DEPARTMENT OF CHEMICAL & ENVIRONMENTAL ENGINEERING: FALL SYMPOSIUM

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University of California, Riverside

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Bourns College
of Engineering

SYMPOSIUM PRESENTERS

Impact of Redox Conditions on the Formation of Hexavalent Chromium in Drinking Water

Michelle Chebeir

Advisor: Haizhou Liu

Chromium commonly exists in two oxidation states in natural environments as well as water treatment and distribution systems as trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)). In trace amounts, Cr (III) is considered to be a nutrient that aids in human metabolic processes whereas Cr (VI) has been shown to be a toxic carcinogen. Recently, the California Department of Public Health set a new maximum contaminant level for Cr (VI) at 10 ppb. This new regulation is anticipated to pose great challenges on the compliance of water treatment facilities. Current water treatment processes typically transform soluble Cr (VI) to particulate Cr (III) before solid removal. However, these processes may not be efficient enough to achieve the low concentrations required, potentially resulting in the re-occurrence of Cr (VI) in treatment and distribution systems.

This study seeks to understand the kinetics of Cr (III) oxidation and formation of Cr (VI) by chlorine in water disinfection conditions. Batch experiments were carried out with chromium hydroxide, chromium oxide, and copper chromite as model Cr (III) sources at varying pHs (6-8) and bromide concentrations (0.1-5 mg/L). At a 10:1 molar ratio of Cr(III) to chlorine, it was found that Cr (VI) was produced with the consumption of chlorine, suggesting that Cr (III) was oxidized to toxic Cr (VI). Increase in pH generally accelerates Cr (VI) formation. Furthermore, the presence of low level bromide catalyzed the formation of chromium (VI) rates by one order of magnitude. Future work will investigate options to minimize Cr (VI) formation.

Investigation of Filtration Mechanisms Involved with Removal of Engineering Nanomaterial from Drinking Water

Chen Chen

Advisor: Sharon Walker

An *in situ*, quantitative experimental system has been designed to study the fate and transport of engineered nanoparticles (ENPs) in porous media. ENPs transport in the subsurface or in engineered filtration processes are being simulated in the system, and the deposition and detachment of particles of fluorescent model ENPs are investigated using an optical microscope and an image-capturing camera. The capture efficiency η, is calculated to quantify the removal of particles in the filter under a range of solution chemistry and flow conditions. Complementary particle characterization is being conducted including dynamic light scattering (DLS) to test particle aggregate size and zeta potential for evaluating particle stability and zero point of charge (ZPC). Interaction forces between ENPs and collector surfaces may be predicted based on traditional DLVO theory, and the colloid transport around spherical collectors were also analyzed used the colloid filtration theory (CFT). A range of aquatic conditions is being tested to capture the range of water quality conditions as would exist in surface and groundwater including multiple salts (KCl and $CaCl_2$), organic matter levels, and residual coagulant levels (iron chloride, iron sulfate, and aluminum sulfate) that would exist in the filtration step of a water treatment plant. This research will better elucidate the fate and transport of ENPs in multiple aqueous conditions, to better define their movement, and ultimately, their removal from engineered and natural systems

Assessing Impacts of Engineered Nanomaterials on Model Colon and Septic Systems

Travis Waller

Advisor: Sharon Walker

As the production and application of engineered nanomaterials (ENMs) continues to grow, the environmental implications are of the utmost importance. Titanium dioxide (TiO_2) is one type of ENM commonly found in foods and consumer products (e.g. sunscreen) with direct access to wastewater treatment facilities; through food consumption and release during bathing of products containing TiO_2, respectively. Studies have reported toxicity is often experienced through bacterial membrane surface interactions often amplified by an increasing ENM concentration in the experimental system. This relates to septic systems as microbial activity drives the degradation of wastewater contaminants and their impairment means greater potential for ground water contamination. Approximately 25% of American homes still rely on decentralized wastewater treatment so therefore this project focuses specifically on septic systems and the impact of ENMs on the septic performance. Prior to reaching septic systems, however, titania particles pass through the human body and the impacts on fate and transport of the particles have been considered. Preliminary studies have been performed to characterize an industrial grade and a food grade TiO_2 when subject to conditions found in a laboratory model human colon.

Examination of Aggregation and Deposition Behaviors by Engineered Nanomaterials in Pristine and Complex Matrices

S. Drew Story

Advisor: Sharon Walker

This doctoral research will examine the structural morphology of aggregates comprised of unique 2-dimensional engineered nanomaterials (ENMs) as well as the more traditional 3-dimensional ENMs. Some examples of 2-D (or planar) ENMs include both carbonaceous materials such as graphene oxide, and inorganic materials such as molybdenum disulfide. Prevalent 3-D ENMs include spherical and amorphous metal oxides, such as titanium dioxide and zinc oxide. Morphology of aggregates, often quantified by fractal dimension, can provide predictive insight regarding the transport behavior, namely, the deposition tendencies. Investigation of morphology of spherical materials typically requires the use of light scattering methods to provide information regarding how densely packed the individual particles are. When examining planar ENMs, the use of multiple microscopic methods will also be needed. Cryogenic transmission electron microscopy (cryo-TEM) will be used in conjunction with atomic force microscopy (AFM) to visually verify the fractal dimension calculations of the light scattering methods, as well as provide information on the parallel stacking of individual plates. This characterization will be done in conjunction with traditional transport studies, including the use of a saturated porous media column by which an attempt will be made to correlate fractal dimension with the deposition rate constant.

Treating Anaerobic Reactor Effluent with Electrically Conducting Ultrafiltration and Nanofiltration Membranes for Fouling Control

Wenyan Duan

Advisor: David Jassby

The anaerobic treatment of industrial wastewater has attracted a significant amount of interest. However, excessive fouling complicates the treatment of anaerobic reactor effluent with membranes, which limits the application of anaerobic membrane bioreactors. Here, we use an anaerobic sequencing batch reactor coupled to ultrafiltration and nanofiltration membranes to treat a high-strength industrial wastewater containing large concentrations of benzyl alcohol, a commercial depainter. We demonstrate that an anaerobic process can successfully be used to degrade this contaminant and application of negative electrical potentials to the ultrafiltration membrane surface prevents membrane fouling and allows for high operational fluxes during the treatment of complex wastewater streams. While the application of a positive potential to the membrane surface increases ultrafiltration membrane fouling, as well as worsens the recovery of the nanofiltration membranes. Overall, our experimental results demonstrate the feasibility of using electrically conducting membranes to prevent membrane fouling during the treatment of anaerobic reactor effluent, while operating at high fluxes.

Magnetic Pickering Emulsions Coupled to Membrane Filtration for Fouling Free Oil/Water Separation

Alexander Dudchenko

Advisor: David Jassby

The ever increasing demand for oil throughout the world has resulted in increased production of oil and produced water. The produced water can be challenging to treat, due to presence of free and emulsified oil. Gravity-based separation can effectively remove the free oil, but not the emulsified fraction. Membrane filtration has been demonstrated to be an effective method of oil removal, producing high quality water. However, membranes suffer from a high degree of irreversible fouling. Here, we present a novel approach to oil/water separation using magnetic Pickering emulsions coupled to ultrafiltration membranes. We demonstrate that crude oil/water mixtures, with concentrations as high as 100 ml/L, can be treated at high fluxes of 100L/m^2 hr for extended periods of time with no significant fouling. The efficacy of this process is independent of water chemistry, with no decrease in performance even at the high ionic strengths (2 Molar) associated with some produced waters. The process employs ferromagnetic nanoparticles, which coat oil droplets, creating a physical barrier preventing coalescence and subsequent membrane fouling. We explore the coated oil droplet properties with atomic force microscopy, demonstrating the presence of the physical barrier separating the oil. The ferromagnetic properties of the emulsions allow for their recovery using a magnetic force, leading to nanoparticle recycling and reuse. The ability to rapidly treat oily wastewater can open new alternatives to deep well injections and evaporation ponds, allowing for reuse in oil extraction operations, discharge into the environment or further post treatment, such as desalination.

Comparison of Pretreatment of Switchgradd by Co-solvent Enhanced Lignocellulosic Fractionation (CELF) to Dilute Acid Pretreatment

Abhishek S. Patri

Advisor: Charles E. Wyman

Over the last few decades, numerous environmental and political concerns have motivated research into renewable, domestic sources of fuels to replace those derived from petroleum. Lignocellulosic biomass represents the most abundant renewable resource and provides the only known route to sustainably produce liquid fuels on a large scale and low cost. Due to its recalcitrant nature, raw biomass hinders enzymatic digestion of the cellulose, thus necessitating pretreatment to deconstruct the plant structure and allow cellulose to be more accessible for enzymes to release fermentable sugars. Several pretreatment methods, including hydrothermal and dilute acid, have been developed to improve enzyme accessibility but are limited in their ability to break lignin bonds, a key contributor to biomass recalcitrance. Recently, we developed a new pretreatment called Co-solvent Enhanced Lignocellulosic Fractionation (CELF) that applies aqueous tetrahydrofuran (THF) to effectively remove lignin and simultaneously achieve high sugar yields from hemicellulose as well as make it possible to realize very high yields from the glucan left in the solids using much lower enzyme loadings than typically possible. In this study we evaluated the pretreatment of switchgrass by dilute sulfuric acid and CELF in terms of impacts on solids compositions, sugar recovery, and the digestibility of the pretreated solids over a range of enzyme loadings for each pretreatment. The results provide insight into overcoming biomass recalcitrance and maximizing saccharification yields.

Understanding and optimizing integration of consolidated bioprocessing with pretreatment for simplified, cost-effective production of fuel ethanol from lignocellulosic biomass

Ninad Kothari

Advisor: Charles E. Wyman

Over 97% of fossil fuel energy consumption for the transportation sector is derived from petroleum-based fuels that are a finite resource. To meet increasing fuel demands and mitigate climate change, dependence on fossil fuels must be reduced. Ethanol made from corn starch and cane sugar is presently the largest volume biotechnology-based product and is attractive as a fuel for internal combustion engines. However, the current technological trend is moving towards utilizing lignocellulosic biomass, which, unlike corn starch and cane sugar, does not compete with food for land. Production of fuel from lignocellulosic biomass, i.e., non-food / feed based feedstocks, offers a low carbon footprint, and recent technological advancements have improved the economics of lignocellulosic biomass utilization for ethanol production. The conventional process for bioethanol production from lignocellulosic biomass involves the following primary steps: 1) size reduction 2) pretreatment, 3) enzyme production, 4) enzymatic hydrolysis (EH), 5) fermentation, and 6) product recovery. Consolidated bioprocessing (CBP) is a potentially cost saving process for simplifying biological conversion of lignocellulosic biomass into ethanol or other products through a combination of enzyme production, enzymatic hydrolysis, and fermentation in a single organism/vessel. *Clostridium thermocellum* and *Caldicellulosiruptor bescii* are promising CBP organisms. Pretreatment may still be needed to achieve high yields. However, it is not known how well physical and compositional characteristics of solids produced by different pretreatment technologies will be amenable to CBP. Therefore, we are examining the ability of *C. thermcellum* and *C. bescii* to solubilize and capture the total sugars in CBP using materials from different leading pretreatment methods, such as hydrothermal, dilute acid, alkali, and solvent-based pretreatments.

Maximum Sugar Yields for THF Co-Solvent Enhanced Lignocellulosic Fractionation (CELF) or Organosolv Pretreatments of Poplar Wood Coupled with Subsequent Enzymatic Hydrolysis

Rachna Dhir

Advisor: Charles E. Wyman

Because lignocellulosic ethanol production typically requires a costly pretreatment step to overcome biomass recalcitrance, advanced pretreatments could significantly reduce overall ethanol production costs. The University of California at Riverside recently invented a novel pretreatment we call Co-solvent Enhanced Lignocellulosic Fractionation (CELF) that uses tetrahydrofuran (THF) in a homogeneous solution with water containing dilute sulfuric acid to achieve very high recovery of hemicellulose sugars in solution and removal of lignin. Furthermore, the highly glucan enriched solids produced by CELF can be readily digested to high glucose yields with much lower economically attractive enzyme loadings than typical for most pretreatments. This study optimized CELF pretreatment of poplar wood to maximize total xylose and glucose yields from the combined operations of pretreatment and subsequent enzymatic hydrolysis and compared the results to maximum total sugar yields from ethanol organosolv pretreatments of the same substrate. CELF pretreatment conditions that achieved the highest combined total sugar yields from poplar wood at high enzyme loadings were determined to be 160°C for 15 minutes with 0.5% H2SO4 as the catalyst at a 1:1 (v:v) THF/H_2O ratio. At these conditions, CELF removed more than 90% of the lignin from poplar and realized xylose plus glucose yields of more than 95% at an enzyme loading of only 15mg/g glucan in raw biomass while organosolv realized a maximum yield 90%. Yield data will be presented over a range of enzyme loadings from 5 to 100 mg protein/g for CELF pretreatment compared to application of ethanol organosolv pretreatment to the same poplar material.

Investigation of aqueous pretreatment and enzymatic hydrolysis of lignocellulosic biomass for understanding recalcitrance

Samarthya Bhagia

Advisor: Charles E. Wyman

A few natural poplar variants carry a rare natural mutation in a lignin biosynthesis gene that alters their cell wall structure and composition. Lignin content and composition have been known to affect sugar yields in poplar, which in turn affect ethanol yields[1]. Several rare varieties carrying the mutation from three different field sites were identified[2, 3] and analyzed by high-throughput pretreatment and co-hydrolysis for their sugar yields. A large variation was found among these plants in their sugar yields for all pretreatment conditions tested. Pretreatment temperature and severity were found to have a large effect on the ranking of the plants based on sugar yields. Further into this project, two plants with the mutation were selected from one of the sites and compared with standard poplar to discover cell wall characteristics that were different between the two plants and the standard. For this procedure, the three varieties were pretreated by low to mild liquid hot water and dilute acid in batch reactors at the same temperature. Enzymatic saccharification was then performed on the pretreated and raw biomass samples at two protein loadings. Glycome profiling[4] showed that xylan in cell walls was more loosely bound in the two rare plants versus the standard. The same was observed from analysis of xylose in the pretreatment liquor, showing 100% recovery for the two rare plants. In the best case, the total sugar yield was 41% higher from mild pretreatment of one of the rare plants compared to the standard. Through this project, we have classified plants for their merits as top poplar biofuel candidates and identified several features that improve our knowledge of biomass deconstruction fundamentals.

Kinetic modeling parameters of THF co-solvent enhanced production of furfural, HMF, and levulinic acid

Nikhil Nagane

Advisor: Charles E. Wyman

The primary feedstock for liquid fuels production is petroleum. Petroleum also provides a platform for synthesis of valuable chemicals and polymers. The historically high price of petroleum products and concern about the impact of fossil emissions of carbon dioxide on global climate change make it important to develop sustainable routes for production of fuels and chemicals. Furfural, 5-hydroxymethylfurfural (HMF), and levulinic acid (LA) are important fuel precursors (FP) that can be derived from lignocellulosic biomass and converted into drop-in fuels compatible with the existing fuel infrastructure. We recently developed a novel co-solvent system we call Co-solvent Enhanced Lignocellulosic Fractionation (CELF) that employs tetrahydrofuran (THF) in solution with water to improve yields of FPs from lignocellulosic biomass. This unique system achieves >87% yields of furfural, removes more than 90% of original lignin, and produces a highly reactive glucan rich solids residue. Therefore, in this study, we developed kinetic data and models for THF co-solvent assisted fuel precursor production from pure sugars and biomass. First, the effect of various operating conditions on carbohydrate breakdown and FP yields were determined. Then, kinetic models were developed from that data to help define reaction conditions that favored the highest yields of each fuel precursor for the THF co-solvent system. In order to understand how CELF improves fuel precursor yields, we identified which kinetic parameters were impacted by the presence of THF.

Determining the Feedstock Production Cost of Agave spp. in Australia for Biofuel Production

May-Ling Lu

Advisor: Charles E. Wyman

Biofuel plays an important role in the curtailing of greenhouse gases (GHG). One crop that holds potential as a biofuel feedstock is agave. Agave, a drought-tolerant plant that thrives in arid and semi-arid regions of the world seems an ideal fit as a biorefinery candidate. Its high water use efficiency and productivity in low precipitation regions allows for marginal land to be cultivated, thus avoiding contentious debates over the use of food for biofuel purposes while potentially providing a renewable and sustainable supply of feedstock for biofuel production. Given its promising features, it is important that the plant be assessed for its economic viability. This presentation reports on the progress of agave feedstock cost estimation using agave field trial data in Queensland, Australia.

Semiconducting to Metallic Phase Change in CVD Produced Monolayer MoS_2

Peter Byrley

Advisor: Ruoxue Yan

As the world moves toward incorporating cheaper earth abundant materials into commercialized electronics, molybdenum disulfide (MoS_2) has become an increasingly important material. When in the bulk form, 2H phase MoS_2 has an indirect bandgap of ~1.3 eV, however, when reduced to one layer it obtains a surprising direct bandgap in the visible range of ~1.8 eV. This is in contrast to graphene's zero bandgap semimetal properties.

Creation of MoS_2 through chemical vapor deposition (CVD) has recently been well documented on a variety of substrates including silica, graphene and even gold. While monolayer MoS_2 can be produced using several routes including mechanical exfoliation and solvothermal methods, CVD produced MoS_2 is of a high enough quality that it can be used for practical devices. Recently, it has also been discovered that phase transformation of MoS_2 from the 2H trigonal prismatic phase (semiconducting) to the 1T octahedral (metallic) phase is achieved through transversal displacement of one of the sulfur planes. This can be achieved and stabilized by several mechanisms including hot electron induction and lithium intercalation. This is important because the 1T phase has been shown to have many times the catalytic activity of the 2H phase for the hydrogen evolution reaction.

I have developed a repeatable CVD process to produce monolayer MoS_2 with varied interesting morphologies and properties. The monolayer MoS_2 I have produced shows excellent photo luminescent properties confirmed by Raman and photoluminescence measurements. It has also been analyzed using SEM and AFM to confirm its existence. This MoS_2 has then been used to look at methods for induced phase change and the resulting change in optoelectronic properties from this.

Organometallic complexes of CVD graphene and single-walled carbon nanotubes

Mingguang Chen

Advisor: Robert Haddon

Chemical vapor deposited (CVD) graphene is a very promising material for the commercial fabrication of electronics and spintronics due to its low cost, large-scale size and amenability to electrical device operation and integrated circuit fabrication. Organometallic modification of transferred CVD graphene has the potential for advanced electronics because it preserves the graphene electronic structure to a large extent while it increases the conductivity. Thin films of single-walled carbon nanotubes (SWNTs) have lower conductivity compared to graphene due to the high resistance of junctions between individual nanotubes. Our group has demonstrated that Cr complexation can lead to electrically conductive interconnects for both semiconducting and metallic single-walled carbon nanotube in the form of (η^6–SWNT)Cr(η^6–SWNT).

My work mainly focuses on fabrication of graphene-transition metal sandwich structures by photochemistry and metal vapor synthesis, study of their unique electronic and magnetic properties by in-situ resistance measurements, temperature dependence and magnetoresistance measurements of the devices.

Contamination of CVD graphene during transfer process has always been an obstacle to the fabrication of high performance devices, especially when it comes to organometallic chemistry. In this work, we employ an ultraclean graphene transfer method to avoid contamination from poly(methyl methacrylate) (PMMA) or other graphene holding layers. Besides, we design a delicate structure to prepare Cr, Mo and W derivatives of graphene. Finally, we are able to make the graphene-Cr-graphene sandwich complexes and explore theirs properties, which may pave the way to advanced applications.

Site Specific Mechanisms for Selective Heterogeneous Catalytic Reactions

Leo DeRita

Advisor: Phillip Christopher

Heterogeneous catalysis is a fundamental driver of economically viable chemical and fuel production processes and optimizing energy efficiency is of paramount importance. The preferred approach is through controlling catalytic selectivity, such as through engineering catalyst geometry. By focusing on the kinetics of single reaction steps, the impacts of catalytic modifications on reactivity are directly measurable offering fundamental insight. The complimentary techniques of *in-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Mass Spectrometry (MS) are used to explore the impact of various approaches to modify catalytic behavior for single elementary steps. It is hypothesized that these insights will provide critical information to aid in the design of catalytic processes with high selectivity.

The desorption of CO from alumina supported Pt nanoparticles of varying size was chosen as an initial probe system due to the ubiquitous role in automotive catalysis and the unanswered question regarding structure sensitivity. Varying the size of catalyst nanoparticles imposes a change in the catalyst geometry, specifically, the relative abundance of sites with varying adsorption energy. Differences in CO-Pt adsorption energy are manifested in the FTIR as separate vibrational modes in the spectra and the intensity at each frequency characterizes the relative abundance of each site type on the catalyst. By comparing two nanoparticle sizes we can observe which sites are active for desorption from our *in-situ* DRIFTS measurements. In conjunction with the DRIFTS measurements, Temperature Programmed Desorption/Reduction (TPD, TPR) experiments have been performed via mass spectrometry to monitor concentrations of desorbing CO and CO_2 during a temperature ramp to directly map the change in CO coverage at each site. The surface chemistry at play is clear as desorbed CO features during TPD correspond with intensity drops in the DRIFTS spectra. Initial results indicate the accepted mechanism for CO oxidation may be excluding a key elementary step, CO dissociation. The observed decrease in CO adsorption on the most active sites following a TPD experiment indicates carbon deposition, supported by the appearance of methane (CH_4) during TPR. It is expected that smaller particle sizes will show more dramatic changes due to higher concentrations of the most active sites.

Exploration of Interfacial Band-bending phenomena induced by Contacting Co-catalysts with Light-absorber for Watersplitting Application

Yibo Jiang

Advisor: Phillip N. Christopher

Photocatalytic watersplitting offers a promising resolution for converting solar energy into easily-storable chemical energy. Cocatalyst-loaded semiconductive light absorbers have been extensively synthesized and trialed for their photocatalytic activity, as it is believed that the use of co-catalysts (i.e., metals or semiconductors) promotes reaction kinetics by lowering the water-cleavage overpotential. Few studies have elaborated on the physical phenomena occurring at these interfaces formed upon contacting different materials or the consequent influences that the formation of these interfaces has on the thermodynamics (overpotential) and kinetics (rate) of photocatalytic watersplitting processes. We hypothesize that the thermodynamics and kinetics are both impacted by the nature of the co-catalyst interface and that thorough elucidation of this mechanisms underlying these effects will enable the design of optimized systems. In this project, gallium zinc oxynitride (GaNZnO) was selected as the semi-conducting light absorber, while catalytic metals (Pt, Rh, Ru, Cr, Ni) and their oxides were chosen as cocatalysts that form two types of heterojunctions: Schottky (M/GaNZnO) and p-n or n-n (MO/GaNZnO) junctions. The performance of each system was tested in overall watersplitting (OWS) during which evolved gases were monitored by Gas Chromatography (GC). Preliminary results showed that all metal cocatalysts failed to initiate the watersplitting reaction; while several metal oxides (RuO_2, RhO_2, and NiO) facilitated the reaction, which clearly indicates the existence of differentiated charge transfer behaviors at catalyst interfaces. The OWS activity improvement of the cocatalysts is ranked from high to low: RhO_2 > NiO > RuO_2. Since hydrogen evolution reaction (HER) is of particular interest, sacrificial reagent-aided half reactions were also performed to explore the effects of cocatalyst loading on hydrogen generated from water. Besides kinetic analysis, the thermodynamic and structural properties of the interfaces will also be characterized via photoelectronic techniques, such as: XPS, UPS, and XRD, and etc. The experimental results will be coupled with material thermodynamic properties as input parameters so as to gain more insights for constructing predictive models in next stage of the project.

Plasmonic Nanowire Optical Probe for Near Field Scanning Microscopy

Sanggon Kim

Advisor: Ruoxue Yan

Near-field scanning optical microscopy (NSOM) is an ultrahigh resolution optical imaging technique. By detecting and utilizing the near-field light before it undergoes diffraction, NSOM retains the full gamut of contrast mechanisms afforded by optical microscopy methods for optical, chemical and structural characterization, while attaining spatial resolution far beyond the classical optical diffraction limit (~500 nm). However, conventional NSOM probes suffer from either extremely low optical transmission (~10^{-6}) or signal-to-noise ratio, both of which significantly limit the speed of image construction. Here, we have developed a novel NSOM probe design based on plasmonic nanowire (NW) waveguides. We have demonstrated a visible light transmission of up to 97% in these probes, which corresponds to 10^6 times enhancement in excitation intensity compared to conventional NSOM probes to allow high speed scanning. In addition to the high transmission, this probe also demonstrated a 10^2 Raman enhancement due to the large electric field enhancement at the tip of the NW, which is 10 times higher than commercial NSOM probes designed for Tip Enhanced Raman Spectroscopy (TERS) scanning. This new probe design also allows for higher device reliability, which is another major limitation for conventional NSOM probes.

Development of Catalytic Technologies for the Conversion of Biomass-Derived Sugars to Fuels and High-Valued Commodity Chemicals

Glen Svenningsen

Advisors: Phillip Christopher, Charles Wyman

This project develops transformational technologies for fuel additives production from inexpensive, abundant cellulosic biomass (corn stover), and is composed of three research areas: 1) novel one-step biological conversion of glucan enriched pretreated lignocellulosic biomass into fructose, 2) advanced approaches to fructose dehydration, and 3) new catalytic approaches to make sustainable fuels that are compatible with the current transportation fuel infrastructure. This research currently focuses on the second area, the dehydration of fructose to 5-hydroxymethylfurfural (HMF) through heterogeneous catalysis.

HMF is a highly desirable platform chemical for the production of fuels and high valued commodity chemicals. Presently, there is no cost-effective synthetic methodology for the production of HMF from sugars. The main cost factor impeding the commercialization of HMF is due to the difficulty of separation and extraction from the high-boiling point aprotic solvents used for HMF production.

High boiling point solvents, such as dimethylsulfoxide (DMSO), consistently demonstrate the highest HMF yields (100% yields). This is due to both the stabilization and catalytic effects associated with DMSO. The stabilization is a key property of DMSO, as it hinders the degradation of HMF to acids and other condensation products, which is a major problem in aqueous-based systems.

The strategy of this project is to utilize polymers which incorporate these solvents as the functional moieties and/or monomers of the polymer. Being fixed into a polymer chain/matrix will allow for easy, economical separation of HMF from solution while still keeping the catalytic and stabilization effects associated with these solvents. These polymers can also be grafted onto the surface of stable metal oxides to engage new surface chemistry by anchoring these functional groups near active catalytic sites on the surface. Additionally, these new materials can be loaded into continuous flow or pack-bed reactors to enhance its viability for commercialization.

Synthesis and characterization of these polymer-based materials were performed via FTIR and TGA studies. Preliminary results of the HMF yields, characterized by HPLC, show enhanced HMF yields from systems without catalysts.

Solid-State Lithiation and Delithiation of Sulfur in Liquid Electrolytes: A New Concept for Designing Lithium-Sulfur Batteries

Chengyin Fu

Advisors: Juchen Guo

We investigate the detailed effects and mechanisms of sub-nano confinement on lithium-sulfur (Li-S) electrochemical reactions in both ether-based and carbonate-based electrolytes. Our results demonstrate a clear correlation between the size of sulfur confinement and the resulting Li-S electrochemical mechanisms. In particular, when sulfur is confined within sub-nano pores, we observe identical lithium-sulfur electrochemical behavior and excellent cycle stability in both ether and carbonate electrolytes. Taken together, our results highlight the critical importance of sub-nano confinement effects on controlling +solid-state reactions in Li-S electrochemical systems.

Mechanism of CO_2 reduction by H_2 on Ru and general selectivity descriptors for late-transition metal catalysts

Talin Avanesian

Advisor: Phillip Christopher

Climate changes resulting from increasing atmospheric CO_2 concentrations, has become a widespread concern in recent years and the search for methods to reduce atmospheric CO_2 concentration has become a high priority research area. Coupling CO_2 sequestration approaches with catalytic hydrogenation of CO_2 to higher value hydrocarbon feedstocks for chemical and fuel production is considered to be a promising route towards environmentally friendly and carbon neutral economy. The main goal of this study is to utilize computational quantum chemistry calculations based on Density Functional Theory (DFT) to develop molecular level insights into the mechanisms that control the performance and selectivity of metal catalysts in CO_2 reduction by H_2. The mechanism of CO_2 hydrogenation was investigated on Ru catalyst surface to address fundamental mechanistic questions and existing debates in literature regarding the CO_2 hydrogenation pathways. By coupling DFT calculations with microkinetic analysis it was shown that the initial CO_2 hydrogenation step leading to CH_4 production occur through CO_2 dissociation and subsequent hydrogenation of CO* to CHO*. The dissociation of CHO* to form CH* and O* was identified as the rate limiting step for CH_4 formation, while the rate limiting step for CO production through the competing reverse water gas shift reaction was identified as CO* desorption. Based on the analysis of energies of competing CHO* dissociation and CO* desorption, O* adsorption energy was found to be an effective descriptor of differences in selectivity between CO and CH_4 production previously observed on late-transition metal catalysts. These mechanistic insights provide critical information to guide the design of catalysts with tunable selectivity for CO_2 reduction by H_2.

Synthesis of Lithium Sulfide Carbon Composites via Aerosol Spray Pyrolysis

Noam Hart

Advisor: Juchen Guo

The high promise of lithium-sulfur (Li-S) batteries has attracted unprecedented interest in recent years. The majority of current investigations concentrates on sulfur-based cathode materials. The use of a sulfur cathode, however, presents several challenges due to the Li metal anode, which is prone to potential dendrite growth, shuttle reactions of Li with polysulfide species and the reductive decomposition of electrolyte components on the Li surface. One holistic strategy to address these problems is to produce batteries with Li_2S-based cathodes, with which high-capacity anodes including Si and Sn can be used instead of Li metal. The electrochemical reaction at the Li_2S cathode is the same as the sulfur cathode in principle. At the anode side, Li forms alloys with Si or Sn at higher potentials versus Li/Li^+ so that the Li dendrite formation can potentially be eliminated. The new batteries of Si-Li_2S and Sn-Li_2S indeed have lower energy compared with Li-S batteries due to the lower cell voltage and the lower anode capacity. Nevertheless, they have much higher specific capacity than current Li-ion batteries.

The Li_2S cathodes also have advantages from the manufacturing standpoint compared with conventional Li metal anodes (typically Li thin foils), which require sophisticated processes (purification, extrusion, passivation, etc.) due to the high reactivity of Li. On the other hand, while sensitive to moisture, Li_2S is nonflammable and oxygen stable so that the manufacturing process may be less demanding. In this study, we present a scalable process to synthesis Li_2S-carbon composite cathodes from various lithium salts and organic carbon precursors via aerosol-assisted spray pyrolysis (ASP). The ASP is a robust method to produce Li_2S-C composites with rational microstructures from different reactants. The design of the composites and their performance will be discussed in detail.

Controlling Catalytic Selectivity on Metal Nanoparticles by Direct Photoexcitation of Adsorbate-Metal Bonds.

Matthew J. Kale

Advisor: Phillip Christopher

Controlling selectivity of chemical reactions on metal surfaces is of paramount importance for the design of efficient, environmentally friendly heterogeneous catalytic processes. Governing relationships between adsorption energies and activation barriers of competing chemical pathways on metal surfaces limit the potential to control selectivity when using thermal energy to drive reactions. It has recently been shown in a few cases that visible light irradiation of metal catalysts can overcome inherent limitations of thermal-driven catalysis, inducing new chemical pathways through electronically excited states. However these photon driven reactions typically occur through a substrate-mediated transfer of photon energy to adsorbate-metal bonds, where the initial photon absorption occurs in the bulk metal states, followed by charge transfer to adsorbates. Since only the bulk metal is involved in the initial photoexcitation step, the wavelength dependent quantum yields follow the absorption spectrum of the metal, and targeted activation of adsorbate-metal bonds (which is required to control the outcome of metal catalyzed reactions) cannot be controlled in a rational manner.

In this work, we show that catalytic processes on metal surfaces can be driven and controlled through direct, resonant photoexcitation of hybridized electronic states formed due to strong chemisorption of CO on Pt surfaces. We investigate the effect of particle size, photon wavelength and intensity, and the surface coverage of the CO and H_2 oxidation reactions. As opposed to the substrate-mediated mechanism, direct photoexcitation of adsorbate-metal bonds occurs at surface Pt atoms that are directly bound to adsorbates. Pt nanoparticle size dependent studies showed that activation of Pt-CO bonds by direct photoexcitation becomes the dominant mechanism driving chemistry on nanoparticle catalysts <5 nm in diameter. By exploiting the resonant, adsorbate specific nature of electronic transitions formed between adsorbates and metal surfaces we show that targeted photoexcitation of catalytic 2.3 nm Pt nanoparticles with 450 nm photons enhances selectivity from 40% to 80% in the preferential oxidation of CO in an H_2 rich environment. It is expected that the development of insights into resonant photon induced electronic transitions between hybridized metal-adsorbate states should allow rational control of catalytic selectivity that cannot be achieved exclusively with thermal energy input.

Catalytic reactivity and in Situ synthesis of stable Rh isolated catalyst sites

John Matsubo

Advisor: Phillip Christopher

Significant recent interest has been placed on identifying and exploiting the unique reactivity of atomically dispersed active metal sites on oxide supports. Synthesizing atomically dispersed active species with high concentration, and stabilization against agglomeration under reaction conditions, is difficult. Focus has been placed primarily on the excellent reactivity of these active sites in reactions where activity is the crucial descriptor of performance. This talk will discuss the reactivity of atomically dispersed Rh active sites on TiO_2 supports in the reduction of CO_2 by H_2. It will be shown that these species are highly stable under reaction conditions and exhibit different selectivity than Rh nanoparticles for CO_2 reduction.[1,2] In addition, environmental conditions were identified that enable reversible tuning of the catalyst morphology *in situ,* resulting in catalysts with high concentrations of atomically dispersed Rh active sites as the only exposed species.

Catalytic CO_2 reduction by H_2 at stoichiometric methanation and H_2-lean CO_2:H_2 feed ratios was explored over various weight loadings of Rh on TiO_2 supports. The concentration of atomically-dispersed/isolated Rh active sites, and Rh atoms sitting at the surface of Rh nanoparticles were quantified using probe molecule Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), coupled with known extinction coefficients. The reactivity results coupled with the DRIFTS measurements strongly suggest that Rh_{iso} sites on the TiO_2 support are active sites almost exclusively for CO_2 reduction to CO, whereas Rh_{NP} sites are active sites almost exclusively for CO_2 reduction to methane. We also found that at high CO_2:H_2 ratios methane-producing Rh_{NP} sites convert to CO-producing Rh_{iso} sites, thereby controlling the instability of catalytic selectivity with time on stream. This process was augmented to completely convert the catalyst into a state with either exclusively exposed Rh_{NP} or Rh_{iso} sites, allowing tuning of selectivity from almost completely methane to completely CO depending on the state of the catalyst. In addition, we determined Rh_{iso} sites produced from the high CO_2:H_2 treatment were very stable under reaction conditions without adding any promoter species.

This study provides critical information towards the design of controllable and stable atomically dispersed Rh catalysts compared to Rh nanoparticles based active sites.

Effect of electron beam-induced irradiation defects on thermal conductivity of single layer graphene

Pankaj Ramnani

Advisor: Ashok Mulchandani

Graphene, a planar sheet of sp^2-bonded carbon atoms arranged in honeycomb lattice, is known to have an extremely high thermal conductivity of >3000 W/mK. Study of thermal transport in graphene is crucially important for diverse applications, such as thermal management in nanoelectronics and thermal conductivity enhancement of composite materials. However, studying the properties of pristine defect-free graphene is not practical since the device characterization and fabrication steps inevitably introduce defects in graphene. Scanning electron microscopy (SEM) and electron-beam lithography (EBL), which are two commonly used techniques for characterization and fabrication of graphene devices, involve exposure of sample to electron beam. This irradiation introduces point defects in graphene which significantly affect the two-dimensional transport of phonons. Due to scattering occurring from the presence of such point-defects, the phonon mean free path and thermal conductivity are significantly affected.

In this work, we explore the effects of electron beam-induced defects on thermal conductivity of single-layer graphene. Large grain single-layer graphene was synthesized using chemical vapor deposition and suspended on a metallic transmission electron microscopy (TEM) grid. Suspended graphene grains were exposed to low energy (20keV) electron beam for certain period of time in several steps to obtain the desired defect density. The defect density was quantified by monitoring the intensity ratios of D/G peak in Raman spectra. After each step of e-beam irradiation, the thermal conductivity was measured using optothermal Raman technique. Briefly, Raman laser was used as a heat source to locally heat the suspended graphene and corresponding temperature rise was measured by monitoring the shift of G peak in Raman spectra. Based on temperature change and power dissipated, the thermal conductivity was extracted by solving the heat-diffusion equation using finite-element analysis (COMSOL Multiphysics). The thermal conductivity of single layer graphene was found to non-monotonically decrease with increasing defect density. At defect density of 1.5×10^{11} cm^{-2} we observed a change of the slope followed by saturation behavior in the thermal conductivity. The non-monotonic decrease can be related to the interplay of the point-defect and grain boundary scattering appearing due to defect clustering. The exact mechanism is currently under investigation.

Rapid Electrodeposition of Thick Lead Telluride (PbTe) Film in Alkaline Solution for Thermoelectric Application

Tingjun Wu

Advisor: Nosang Myung

Waste heat recovery is a crucial step to improve the energy generation and utilization efficiency. Thermoelectric (TE) materials, which can directly convert rejected or waste heat into usable electric power, has been extensively developed for this issue. Thick-film-based devices have advantages over conventional TE module because of its compact size. By shrinking the size of thermoelectric devices, it expands its capability to handle a wider range of thermal and power management microelectronic systems. The combination of electrochemical deposition of compound semiconductors (metal tellurides) with standard integrated circuit technique makes fabrication of thermoelectric microdevices possible. However, the commonly used baths for electrochemical deposition of metal telluride are acidic baths, in which the deposition rate is limited by the solubility of Te (+IV). For instance, it can take more than 24 hours to deposit a 100 µm thick, compact film.

In our work, we demonstrated a rapid deposition process (100 µm/h) to synthesize dense thick PbTe film (>50 µm) for thermoelectric applications. Control over the composition of the thick PbTe film was achieved by tuning the electrodeposition conditions, such as the ratio of [TeO_3^{2-}]/[Pb^{2+}] and [$EDTA^{4-}$]/[Pb^{2+}] in the electrolyte, pH, as well as the applied potential, agitation and temperature. The electrodeposition mechanism of PbTe was examined. The electrical and thermoelectric properties of thick PbTe films were investigated.

The Microstructure and Mechanical Properties of Gastropod Shells

Christopher L. Salinas

Advisor: David Kisailus

Nature has evolved a variety of highly specialized mineral and organic composite microstructures to suit a wide variety of environmental pressures facing different animals. A commonly observed architectural motif is that of the fiber reinforced composite microstructure, which is observed in animals across many different phyla, for example the structures found in the teeth of chitton, arthropod exoskeletons, and in the crossed lamellar structure that is commonly found in the shells of gastropods. The crossed lamellar structure in the shells of the gastropod has evolved to be lightweight, tough, and efficient energetically to produce. In addition gastropods have evolved a number of unique shell adaptions to excel at many different ecological niches such as spines to avoid crushing predators, or in other cases flared lips to provide peeling resistance, or the ability to diffuse bioluminescent light produced by the body of the snail, such as the *Hinea brasiliana* when it is disturbed by a predator. The properties of the *H.brasiliana* shell were investigated by synchrotron 2d-xrd, nanoindentation, scanning electron microscopy, and optical microscopy in addition the shells of the non-bioluminescent *P.sulcatus* and *S.gigas* were investigated. The crossed lamellar microstructure has a unique morphology and crystalline orientation. The unique nanostructure enhances the toughness of the shell and provides a superior defense against predation compared to other shell microstructures.

Understanding Emissions from Wastewater Treatment Processes and Their Impact on Regional Air Quality and Health

Pedro Piqueras

Advisor: Akua Asa-Awuku

As water resources become scarce and population grows, the construction and use of wastewater treatment plants is increasing significantly. Wastewater treatment plants (WWTPs) are common in urban environments and their aerosol emissions have been associated with local and regional health burden. Known toxic compounds, bacteria, fungi, endotoxins and viruses have been observed in WWTP aerosols in the past, but their concentration and classification are still dubious. The airborne exposure route is also still poorly established due to the lack of information on aerosol characterization and transport.

We have measured particle concentration and size distributions from two laboratory scale bioreactors; a bioreactor with an air diffuser and a bioreactor with only a mixer. These bioreactors simulate both aerobic and anaerobic biological processes in the secondary stage of water treatment. The inside of the bioreactors contains sludge from an aeration basin from a WWTP in Redlands, California. They are fed 3,000 mg/L of COD every two days by using a dilution of molasses as the influent. This COD is fully degraded after the two-day cycle.

Results suggest that aerobic processes generate more particles through bubble bursting. Increasing the aeration flow rate increases the particle number, however the size distributions of particles produced remains the same. The results will later be extrapolated to real field measurements at Orange County Sanitation District aerated basins.

To our knowledge, these are the first real-time measurement of ultrafine particles measured from WWTPs systems and it will attempt to fill some of the gaps in scientific literature so that regulatory laws can be implemented in order to establish a safe and non-polluting environment when treating wastewater.

Modification of Droplet Sizes Due to Mixing in Anthropogenic Aerosols

Emmanuel Fofie

Advisor: Akua Asa-Awuku

Cloud droplet size influences the optical depth of clouds and hence particle scattering and the resulting estimates of global cloud radiative forcing. Yet, the sizes of droplets formed from the activation of aerosols either in their pure states, externally or internally mixed is not well characterized. In this study, we explore the effects of organic anthropogenic aerosol such as succinic acid, malonic acid, oxalic acid and soot (Black carbon) on cloud droplet sizes. The final droplets sizes are measured from pure and mixed aerosol species. Aerosol activate, form cloud condensation nuclei (CCN) and their droplet growth is characterized according to their mass accommodation coefficient and mixing states. A custom built flowtube was employed to achieve the different mixing states of the aerosol and NIST-certified borosilicate glass beads were used to verify the sizing of the optical particle sizer of the DMT, Inc. cloud condensation nuclei counter (CCNc). A coupled analysis of laboratory CCN experiments and simulation data from the continuous-flow streamwise thermal gradient CCN (CFSTGC) model showed a distinguishable and repeatable divergence in the sizes of CCN when exposed to the same supersaturation and time, with water vapor depletion effects considered. The results suggest that the final droplet sizes of activated aerosol depends on the chemistry of the aerosol represented by the hygroscopicity parameter, κ, as well as the mass accommodation coefficient. The amount of each aerosol species in the atmosphere and their mixing states may therefore have to be considered when computing the earth’s radiative forcing.

Ozone and Secondary Organic Aerosol (SOA) Formation from Select Low Vapor Pressure-Volatile Organic Compounds (LVP-VOCs)

Weihua Li

Advisor: David Cocker III

A low vapor pressure-volatile organic compound (LVP-VOC) is a chemical “compound” or “mixture” that has relatively low vapor pressure and high boiling point. LVP-VOCs are essential components in consumer products used to meet product functionality and also volatile organic compound (VOC) limits. However, LVP-VOCs may still be present in the atmosphere through evaporation over extended periods of time and form secondary organic aerosol (SOA) after photo-chemical oxidation. Therefore predicting the LVP-VOCs’ behavior in the atmosphere and their contribution to ambient fine particulate matter are very important.

Teflon indoor chambers are ubiquitous in the study of gas phase atmospheric chemistry and SOA formation from oxidation of LVP-VOCs. However, SOA formation can be significantly underestimated due to deposition of particles and SOA-forming vapors to chamber walls. Losses of particles to chamber walls are taken into account by current SOA formation models, but there has been little evaluation of the chamber surfaces in influencing LVP-VOCs availability and SOA formation. The goal of this study is to understand SOA forming-potential and growth from selected LVP-VOCs as they partition between gas-phase, chamber surfaces, and particle surfaces. This study will provide a firm experimental foundation for evaluating current VOC exemption rules.

The work utilizes the advanced environmental chamber facility located at CE-CERT, which is designed to investigate atmospheric reactivity, ozone formation, and SOA formation at low atmospheric concentrations. The chamber facility is ideally suited for studying atmospheric impacts of LVP-VOCs due to its precise environmental controls and largest volume to surface area compared with any other indoor chambers.

Greenhouse Gases and Particular Matter Emissions from Heavy-duty Diesel Vehicles

Yu Jiang

Advisors: David Cocker III, Kent Johnson

Greenhouse gases emissions can trap heat from the sun and keep the surface of earth warm, which result in climate change and global warming. Transportation is the important source to contribute to greenhouse gases. In this presentation, it will focus on greenhouse gases (CO_2 and CH_4) and short-lived emissions (O_3 and Black Carbon). These emissions lead to lots of adverse effects, for example GHGs gases are responsible for global warming, NO_X and HCs are precursors for O_3, toxic substances of PM and HC threat human's health and so on.

The Heavy-duty trucks are the most efficient transportations worldwide today. Diesel engines contribute significantly to the emissions inventories CO_2, CO, HC, NO_X and PM due to their high vehicle emissions rates and high vehicle miles traveled. EPA has implemented a serious of standards to control diesel emissions. Current diesel engines must meet emissions standards of 2007 for PM and 2010 for NO_X, which contributes to the development of diesel engine after-treatment systems, diesel particulate filter (DPF), selective catalytic reduction (SCR) and diesel oxidation catalysts (DOCs). Characterization of in-use emissions of on-road heavy-duty trucks is an important element of obtaining accurate emissions inventory estimates. Data on in-use emissions measurements of these modern diesel engines is limit. The goal of the presentation is to obtain data on class 8 trucks with the newest emission control strategies over in-use cycles on a heavy-duty chassis dynamometer.

Total 4 vehicles will be tested in this proposal. The engine manufacturer will be Cummins, Detroit Diesel, Mack and Navistar. All vehicles are required model year 2014+ and mileage is below 50000 miles. The testing trucks are preformed four phases of the Heavy Heavy-Duty Diesel Truck (HHDDT) schedule and Heavy Heavy-Duty Diesel Truck-Short (HHDDT-S) developed by the California Air Resources Board on CE-CERT Heavy Duty Chassis Dyno meter. The results showed that after-treatment system attributed to reduce most NO_X and PM emissions and met EPA standards.

Incremental Secondary Organic Aerosol Formation at Simulated Atmospheric Reactivities

Mary Kacarab

Advisor: David Cocker III

Two surrogate mixtures of anthropogenic and biogenic volatile organic compounds (VOCs) were developed to study the effects of individual compounds on secondary organic aerosol (SOA) formation in simulated urban atmospheres with varying levels of biogenic influences (e.g. a Los Angeles atmosphere vs. an Atlanta atmosphere). Environmental chamber simulations were designed to enable the study of the incremental aerosol formation from select anthropogenic (aromatic) and biogenic (terpene) precursors under chemical conditions created by the surrogate mixtures. The surrogate reactive organic gas (ROG) mixtures were based on that used to develop the maximum incremental reactivity (MIR) scales for O_3 formation in Southern California urban atmospheres. Multiple surrogate experiments (with and without the SOA precursor) were performed in the University of California Riverside (UCR) College of Engineering Center for Environmental Research and Technology (CE-CERT) dual $90m^3$ environmental chambers. SOA incremental aerosol yields and aerosol properties such as density, volatility, and elemental chemical composition data will be presented. It was found that the aerosol yields from individual precursors varied in the different controlled reactivity systems and with individual precursor experiments, thus demonstrating that the overall reactivity of the system can dictate how an individual precursor will behave. Incremental yields, SOA characteristics, and O_3 formation will be compared between the two surrogate ROG mixtures and against data from previous single VOC studies conducted following traditional VOC/NOx models. Comparison between the incremental effects of VOCs on SOA formation and properties are important when evaluating how to best extrapolate environmental chamber observations to the ambient atmosphere and provides useful insights into current SOA formation models.

Impact of Molecular Structure on Secondary Organic Aerosol Formation from Aromatic Hydrocarbons

Lijie Li

Advisor: David Cocker III

Aromatic hydrocarbons account for 20%-30% of the VOC in the urban atmosphere and are major contributors to anthropogenic SOA. Previous studies mentioned that SOA formation from aromatic hydrocarbons photooxidation are related to their molecular structure. However, the impact of molecular structure is not comprehensively studied and remains elusive especially under atmospherically relevant low NO_x conditions. This study generalizes the relationship between aromatic alkyl groups (number and location on aromatic ring) and SOA formation based on hundreds of chamber experiments from 17 different aromatic precursors under low NO_x conditions. We found that SOA yield, physical property (density and volatility) and chemical compositions are strongly depend on aromatic molecular structure. A novel method is found to quantify the relationship of SOA yields and chemical composition with the number of alkyl group. Therefore, the concept of low and high yield of aromatics is reevaluated. Alkyl group location impact on SOA formation from aromatic hydrocarbon is also confirmed and extended. ^{13}C isotope enriched aromatics are used to confirm the contribution of alkyl group location to SOA formation. Three mass spectrometers including ToF-HR-AMS, PTR-MS (Proton Transfer Reaction – Mass Spectrometry) and SIFT (Selected-ion flow-tube mass spectrometry) are used to demonstrate alkyl group position impacts on SOA formation and composition during photooxidation. This work provides fundamental information for government regulations and contributes to the improvement of global modeling on aerosol formation, climate change and health impact.

Critical Time for CCN Activation of Biogenic Precursors

Ashley Vizenor

Advisor: Akua Asa-Awuku

Particles that can uptake water and form cloud droplets are referred to as cloud condensation nuclei (CCN). The hygroscopicity, or ability of a particle to activate is traditionally quantified by a single parameter, kappa. Here we examined the photooxidation of two biogenic compounds, isoprene and longifolene using the UCR CE-CERT Environmental Chamber. A TSI SMPS ran in parallel with a Droplet Measurement Technologies Cloud Condensation Nuclei Counter (CCNC) was used to observe the hygroscopicity of resulting secondary organic aerosol (SOA). Traditional CCN analysis is performed by dividing the number of particles activated by the total number of particles (condensation nuclei, CN). The point at which the ratio equals 0.5 is used to identify the critical supersaturation at which 50% of the particles activate for a given diameter. Alternatively, the critical diameter at which 50% of particles for a given supersaturation can be identified. This critical supersaturation and the corresponding dry diameter are then used to calculate kappa. However, this calculation assumes that the hygroscopicity of particles stays constant for a given precursor gas. The CCN to CN ratio at given diameters and supersaturations was calculated and plotted against photooxidation time to observe if this assumption holds true.

A New Mobile Atmospheric Chamber: Atmospheric Aging of Vehicle Emissions

Diep Vu

Advisor: Akua Asa-Awuku

A new Mobile Atmospheric Chamber (MACh) has been developed to investigate the Secondary Organic Aerosol (SOA) forming potential of emissions generated from emerging vehicle technologies and renewable fuels. MACh was designed and constructed in house and then integrated with the infrastructure of the atmospheric processes and vehicle emissions research laboratories (APL and VERL, respectively) at the Center for Environmental Research and Technology (CE-CERT). This provides real time physical and chemical characterization of both fresh and aged emissions sources from driving cycles that are representative of real world driving conditions in a repeatable and controlled environment.

MACh consists of a single collapsible ~ 30m^3 2 mil FEP Teflon film chamber, thereby making it one of the largest mobile reactors currently available. The chamber is suspended in a mobile aluminum frame that is positioned in the test cell where the emissions are collected and then transported to APL to be aged with black lights. Photochemistry is completed using a controlled light source consisting of 600 UV lights yielding a total of 9 kW at 300-430nm with a peak intensity of 365nm. State-of-the art gas and particle phase instrumentation are used to measure the chemical activity in real time as the fresh emissions are aged through photochemical oxidation. Results of initial characterization experiments will be presented.

Classical Density Functional Theory for the Optomized Pairing of Electrolytes with Porous Carbon Electrodes in Ionic Liquid Supercapacitors

Justin Neal

Advisor: Jianzhong Wu

The future of our climate depends on the reduction of carbon emissions to the atmosphere. The development of more effective methods and devices to store and transport energy represents a vital step toward the prevalent use of renewable energy that would significantly contribute to the reduction of carbon emissions. As illustrated by Helmholtz over 150 years ago, the electric double layer (EDL) capacitance is inversely proportional to the length scale of ion distributions near a charged surface, larger than that of a conventional dielectric capacitor by many orders of magnitude. EDL capacitors, also known as supercapacitors, have been used broadly for energy storage along with porous electrodes (mostly activated or carbide derived carbons) and ionic liquids to maximize the energy density. Their performance is sensitive not only to the pore geometry (e.g., slit, cylindrical, or spherical) and size distribution but also to the molecular characteristics of a matching ionic liquids and composition. This thesis is devoted to a systematic analysis of all pertinent parameters that can be utilized to optimize the device performance. The classical density functional theory (CDFT), coupled with generic models of electrolytes and electrodes, is applied to shed insight into the microscopic details underlying the interaction between the structure of porous electrodes and the characteristics of ionic-liquid mixtures. The distribution of pores in porous electrodes is especially emphasized in conjunction with the variables defining an ionic-liquid mixture such as: size and charge asymmetries, anisotropy of individual ions, electrolyte composition, and ion valence. The diverse parameter space makes it too time consuming for a thorough examination only by experiments or atomistic molecular dynamics simulations. In contrast, the versatility of classical density functional theory enables the most efficient characterization of each variable in this multifaceted problem. This work is supported *via* collaboration with researchers at the DOE Energy Frontier Research Center on Fluid Interface Reactions, Structures and Transport (FIRST). A recent interesting development concerns the absorption of asymmetrically sized ionic liquid mixtures in slit pores. This found a pronounced increase in capacitance resulting from intercalation of smaller anions between cations, packing them closer together and promoting greater energy density.

Molecular Density Functional Theory for High-throughput Predictions of Solvation Free Energies

Shijie Sheng

Advisor: Jianzhong Wu

Solvent effects are fundamental to understanding all chemical processes and reactions in aqueous and organic environments. Despite enormous activities in this field, quantitative solvation calculations remain an enormous intellectual challenge. While molecular dynamics (MD) simulation provides reliable solvation free energy predictions, its computational time is expensive for a large number of solutes. This project aims to establish a theoretical platform for high-throughput predictions of solvation free energies in liquid water and octanol systems based on the molecular density functional theory (MDFT). Unlike conventional theories, for example, van der Waals equation of state that takes the mean-field approximation, MDFT accounts for two-body correlations and thus provides more accurate predictions. To apply MDFT, we first determine the solute structures from quantum mechanics (QM) calculations. Secondly, the direct correlation functions (DCFs), a pivotal input of MDFT, are accurately sampled from MD simulations for bulk water and octanol. Finally, the solvation free energies are calculated and calibrated with experimental data for a large library of organic molecules. In additional to neutral solutes, we apply a similar method to charged systems including monovalent ions. Finally, we investigated the temperature dependence of solvation free energies using DCFs from the reference interaction site model (RISM). This analytical tool provides reasonable DCFs compared with that from MD simulations for different water models. With the DCFs from RISM as an input, we use MDFT to predict the solvation free energies at different temperatures 277K, 298K and 313K. All of the three sets of data compare well with the experimental values. In conclusion, the theoretical tool used in the project provides accurate and fast prediction of solvation free energies in water systems. The same method will be applied to other solvents like octanol in the future to expand its applications.

Classical Density Functional Theory for Methane Adsorption in Metal-Organic Framework Materials

Yun Tian

Advisor: Jianzhong Wu

Natural gas is considered as a promising alternative to petroleum as the next generation of primary transportation fuel owing to relatively smaller carbon footprint and lower SO_x/NO_x emissions and to fast developments of shale gas in recent years. Since the volumetric energy density of methane amounts to only about 1% of that of gasoline at ambient conditions, natural gas storage represents one of the key challenges for prevalent deployment of natural gas vehicles (NGVs). In this work, we present a molecular thermodynamic model that is potentially useful for high-throughput screening of nanoporous materials for natural gas storage. We investigate methane adsorption in a large library of metal-organic frameworks (MOFs) using four versions of classical density functional theory (DFT) and calibrate the theoretical predictions with extensive simulation data for total gas uptake and delivery capacity. In combination with an extended excess entropy scaling method, the classical DFT is also used to predict the self-diffusion coefficients of the confined gas in several top-ranked MOFs. The molecular thermodynamic model has been used to identify promising MOF materials and possible variations of operation parameters to meet the ARPA-E target set by the U.S. Department of Energy for natural gas storage.

Spore-based Biocatalysis for Improved Stability and Cofactor Regeneration

Long Chen

Advisor: Xin Ge

Enzymes are widely used in chemical synthesis of medicines and biofuels, but largely limited by their costly purification, low stability, and lack of reusability. In this study, we intend to address these issues by immobilizing enzymes on surface of *Bacillus subtilis* endospores. Particularly, xylose reductase (XR) and phosphite dehydrogenase (PTDH) were successfully displayed on spore surface via the cohesin-dockerin interactions, and their thermostability and reusability were tested and compared with free enzymes. It was found that compared with cotB/C, cotG displayed the highest amount of enzymes, equivalent to 1.7×10^3 enzyme molecules per spore. The thermostability of immobilized XR was enhanced 3.2 and 5.7 times at 25 °C and 37 °C, respectively, compared with free XR. When both XR and PTDH were displayed through two pairs of cohesin-dockerin derived from *Clostridium thermocellum* and *Ruminococcus flavefaciens*, the regeneration of NADPH was achieved successfully. We further manipulated the ratio between XR and PTDH by changing the copy number of *R. flavefaciens* cohesion, which is associated with PTDH. After being confirmed by Western Blot, overall reaction rate in the case of XR/PTDH = 1:3 ratio was 1.6 times of 1:1 ratio. In the future, we plan to build secondary cohesin-dockerin scaffoldins, in order to increase the loading density of enzymes on spore surface, and to achieve enhanced substrate channeling. In conclusion, spore-based enzyme display technologies hold promises for wide applications in biocatalysis.

Development of a colorimetric assay to assess ester production and enable engineering of ester synthesis in the yeast *Kluyveromyces marxianus*

Ann-Kathrin Loebs

Advisor: Ian Wheeldon

Ethyl acetate and other short-chain volatile esters have great industrial potential and the global demand of ethyl acetate is at 1.7 million tons annually. Currently, production of ethyl acetate solely relies on energy–intensive processes that are dependent on fossil fuels and are thermodynamically unfavorable. Microorganisms have high potential as production units for commodity chemicals and biofuels as they are able to convert varieties of substrates into fuels and fuel precursors and are thus not depend on fossil fuels. Recent accomplishments in the fields of protein and metabolic engineering have enabled tuning of a microorganism towards high yield, high titer production of specific chemicals. A strong candidate for ethyl acetate synthesis is *Kluyveromyces marxianus* because it has several advantages compared to traditional yeasts, making it especially suitable for industrial applications. Aside from its recognition as GRAS (generally recognized as safe) organism, it can be cultured at elevated temperatures, lowering the risk of contamination. Furthermore, *K. marxianus* is characterized by its very fast growth that is nearly twice as fast as the growth of the model yeast *Saccharomyces cerevisiae*. Along with its ability to metabolize a variety of substrates *K. marxianus* is an excellent candidate for biotechnological production of chemicals. Previous research suggests that *K. marxianus* produces a great amount of ethyl acetate during fermentation. To identify ethyl acetate production pathways and increase yield of ester production in *K. marxianus* it is necessary to genetically modify the yeast and subsequently screen a large number of colonies for ethyl acetate production. Traditionally ethyl acetate production has been assayed by headspace gas chromatography, a low throughput method, which is tedious and time-consuming. To enable high throughput screening of ester producing yeast strains a simple and rapid colorimetric assay was developed. Here ester detection is based on the formation of ferric hydroxamate, a stable red colored complex. The assay has found to be roust and sensitive and can be applied to samples from yeasts and bacteria. Using this newly developed ester detection assay we are able to quantify ethyl acetate production yields of different *K. marxianus* strains in a simple and time-efficient manner.

Enzyme-DNA Nanostructures for Enhanced Hydrolysis of Organophosphates

Aaron Toop

Advisor: Ian Wheeldon

Organophosphates are a widely used component in many pesticides as well chemical weapons. These molecules work as acetylcholinesterase inhibitors causing loss of muscle function and eventually death by respiratory failure. While these chemicals have proven useful in agriculture for the extermination harmful insects, organophosphates have infected the surrounding soils and are being stockpiled as a chemical weapon. Safe and effective ways to destroy of these stockpiled and environmentally dispersed organophosphates is a main objective for the US Military. The most common method for removing these stockpiles currently is incineration, which has several draw back including cost, energy sustainability, and the release of toxic compounds into the environment. Phosphotriesterase (PTE) found in soil bacteria has been shown to effectively hydrolyze organophosphates into less toxic products. While PTE has a high affinity for paraoxon, the reaction can be made more efficient through the use of posttranslational modifications. It has been shown that DNA interacts with small molecules through several different mechanisms including groove binding, intercalation, and coulombic interactions. Manipulating these mechanisms by changing the DNA sequence as well as creating small nanostructures of different geometries allows for the effective control of the local substrate concentration. DNA sequences and structures were designed based on data collected from computer simulations, FTIR, and circular dichroism experiments. The data collected allowed for the determination of the most likely mechanism binding and showed it to be grove binding. Using a bifunctional crosslinker to activate the DNA will allow it to be conjugated to the enzyme creating an Enzyme-DNA nanostructure. Initial kinetic experiments have shown parameters of the wild-type PTE-S5 enzyme to be in agreement with published results. Further experiments will characterize the enhancement of hydrolysis caused by the DNA, as well the demonstrating the effective control of specific substrate concentration near the enzyme. DNA tiles will be used to investigate the control of reaction intermediate diffusion along cascade reactions.

POSTER PRESENTERS

Development of Novel Simultaneous Saccharification and Isomerization (SSI) Technology to Enhance Fructose Production for Catalytic Conversion into Drop-In Fuels

Christian Alcaraz

Advisor: Charles Wyman

Secondary fuel precursors (SFP), e.g., furfural, HMF, and levulinic acid, made from sugars in cellulosic biomass can be thermo-catalytically converted into "drop-in" fuels, i.e., hydrocarbons that are compatible with the existing fuel infrastructure. Biological saccharification of glucan using *C. thermocellum* promises to release glucose from glucan in biomass with high yields without the need for a separate enzyme productions step, thereby potentially reducing the cost compared to traditional cellulase enzymes. However, catalytic processes can realize higher SFP yields from fructose than from glucose. Thus, the objective of this research is to develop a novel approach called simultaneous saccharification and isomerization (SSI) to convert the glucose released by *C. therm* saccharification into fructose in a single step. In particular, biomass hydrolysis by *C. thermocellum* supplemented with β-glucosidase to reduce glucan consumption will be coupled with simultaneous conversion of that glucose into fructose by glucose isomerase. Advantages of producing fructose directly from cellulose by employing wild type *C.thermocellum* through SSI include 1) elimination of separate enzyme production, 2) negligible or no requirement for adding expensive fungal cellulases, 3) no need for genetic engineering, and 4) elimination of a separate isomerization step. As a first step in developing this novel concept, 50 g/L and higher concentrations of Avicel® PH101 cellulose were saccharified by *C. thermocellum* supplemented with exogenous β-glucosidase and a commercial glucose isomerase at 60°C to 70°C and pH of 4.5 to pH 7.5. The breakdown of cellulose was monitored by HPLC to determine conversion of cellulose to sugars and the selectivity of the sugars released to fructose. The next step will be application of SSI to glucan-enriched and highly digestible solids produced by our novel pretreatment called THF Co-solvent Enhanced Lignocellulosic Fractionation (CELF) when applied to corn stover at optimum SSI conditions.

Applications of 2-Dimensional Gas Chromatography coupled with Time of Flight and Mass Spectrometry

Harshal Vijay Gade

Advisor: Kelley Barsanti

Many of the products we use in our life are mixtures. From the butter on our toast and glass of juice next to it, to the petrol in our cars, countless commonly used products can be separated, analyzed and quantified. Analysis of the constituents can help us understand the detailed properties of the entire product. From there, we can modify properties and generate new applications of common products. Two-Dimensional Gas Chromatography coupled with Time-of-Flight Mass Spectrometry (GC×GC/TOFMS) is one such separation instrument that is applied in countless chemical industries. The GC×GC/TOFMS has two separation columns coupled by a modulator that controls the flow rate of sample material from the first to the second column. The entire sample material gets subjected to both separations often allowing more detailed analysis than can be achieved with one-dimensional GC/MS, particularly when samples are complex. One such application, relevant to the modern world, is analysis of crude oils and other fuels which are very complex in nature. Fuels can be separated depending upon properties such as viscosity, hydrocarbon composition, unsaturation and degree of molecular branching. To satisfy the rising demands for fuels and to meet more stringent regulations, the petroleum industry faces the challenge of evaluating various complex crude oils, generating new cuts and upgrading heavier cuts, all of which lead to different petroleum products with various properties. These efforts are not possible unless the separation and characterization of individual components of complex crude oil mixtures and petroleum products can be achieved, which is greatly facilitated by instrumentation such as GC×GC/TOFMS. GC×GC/TOFMS can also be used to study fuels after combustion. In this work, composition of different fuels will be analyzed using GCxGC/TOFMS. Samples will be taken prior to combustion; post combustion samples will be taken from emissions of vehicles under different operating conditions, including using different control technologies. The post-processed data, describing gas and particle composition of fuels and combustion emissions will help scientists and engineers to better understand and mitigate various health and environmental effects of vehicle emissions.

Synthesis and application of highly reactive TiO_2 nanocrystals to catalytically remove toxic hexavalent chromium

Gongde Chen

Advisor: Haizhou Liu

Hexavalent chromium, Cr (VI), naturally occurring or coming from Industrial effluent, is high toxic and carcinogenic. California regulated the Maximum Contaminant Level (MCL) for hexavalent chromium at 10 μg/L for drinking water. Concerns about Cr (VI) on human health and environment require the transform the more toxic hexavalent form of chromium to the less toxic trivalent form.

In this project, TiO_2 nanocrystals with high reductive power were synthesized for the first time by inexpensive thermal hydrolysis reactions and used as the catalysts for the reduction of Cr (VI) to Cr (III) under UV irradiation. Electrons coming from conduction band of TiO_2 were utilized as the reductive reagent for the removal of Cr (VI). The intrinsic nanostructures of the prepared TiO_2 nanocrystals can trap the photo-generated holes and effectively donate electrons for the reduction reaction. This unique feature is able to prevent the introduction of commonly used organic scavengers for holes. Fast elimination of Cr (VI) can be achieved on the time scales of seconds and high reductive capacity by the TiO_2 nanocrystals was achieved. The performance of catalyst was maintained in complex water chemical matrices without interference by inorganic species and organic compounds commonly present in source water. The outcome of this study will lead to the development of a cost-effective and highly efficient chromium removal technology.

A Kinetic Study of the Light-Induced Desorption of CO from Active Heme Sites of cytochrome *c*: bovine heart

Sergei Hanukovich

Advisor: Phillip Christopher

Photocatalysis provides a novel means of controlling a single step in a complex reaction mechanism, which cannot be achieved by varying temperature or pressure. Such control can play an important role in optimizing reaction selectivity dramatically. With ever growing interest in the production of efficient biofuels, it has become important to study the effect of wavelength specific photons on bio-catalysts. Cytochrome *c* was studied due to its important role in the human body and the extensive research that has already been conducted on it.

We worked to develop a fundamental understanding of the kinetics associated with the desorption of CO from cytochrome *c* active sites as functions of light wavelength and intensity. The cytochrome *c* was first reduced, which worked to change the charge state of Fe. Then the pH of the enzyme was lowered (< 3) to denature the enzyme and allow for CO to readily diffuse to the Fe centre. Using a UV-Vis, a CO gas line, and a Newport light source, we were able to adsorb and desorb the CO from cytochrome *c* as well as measure the solution's absorption spectra.

Upon adsorption, CO formed a weak, linear bond with Fe in the heme group of cytochrome *c*. Formation of the CO-Fe bond created hybrid orbitals between the two molecules that significantly changed the system's absorption spectra. The other, minor spectral changes were attributed to the formation of new, vibronic energy levels. When the system was exposed to light, the CO-Fe bond was readily broken and it is believed (more studies needed) that the CO diffused through the heme's Cu centre before effectively desorbing from cytochrome *c*. Quantitatively, we were able to show that the absorbance spectra and the light kinetics spectra follow similar, expected trends due to different electronic transitions associated with the ligands' π bonds. It should be noted that CO adsorption to Fe sites on an enzyme experienced similar light-induced kinetics to that of CO adsorption to a Pt surface as shown in previous research by Matt Kale.

Plasmonic Resonances: Size and Shape Dependencies in Na Nanoparticles Using Real-Time Density Functional Tight Binding (DFTB) Methods

Niranjan Vasant Ilawe

Advisor: Bryan Wong

Recent advances in the study of local surface plasmon resonances (LSPRs) has led to the emergence of novel applications in the fields of chemical and biological sensing, optical transmission, nanophotonic devices, and energy harvesting. Crucial to the advancement of such applications is the control of LSPRs in metallic nanoparticles by varying their shape, size, composition, and surrounding environment.

The theoretical description of these plasmonic resonances is challenging in metallic nanoparticles, especially between the 2 to 10 nm sizes, where the LSPRs become sensitive to the quantum nature of electrons. In this regime, the system is too small to be accurately described using classical electrodynamic theories but still too large for ab-initio quantum mechanical calculations. We describe and utilize a real-time density functional tight binding (DFTB) based method to predict the optical properties of Na nanoparticles and to analyze their dependence on size and shape. DFTB is an approximate quantum mechanical method derived from density functional theory (DFT) based on a second-order expansion of the DFT total energy expression. This formalism maintains the accuracy of time dependent density functional theory (TD-DFT) but at a fraction of the computational cost.

The shape and size dependence of LSPRs in Na nanoparticles of spherical and icosahedral shapes are studied using real-time DFTB calculations. Na nanoparticles containing 13 to 1827 atoms with corresponding diameters from 0.7 nm to 6 nm are analyzed using the DFTB method. The preliminary calculations of absorption spectra and plasmon energies reveal two interesting trends for the two shapes of NP. For spherical particles, plasmon energies decrease with increasing particle size from 0.7 to 6 nm, while for icosahedral particles a nonmonotonic trend from a blue shift to red shift and back to blue is observed as the particle size increases. These preliminary observations furnish ample motivation for exploring the size and shape dependence of LSPRs further. We propose to study this phenomenon for a wider variety of shapes and sizes. In addition, we are also interested in local field enhancements produced by surface plasmon couplings for single nanoparticles as well as the more interesting case of dimers.

Harvesting energy from desalination concentrate via Electric double-layer capacitor

Tushar Jain

Advisor: Haizhou Liu

Many parts of the world, including California, is facing one of the most severe drought on record. Desalination of ocean water is seen as one of the alternatives for supplying freshwater compared to other conventional options. All the available desalination units such as reverse osmosis or flash distillation produce a large amount of concentrate.

High salinity level in desalination concentrate means high chemical energy. If harvested, this chemical energy can be transformed to more useful form of energy. The proposed idea aims at developing a new technology for beneficial use of desalination concentrate.

Capacitive mixing (CAPMIX) is a novel technique based on the use of naturally occurring electric double layer (EDL) inside the porous capacitor. In CAPMIX, the generation of energy is directly linked to the mixing process, so there is no need for intermediate processes nor conversions, which simplify its application. The EDL capacitor is made of two porous carbon electrodes immersed in salt water. The electrodes are then connected to a power supply so that one becomes negatively charged and the other positively charged. Since salt water consists of positively charged sodium ions and negatively charged chloride ions, the positive electrode attracts the chloride ions and the negative electrode attracts the sodium ions. With the help of the electrostatic force keeping the oppositely charged ions near their respective electrodes, the EDL capacitor can store a charge.

To extract the charge, fresh water is pumped into the device, causing the sodium and chloride ions to diffuse away from the electrodes against the electrostatic force. In other words, the work done by the fresh water to extract the salt water is converted into electrostatic energy, appearing as an increase in voltage between the electrodes. Overall, the system transforms mechanical work (the mixing of the salt and fresh water) into electrostatic energy that can be extracted as usable power. The only energy required by the system is the initial power source to jumpstart the capacitor, and power to pump fresh and salt water into the device.

Synthesis and Characterization of Selectively Attached Gold Nanoparticle Buckypapers.

Rahul Jay

Advisor: Juchen Guo

Carbon Nanotube-metal nanoparticle (CNT-M's) composites have been subject for serious research in the past decade. These CNT-M's have been proposed to have wide variety of applications such as glucose bio sensors, voltammetric detection of mercury, water treatment etc. This study focuses on synthesizing of a buckypaper consisting of these CNT-M (where M is gold (Au)) composites. A buckypaper is a thin sheet of aggregated CNT's, there applications include vehicle and personal armor, next generation electronics etc. synthesizing of these CNT-Au composite buckypapers consists of three major steps. **1.** As obtained pristine CNT's (single walled and muti walled) were oxidized in a piranha solution to form modified CNT's with hydroxyl and carboxyl functional groups on the nanotube walls. These modified nanotubes where then washed and dried. **2.** The modified CNT's where dispersed in water with a final concentration of .5 mg/ml. The dispersed CNT's were vigorously stirred at 70^0C. A 4mg/ml gold chloride tri-hydrate ($HAuCl_4.3H_2O$) solution was added dropwise into the vigorously stirring solution. The gold salt to CNT ratio was calculated to be 10:1. The temperature of the stirring solution was increased to 80^0C after the addition of the gold salt solution and left overnight. The solution was washed and filtered to wash off the acidic content in the gold solution and re suspended in water with a concentration of .5 mg/ml. TEM samples were taken after this step to confirm the presence of Au nanoparticle on the CNT walls. **3.** Sodium dodecyl sulfate (SDS) surfactant was added to the CNT-Au composite suspension, were the SDS:CNT-Au ratio is 5:1. SDS aids in the well dispersed stable suspension of the composite in water which aids in the filtration process. The new suspension was thoroughly sonicated in high frequency for 1.5 hours, the well dispersed suspension was then filtered out through a polycarbonate low poresize filter membrane once dry the buckypaper was peeled off the membrane and heated in argon at 350C for 2 hours to burn away the SDS. TGA data was also recorded for the decomposition of the surfactant during the heating process.

Improvement of dye-sensitized solar cells by reducing Zn^{2+}/dye complex formation between ZnO nanowires grown by chemical vapor deposition

Kichang Jung

Advisor: Nosang Myung

Crystal aggregation of the Zn^{2+}/dye complex is a known issue for dye-sensitized solar cells (DSSCs) made of ZnO nanowires (NWs). The formation of Zn^{2+}/dye complex impedes the effective electron transfer from the dye to the ZnO photoelectrode. Although ZnO possesses high electron mobility and low recombination probability, DSSCs using ZnO show relatively lower conversion efficiency than those devices using TiO_2 due to the Zn^{2+}/dye formation. The instability of ZnO in acidic dye solution is expected to induce the formation of Zn^{2+}/dye complex because the bonding between Zn and O atoms are broken at the interface of the ZnO and the acidic dye solution. Eventually, Zn atoms are oxidized and released from the ZnO material, forming the Zn^{2+}/dye complex, by combining with the dye molecules. In this research, we focused on reducing the formation of Zn^{2+}/dye complex to improve the efficiency of DSSCs using ZnO NWs grown by chemical vapor deposition (CVD).

The ZnO NWs were synthesized on fluorine-doped tin oxide (FTO) substrate by CVD method in a tube furnace, using Zn powder as the precursor. The synthesis was conducted under 450°C with a mixture of oxygen and nitrogen gas (1:25 ratio by volume). The synthesized ZnO NWs were immersed into the N719 solution in ethanol, at room temperature. By adjusting the soaking time, the amount of Zn atoms released from the ZnO material was controlled. The electrolyte based on iodide/triiodide redox couple was used as a hole transport layer. The Pt on the FTO:glass substrate was used as counter electrode. As a baseline reference, a device using TiO_2 (DSL18NR-T paste) as its photoelectrode was fabricated to compare against the efficiency of the ZnO devices.

The photovoltaic characterization of the fabricated DSSCs showed that the short circuit current of ZnO devices is relatively lower than that of TiO_2, while the open circuit voltage was similar. Specifically, the ZnO cells where the immersed time was the longest showed the lowest short circuit current. From our results, we were able to confirm that the formation of Zn^{2+}/dye complex between the ZnO nanowires negatively impact the efficiency of the ZnO devices.

Electrochemical Control of Biologically Inspired Catalytic Cascades

Louis Lancaster

Advisor: Ian Wheeldon

Much of the current work in protein engineering focuses on making modifications to the structure of proteins to enhance reaction kinetics or broaden substrate specificity. This kind of work is especially beneficial when the reaction of interest can be done with a single protein, but the rate enhancements have diminishing returns across a multienzyme cascade reaction. The overall rate of a cascade reaction can be further enhanced by controlling the diffusion of substrates from one active site to the next. Our work focuses on using design rules elucidated from studies of natural bifunctional enzymes and engineered multienzyme systems to build nanostructured hybrid cascade reaction systems utilizing organic catalysts in conjunction with biocatalysts. TEMPO and its derivatives are used as the organic catalysts covalently bonded to a thermostable alcohol dehydrogenase from *P. furiosus,* AdhD, and the KDPG aldolase from *E. coli.* Various crosslinking chemistries will be exploited to alter which amino acid residues are used for bonding and the distance between the active sites. This allows for the tuning of the spatial orientation of the catalysts to promote substrate channeling and enhance reaction kinetics. Electrochemical methods are used to characterize and control reaction kinetics, while also minimizing over oxidation of the intermediates. Future work will focus on designing more variations of hybrid cascade systems. We also intend to incorporate them the hybrid catalysts into more complex engineered multienzyme systems capable of adapting to various reaction substrates and conditions.

Doping Characteristics of Semi-Conducting Single Walled Carbon Nanotubes

Guanghui Li

Advisor: Robert Haddon

Although semiconducting single-walled carbon nanotubes (SC-SWNTs) have attracted much attention due to their exceptional electronic characteristics and promising applications in nanoscale electronic devices, they are naturally doped p-type under ambient conditions. While an individual carbon nanotube has high conductivity and mobility, the fabrication and application of single nanotube based electronic circuits is still technologically impractical. In order to fully develop the potential of SC-SWNTs in field-effect transistors (FET), chemical sensors, complementary metal-oxide-semiconductor (CMOS) logic circuits and photodetectors (PD), it is important to gain control over the mechanism of conduction (p-type or n-type). Thus we seek to fabricate thin-film electronic devices in which it is possible to adjust the position of the Fermi level. In this work, we doped SC-SWNT thin films with benzyl viologen (BV) and obtained air-stable n-type SC-SWNT films which show high conductivity, which is a promising step toward nano-electronic device fabrication and potentially provides a powerful strategy to integrate n-type with p-type s-SWNTs and enable the preparation of electronic circuitry containing p-n junctions.

Classical Density Functional Theory (cDFT) Study of Impurity Effect on Ionic-Liquid-Based Supercapacitors

Kun Liu

Advisor: Jianzhong Wu

Electric-double-layer capacitors (EDLCs), also known as supercapacitors, are electrochemical devices that store energy by adsorption of ionic species at the inner surface of porous electrodes. Compared with aqueous electrolytes, ionic liquids (ILs) have the advantage of larger potential windows, making them attractive for the next generation of EDLCs with superior energy and power densities. For electrochemical applications, trace amount of impurity (e.g. water, alkali salts, and organic solvents) may affect the key properties of ionic liquids and such effects may be dramatically amplified on their electrochemical performances.

This work aims to provide a comprehensive analysis of the impurity effects on ionic-liquid supercapacitors by using the classical density functional theory (cDFT). A slit pore model is employed for porous electrode in contact with an ionic liquid containing an arbitrary impurity. For simplicity, course-grained models are used for the impurity molecules, cations and anions of ILs. A special emphasis is placed on the effects of both electrolyte and materials impurities on the ionic distributions and the capacitance of various porous electrodes.

The results revealed that, even at very low concentration of impurity in the bulk, the impurity molecules tend to accumulate within subnanometer distance from the charged electrodes due to the binding energy between the impurity and the electrode surface and the distributions of ions in the double layer are affected by the presence of impurity. The impurity dominates the pore wall, excluding much of the conventional anion/cation from the pore and causes a loss in the capacitance. Meanwhile, the oscillatory behavior of capacitance inside nanopores vanishes in the presence of surface affinitive impurities. These predictions await experimental verification.

Selection of Inhibitory Antibodies Using Next Generation High Throughput Sequencing

Tyler Lopez

Advisor: Xin Ge

Matrix metalloproteases (MMPs) are of rising interest in the treatment of cancer due to their roles in tumor growth and invasion. Current enrichment methods for monoclonal antibodies inhibiting specific MMPs involve phage panning and classical ELISA screening, which are usually associated with suboptimal growth conditions and insufficient expression levels of antibody clones. As the result, a significant proportion of potentially inhibitory clones might not be identified using classical screening procedures. As one of the most powerful bioinformatics techniques, Next Generation Sequencing (NGS) allows the rapid analysis of hundreds of millions of individual antibody clones in parallel. By monitoring the enrichment of clones along several rounds of phage panning, we hypothesize that more inhibitory clones can be identified than phage/ELISA studies. Four antibody libraries developed by phage panning against MMP-14 were analyzed using a MiSeq next generation sequencer. A total of 410,756 sequences from the original library, 19,488,812 from the first round, 11,761,506 from the second round, and 50,457 from the third round were analyzed to identify clones with high abundances (>0.001% of the total library). The top ten abundant clones from rounds 2 and 3 were selected for cloning and further testing on their inhibitory functions. Interestingly we found that the prominent clones in round two contained cysteine residues which may result in the formation of disulfide bonds. These disulfide bonds can create a fixed loop structure capable of infiltrating the concave structure of the MMP-14 active site. Another major feature found in almost all prominent clones from rounds two and three is an abundance of positive amino acids which will preferentially bind to the negatively charged active site. So far, at least two of the clones identified are inhibitors of MMP-14.

Characterization of potential surrogates for produce pathogens

Holly Mayton

Advisor: Sharon Walker

Despite the modernization and industrialization of agriculture, pathogenic contamination of fresh produce continues to cause significant foodborne illness outbreaks in the U.S. and around the world. Additionally, increasing environmental challenges have lead to increased usage of manures and recycled irrigation waters in crop production, but these may increase opportunity for bacteria like *Salmonella sp.*, *Escherichia coli O157:H7* and *Listeria monocytogenes* to come in contact with our food. Studies have shown that these pathogens have the ability to attach and survive on produce and handling surfaces. Thus, understanding these pathogens' attachment mechanisms has become a research priority in food safety. However, a growing body of literature suggests that current indicator organisms used in laboratory research are not sufficient representatives of these pathogens in any given environment. Therefore, this study seeks to identify chemical and physical properties of twenty-one potential indicator organisms when grown in both high and low nutrient conditions. Each bacteria sample was grown for eighteen hours and harvested in the stationary phase. Electrophoretic mobility, relative hydrophobicity, and surface charge density were measured using ZetaPALS analyzer, microbial adhesion to hydrocarbons test, and potentiometric titration respectively. The study found that the bacteria species' electrophoretic mobility did not vary greatly with growth conditions, with a few exceptions. Bacteria generally showed significant increases in relative hydrophobicity and surface charge density when grown under lower nutrient conditions. The majority of the data collected was within the expected range for produce pathogens, which is promising for future identification of surrogates.

Removal of Nitrate from Contaminated Water by Electrochemical Reduction on Electrically Conducting Ultrafiltration Membranes

Katherine Muller

Advisor: David Jassby

Nitrate in drinking water poses a serious public health risk which affects water sources in California and around the world. The environmental risks of nitrate are twofold: as a contaminant in drinking water it threatens the health of infants and pregnant women, and in lakes and coastal regions it contributes to algae blooms, eutrophication, and hypoxic "dead zones." However, nitrate is an extremely stable and soluble contaminant, which makes cost-effective removal very difficult. Ultrafiltration (UF) membrane systems provide a highly efficient and economically viable method of water purification, but cannot remove nitrate. I propose that an electrically conducting UF (ECUF) membrane can be designed that will electrochemically reduce nitrate in low-pressure UF systems, which particularly benefits impoverished or rural communities that do not have access to reverse osmosis water treatment.

A study of the Methodology for Assessing Anaerobic Ammonium Oxidation Reactor Start-up Rate

Stephen Robert Opot

Advisor: Mark Matsumoto

Anaerobic Ammonium Oxidation (Anammox) is a relatively new alternative for ammonia removal from wastewaters with low carbon to nitrogen (C/N) ratio. Despite its advantages over traditional nitrification–denitrification systems, one persistent problem is the low growth rate of bacteria resulting in long and difficult start-up periods. Therefore, a methodology for assessing the start-up rate will greatly enhance the use of this technology. In providing the methodology, the influence of key process variables such as pH, feed cycles, C/N etc. on specific nitrogen removal rate will be assessed. Currently, a mixed microbial culture capable of actively oxidizing ammonium to dinitrogen gas in the absence of oxygen, using nitrite as the electron acceptor, is being enriched in two bench scale Sequencing Batch Reactors (SBRs), R1(42 days old) and R2 (5days old). The two SBRs were seeded with biomass from a local pilot scale plant (Degremont Technologies at Hyperion Treatment Plant in Los Angeles, CA) treating thermophilic digester centrate with extreme ammonium concentrations. Analysis of alkalinity, suspended solids, and volatile suspended solid are conducted following the standard methods for examination of wastewater. NH_4^+-N concentrations are determined using the standard phenate method, while NO_2^--N and NO_3^--N concentrations are measured using ion-chromatography. Stoichiometric analysis is employed to estimate the nitrogen removal rate (NRR). The process temperature, pH, DO, and oxidative redox potential (ORP) are monitored using electrode probes. Zone settling test is used to determine the granules' settling velocity (S.V). Biomass will be identified and quantified using Fluorescence Insitu Hybridization (FISH) and 16S rRNA gene analysis using q-PCR. For R1, preliminary results depict the maximum nitrogen removal rate as 0.11 kg N L^{-1} day^{-1} with a maximum specific nitrogen removal rate of 0.42 g N/ (g.VSS day). During the enrichment period, Anammox activity was slight inhibited by pH and DO with optimum activity realized at 7.53 and 1.96mg/L values respectively. Fine tuning of feed influent NH_4^+/NO_2^- ratio has allowed Anammox activity to be maintained with sludge granules S.V of 3.12ft/hr. The system has achieved a feed ratio of 1:1.38 which relates favorably with previously reported ratios of 1:1.32 (Lopez et al, 2008).

On-road real-time sensing for select atmospheric cations and gaseous species

Xinze Peng

Advisor: David Cocker III

Concern has been raised that some atmospheric pollutants might have an impact on the performance of Honda’s fuel cell car. Ammonium (NH_4^+) and sodium (Na^+) cations will displace hydrogen ions (H^+) in the fuel cell’s Proton Exchange Membrane (PEM), while SO_2 and NO_X will react with the platinum anode. Ammonia might attack the cathode directly and it can also be a potential source of ammonium cations. Although the South Coast Air Quality Management District (SCAQMD) provides us the concentrations of all these pollutants, it is possible that these concentrations are higher on the road. Therefore, a short-period intensive study is proposed to identify transient and average exposure levels to these species on Southern California roadways and compare these values to local air monitoring station data.

A mobile sensing platform will be built for high time resolution sensing of roadway NH_4^+, Na^+, SO_2, NO_X and ammonia, coupled with video and GPS to identify transient and average levels of these species identified on Southern California roadways. This platform will be equipped with an Aerodyne Aerosol Mass Spectrometer, a Selected Ion Flow Tube Mass Spectrometer, NO_X analyzers and SO_2 analyzers. A 3-dimensional map will be created of location and observed species throughout Southern California by linking GPS location to observed species. Also, video graphic recordings will allow identification of vehicles and estimated following distances during major transients for each of the species.

Graphene-Molybdenum hybrid for bio-chemical sensing devices

Tung Pham

Advisor: Ashok Mulchandani

Two-dimensional (2D) nanomaterials, such as graphene, hold great potential for next-generation electronics owing to their unique properties such as high carrier mobility, fast response time and high transparency. However, the absence of an electrical band gap in graphene limits its applications as a field-effect transistor (FET). To overcome this limitation, other 2D nanomaterials such as transitional metal dichalcogenides (TMDs) have been studied and attracted significant research interests. TMDs consist of 2D stacked layers of covalently bonded transition metal and dichalcogenide atoms arranged in a hexagonal lattice where adjacent layers are held together by relatively weak van der Waals forces. MoS_2 is one such example of TMD that exhibits a direct band gap of 1.8 eV for single layer MoS_2 and an indirect band gap of 1.2 eV for bilayer and few layers. FETs based on single-layer MoS_2 exhibit an on/off ratio of $> 10^8$ at room temperature. However, unlike graphene-based FETs which typically exhibit a high mobility of 5,000 - 10,000 $cm^2V^{-1}s^{-1}$, MoS_2-based FETs show a much lower mobility of ~100 -200 $cm^2V^{-1}s^{-1}$.

One possible way of tailoring the electrical properties of a material is by stacking individual layers of different 2D materials to form a vertical heterostructure. In this work, we explore the electrical properties of graphene - MoS_2 hybrid films synthesized by direct growth of single-layer and multi-layer MoS_2 on graphene using chemical vapor deposition (CVD). By taking advantage of the high charge carrier mobility of graphene and the finite band gap of MoS_2, we fabricate FETs which consist of graphene - MoS_2 hybrid as the conducting channel. Finally, we explore the potential of this new hybrid structure as a platform for electro-chemical sensing by testing its selectivity and sensitivity for different volatile organic compounds (VOCs).

Secondary Organic Aerosol (SOA) Forming Potential from Emerging Light-Duty Gasoline Direct Injection Vehicles

Patrick Roth

Advisor: Akua Asa-Awuku

Motor vehicles are large contributors of volatile organic compounds (VOC), NO_x, CO, and Particulate Matter (PM). Primary organic aerosol (POA) and gas phase compounds significantly contribute to the production of secondary organic aerosol (SOA) which may adversely affect health, agriculture, and global climate. SOA accounts for a majority of the PM in the atmosphere.

Information on SOA formation from modern light duty gasoline vehicles such as (GDI) vehicles is limited, and therefore is not fully understood. With the increased pressure to meet fuel economy standards, the market for gasoline direct injection GDI equipped vehicles is expected increase to approximately 60% by 2016 in the US. GDI engines have been shown to produce higher soot and total hydrocarbon (THC) emissions when compared to PFI, therefore it is vital we understand the impacts of primary emissions and subsequent SOA forming potential.

A new mobile atmospheric chamber (MACh) in UCR's Center for Environmental Research and Technology (CE-CERT) facility has been developed to characterize primary and secondary aerosol emissions. With a volume of $30m^3$, MACh is one of the largest mobile reactors available in the world. The chamber is contained in a lightweight aluminum frame on wheels. This allows the chamber to be positioned close to the combustion source where direct emissions are collected. MACh provides a unique opportunity to observe the effects of modern vehicle technology, advanced control technologies, vehicle age, and new fuel formulations on both primary and photochemical aged emissions in a controlled and repeatable environment.

Methane Bi-reforming in a Heat Exchanger Platform Reactor

Partho Sarothi Roy

Advisor: Akua Asa-Awuku

CO_2 emitted from industrial sources are released to the air which is known as the component for most radiative forcing increase by emission of this planet. The emitted CO_2 can be captured and then mixed with natural gas (CH_4) and steam to convert into valuable product by performing the bi-reforming (steam reforming and dry reforming) reactions thermo-chemically. ASPEN Plus process simulator was used for studying the reforming of CO_2-CH_4-steam mixture. The simulation runs were conducted in the CH_4 to CO_2 ratio of 40:60, 50:50, 60:40, CH_4 to steam ratio of 1.00~2:00 with 0.25 incremental interval, and in the temperature range of 923~1123 K. Primarily, the reforming data were obtained for CH_4 and CO_2 conversion, product yield, process thermal efficiency through Gibbs free energy minimization. For almost all of the cases, the CH_4 conversion at 1048 K was more than 99%. The CO_2 conversion was increasing with the decreasing steam to methane (S/C) ratio and increasing temperature. The most interesting point for steam conversion was initially increasing (mostly steam reforming) and finally decreasing trend (mostly dry reforming) with a transition temperature depending on the S/C ratio. Process thermal efficiencies were increasing with temperature, with a maximum efficiency at in between 1023 and 1073 K, and then it showed decreasing trend. The equilibrium data are to be compared with experimental data over different [Pd-Rh/($CeZrO_2$•Al_2O_3)]/metal foam catalyst. Dry reforming and bi-reforming catalyst synthesis complete. The physical characterization of these new catalysts is ongoing. Dry reforming & bi-reforming experiments over the catalyst by using the Heat Exchanger Platform (HEP) reactor is nearing completion. Experimental data from HEP reactor will be used to update the process simulation and to identify the optimum conditions at desired reaction temperatures for all the catalysts.

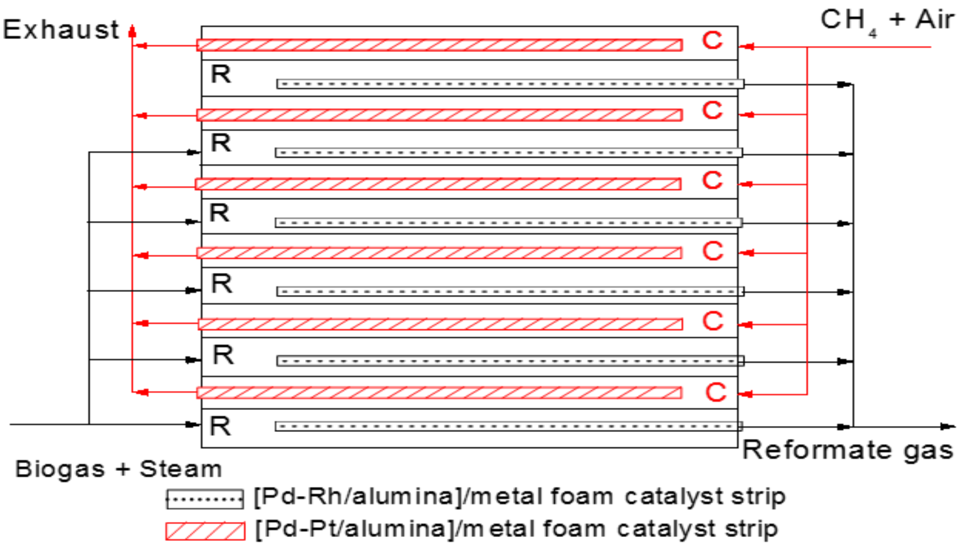

Figure. Schematic diagram of the microchannel-structured HEP reactor system for steam reforming of biogas coupled with catalytic combustion of methane.

Engineering of *Yarrowia lipolytica* for the production of dicarboxylic acids

Cory Schwartz

Advisor: Ian Wheeldon

Yarrowia lipolytica has been the focus of a wide range of metabolic engineering studies due to its ability to make and accumulate lipids to a high level. In this work, we engineer a single plasmid CRISPR-Cas9 system for *Y. lipolytica* that facilitates rapid, markerless gene disruption and gene insertion. Functional CRISPR-Cas9 systems require nuclear localized Cas9 and single guide RNA (sgRNA). To facilitate nuclear localization of Cas9, a codon optimized Cas9 from *S. pyogenes* was designed and the nuclear localization tag SV40 was fused to the C-terminus. For sgRNA expression, a range of different promoters were tested. The constitutive TEF promoter, an RNA polymerase II promoter, was used in conjunction with self-cleaving ribozymes to express the mature sgRNA. Five different RNA polymerase III promoters, including three synthetic promoters, were screened as well. The efficiency of the optimal sgRNA expression system to functionally disrupt the *pex10* gene, essential for growth on oleic acid and used as a reporter gene, reached 95%. In order to facilitate homologous recombination, the *ku70* gene was then disrupted. It has been shown that disruption of *ku70* greatly increases the rate of homologous recombination in *Y. lipolytica*. A two plasmid system, in which one plasmid contains the CRISPR system and the other a homologous recombination donor sequence with a Ura3 marker, was then tested in both the wildtype and the *ku70* deficient strain. The rate of homologous recombination was quantified, and was as high as 100% for the *ku70* deficient strain. Markerless homologous recombination was then attempted.

Water Reuse for Agriculture

Quynh Tran

Advisors: David Jassby, Kurt Schwabe

Water scarcity has become a problem in semi-arid and arid regions. Since the major water use is for irrigation, it is very important to consider alternative irrigation sources for areas with limited freshwater resources.

One potential irrigation water resource is treated wastewater for agricultural fields located near urban centers. Treated wastewater is defined as treated municipal sewage from which excess plant nutrients, organic compounds and pathogens have been removed. In addition to water, treated wastewater contains an appreciable amount of nutrients necessary for plants growth, and can reduce the need for synthetic fertilizer. However, treated wastewater contains high concentrations of salts, heavy metals, and pathogens, which might cause adverse effects to human, plants and soils. The scope of this project is to develop a regional water reuse decision-support model (RWRM) using GAMS software to evaluate the impact of using treated wastewater for agriculture and help water district managers and irrigators to make informed and cost-effective decisions. The model will evaluate different wastewater treatment technologies and their impact on municipal wastewater effluent qualities as well as the benefits and costs of these options.

Characterizing the Oxidation of Alcohol Amines by the Nitrate Radical

Paul Van Rooy

Advisor: David Cocker III

Alcohol amines are used in control technologies designed to capture and sequester carbon dioxide from the flue gas of coal-fired power plants. As this carbon capture process becomes more common, it is important to understand the potentially detrimental environmental and human health impacts associated with the release and subsequent reaction of these compounds in the atmosphere. A number of experiments were conducted in a 37.5 m^3 Teflon atmospheric chamber to characterize the oxidation by the nitrate radical of several alcohol amines including monoethanolamine, 2-methylaminoethanol, and dimethylethanolamine. A scanning mobility particle sizer was used to determine the size distribution and concentration of the produced aerosol. Both gas-phase and particle-phase chemical composition were measured using a selected ion flow tube mass spectrometer and a high resolution – time of flight – aerosol mass spectrometer, respectively. The scanning mobility particle sizer measured a significant concentration of particulate matter during the alcohol amine experiments. The chemical composition of the formed aerosol varied with each amine. Gas-phase nitramines, possible carcinogens, were observed in some of the experiments. Amine nitrate salts were the dominant aerosol produced. Amine oligomers were also observed. The particulate matter concentration and chemical composition of the formed aerosol implicate alcohol amines may contribute to climate forcing as well as adverse human health impacts.

Spore-based Biocatalysis in Organic Solvents

Elmer Wei

Advisor: Xin Ge

Biocatalysis in organic solvents is an alternative to biocatalysis in water with the potentials for enhancement of enzyme properties and development of new reactions and processes. Unfortunately, at the same time, a pure organic solvent system works unfavorably to the conformation and function of most enzymes. Methods of improving such enzymes' performance in organic solvents include enzyme immobilization, optimal organic solvent choice, and the ratio of said organic solvent and water. *Neurospora crassa* xylose reductase (ncXR) and *Pseudomonas stutzeri* phosphite dehydrogenase (PTDH) have been found to make an efficient cofactor regeneration system with promising large-scale industrial applications for its reduction of cofactor cost. Furthermore, these enzymes can be expressed and immobilized on *Bacillus subtilis* spores for enhanced performance in conventional aqueous system. This research will test the stability and activity of spore-based biocatalysts in organic solvents. Activity will be determined by UV spectrophotometry via the consumption or production of the cofactors, and the confirmation of products will be determined by high performance liquid chromatography. The results of the experimental system will be compared with those of the control aqueous system. Further optimization such as adjusting choice of organic solvent, ratio of organic solvent to water, and ratio of ncXR to PTDH will be performed for the development of a more efficient and effective cofactor regeneration system.

A study of core-shell structure for high-performance li-ion battery

Zheng Yan

Advisor: Juchen Guo

Silicon (Si) is considered as a very promising anode material for high-performance Li-ion batteries. It has specific capacity of ~4200 mAh/g, which is beyond challenge. Moreover, Silicon is the eighth most common element in the universe by mass. However, two major defects of silicon anode need to overcome before commercial production. First, the huge volumetric expansion and contraction resulted by Si−Li alloying/ dealloying, which can cause a continuous decomposition of the electrolyte. Second, Silicon (Si) has a relative low electronic conductivity, so electron transfer mainly depends on diffusion. So there are a lot of applications about encapsulation of inorganic nanoparticles with polymers. In these cases, our primary goal is to improve the stability of the encapsulated particles. In my experiment, our group's objective is to maintain the silicon volume in the charging process, caused by the formation of Lithium-Silicon alloying. So we introduced the Silica/Polystyrene composites, and further carbonized it then get Silica-Carbon composite. Finally, we use magnesium to reduce the silica-carbon then we get Silicon-carbon composite.

In order to get the formation mentioned above, first step is to using Stöber's method to make nano-sized silica particles, then grafting MPS on silica particles. Next step is to polymerizing Polystyrene/Polyacrylonitrile to chemically boned to the modified silica surface. Third step is carbonization. Fourth step is magnesiothermic reduction of Silica to Silicon. After these, final anode material is synthesized, then making battery.

During all these steps, Data such as XRD, SEM, TEM, TGA and electrochemical performance are needed to be collected.

In summary, we encounter lots of challenges. For the polymerization procedure, we tied three methods and finally found an optimal one. As for the magnesiothermic reduction, we are still trying different amount of magnesium and temperature to reach the most ideal reduction condition.

Study of the Viability of Dimethyl Carbonate as an Alternative Fuel for the Transportation Sector

Jiacheng Yang

Advisors: David Cocker III, Tom Durbin

Diesel vehicles and engines play a vital role in the transportation sector and the overall economy. Diesel engines have the advantages of better fuel economy and higher power output compared to gasoline engines. Most air quality issues in cities are associated with the burning of fossil fuels in internal combustion engines, including a large fraction of pollutants from diesel engines. Diesel engines generally have lower emissions of hydrocarbons (HC) and carbon monoxide (CO) compared to gasoline engine. However, diesel engines also have higher emissions of particulate matter (PM) and nitrogen oxides (NOx), and it is hard to reduce these pollutants simultaneously without exhaust aftertreatment, which leads to extra cost.

There is an increasing urgency in finding ways to control tailpipe emissions for diesel engines to meet the increasingly stringent emissions standards being implemented all over the world, while improving their fuel economy and maintaining costs at reasonable levels. Alternative diesel fuels are another important option that offers the potential to reduce pollutant emissions, petroleum use, and greenhouse gases (GHGs). Alternative diesel fuels can be a lower cost option for reducing emissions compared to exhaust aftertreatment devices, especially in developing countries with more severe air quality problems.

Dimethyl carbonate (DMC) as an alternative diesel fuel that can be produced sustainably from a variety of renewable biomass sources in either domestic or foreign markets. This study is to conduct a preliminary evaluation of the viability of DMC as a transportation fuel. 5%, 12.5%, 20%, and 30% DMC diesel blends have been made and tested on a 1991 Detroit Diesel Corporation (DDC) 4 stroke, 6 cylinder diesel engine at CECERT's Heavy-duty engine dynamometer in accordance with the Federal Test Procedure (FTP). Standard emissions measurements of total hydrocarbons (THC), CO, NO_x, PM, particle number (PN) and carbon dioxide (CO_2) were made for each test.

Removal of surfactant-stabilized oil with γ-Fe_2O_3 magnetic nanoparticles

Xiaobo Zhu

Advisor: David Jassby

Wastewater containing emulsified oil is difficult to treat due to the presence of highly stable oil droplets stabilized by surfactants. New technology is needed to separate the emulsified oil droplets from the wastewater. We hypothesize that nanoparticles can stabilize the oil droplets to form Pickering emulsions, and that those emulsions can be more easily removed. The stability of Pickering emulsions is related to the functionalities of the nanoparticles. We use magnetic nanoparticles (y-Fe_2O_3) with different polymer modifications to remove emulsified oil droplets stabilized by ionic and nonionic surfactants under three water conditions: millipure water, 10 mM NaCl, and 10 mM $CaCl_2$ solutions. Particles were characterized by FT-IR and TGA, and the removal efficiency was characterized by Total Organic Carbon (TOC) analysis.