DEPARTMENT OF CHEMICAL & ENVIRONMENTAL ENGINEERING: FALL SYMPOSIUM

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SYMPOSIUM PRESENTERS

Wastewater Reuse for Agriculture: Development of a Regional Water Reuse Decision-Support Model (RWRM) for Cost-Effective Irrigation Sources

Quynh K. Tran
Advisor: Dr. David Jassby

Water scarcity has become a critical problem in many semiarid and arid regions. The single largest water use in such regions is for crop irrigation, which typically relies on groundwater and surface water sources. With increasing stress on these traditional water sources, it is 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. In addition, treated wastewater can contribute an appreciable amount of necessary nutrients for plants. The suitability of reclaimed water for specific applications depends on water quality and usage requirements. The main factors that determine the suitability of recycled water for agricultural irrigation are salinity, heavy metals, and pathogens, which cause adverse effects on human, plants, and soils. In this paper, we develop a regional water reuse decision-support model (RWRM) using the general algebraic modeling system to analyze the cost-effectiveness of alternative treatment trains to generate irrigation water from reclaimed wastewater, with the irrigation water designed to meet crop requirements as well as California's wastewater reuse regulations (Title 22). Using a cost-minimization framework, least-cost solutions consisting of treatment processes and their intensities (blending ratios) are identified to produce alternative irrigation sources for citrus and turfgrass. Our analysis illustrates the benefits of employing an optimization framework and flexible treatment design to identify cost-effective blending opportunities that may produce high-quality irrigation water for a wide range of end uses.

Recovery of Phosphorus and Salt Removal from Reverse Osmosis Concentrate in Brine Line

Tushar Jain
Advisor: Dr. Haizhou Liu

The inland empire Brine Line was installed by Santa Ana Watershed Project Authority in collaboration with Orange County Sanitation District to export salt from the inland districts of Southern California to the ocean. It transports the salty wastewater concentrate from groundwater reverse osmosis process and the wastewater generated from the industries, boiler blowdown and power plants. The supersaturation of inorganic salts due to high-rejection membrane processes cause crystallization of sparingly soluble inorganic salts of calcium, magnesium, phosphate, carbonate and silica. Scaling in the brine line is a huge problem as it affects the distribution and can require expensive maintenance if left unaddressed.

Phosphorous is a valuable element that is essential as a fertilizer in agricultural and food industry. However, it has been speculated that the world phosphorus production from phosphate rock will inescapably decrease due to the depletion of its natural reserves. Reverse osmosis (RO) concentrate has a considerable level of phosphorous, estimated to be around several mg/L. High phosphorus content due to concentrate disposal can lead to eutrophication in receiving water bodies.

We propose to extract the phosphorus from the inorganic concentrate by precipitating it in the form of its calcium salt, hydroxyapatite (HAP). RO processes dose the feed with antiscalants to avoid scaling on the membrane surface due to concentration polarization. Thus, the effects of presence of antiscalant will be evaluated on the precipitation of HAP. A thorough study of precipitation kinetics and crystallization mechanism have been proposed in this study. Impact of silica is also studied in order to study the effect of induced precipitation. These extent of precipitation are measured in the form of turbidity of the system measured by using a HACH 2100-N turbidimeter.

It was observed that the presence of antiscalant delayed the precipitation due to its chelating effect. The addition of silica does increase the precipitation rate and thus it can be implemented to induce the precipitation of HAP and recover it as a calcium salt.

Investigation of Produce-Associated Pathogens and Potential Surrogates: Characterization and Mechanisms of Attachment and Removal

Holly Mayton
Advisor: Dr. Sharon Walker

Despite modern agricultural practices, pathogenic contamination of fresh produce continues to cause significant foodborne illness outbreaks in the U.S. and around the world. Additionally, the recent trend towards more sustainable food production has led to increased usage of manures and recycled irrigation waters in crop production, which may increase opportunity for bacteria like *Salmonella sp.* Typhimurium and *Escherichia coli* O157:H7 to come in contact with our food. Bacterial survival, proliferation, and resulting foodborne illness outbreaks from agricultural processes begins simply with adhesion to a surface, followed by persistence in the face of washing. Thus, understanding these pathogens' characteristics and attachment mechanisms has become a research priority in food safety. However, a growing body of literature suggests that current indicator organisms used to assess industrial sanitation processes are not sufficient representatives of relevant pathogens in any given environment. In order to identify better surrogates,18 potential non-pathogen indicator organisms were characterized by their chemical and physical properties when grown in both high and low nutrient conditions, and compared to two pathogens and a current quality control indicator organism. Each bacteria sample was grown for eighteen hours and harvested in the stationary phase. Electrophoretic mobility, relative hydrophobicity, size, surface charge density, and extracellular polymeric substance (EPS) were characterized using ZetaPALS analyzer, microbial adhesion to hydrocarbons test, light microscopy, potentiometric titration, and colorimetric methods, respectively. This work has found that quality control surrogates currently used in industry and lab environments differ from pathogens in their physiochemical properties in some ideal and realistic growth environments. To adequately test disinfection systems, use of multiple surrogates may be necessary to mimic the characteristics of multiple pathogens of concern. Therefore, future work will utilize two potential surrogates that best mimic *Salmonella sp.* Typhimurium and *Escherichia coli* O157:H7 to compare attachment and detachment mechanisms. A parallel-plate flow cell and fluorescent microscopy will be used for direct visualization and enumeration of pathogen and surrogate cells on spinach leaf surfaces, under various water chemistry, hydrodynamic, and disinfection conditions. This work will ultimately contribute to more scientifically rigorous food safety policies that protect public health and efficiently utilize agricultural resources.

Studies on Performance and Kinetic Analysis of Anaerobic Ammonium Oxidation process

Stephen Robert Opot
Advisor: Dr. Mark R. Matsumoto and Dr. David Jassby

Excess nutrients from wastewater discharged in open waters lead to eutrophication, hypoxia, and oceanic red-tide, which are major threats to public health. Anaerobic Ammonium Oxidation (Anammox) is a relatively new alternative for ammonia removal from wastewaters with low carbon to nitrogen ratio. Compared to conventional N-removal process, the anammox process has the potential to significantly reduce energy and chemical demand in wastewater treatment plants.

Widespread utilization of anammox process is impeded by two bottlenecks: very slow growth and the risk of process instabilities associated with anammox bacteria. Start-up and long-term process stability could be improved by inoculation if the conditions for competition between different anammox bacteria were known. Competition among bacteria during acclimatization provides a great challenge in determining optimum concentrations and operational levels for controllable process parameters. The anammox reaction is also a tightly coupled cyclic catabolic process, which also makes it vulnerable to disturbances. Collectively, the setbacks hinder assessment of performance during start-up.

The study's aim is to monitor anammox N-removal rate within the context of a kinetic model in a sequencing batch reactor, and to obtain key kinetic parameters from experimental data. To evaluate start-up which is the time taken to attain maximum specific anammox activity (S.A.A) at maximum nitrogen load rate (steady state), the model may be used to predict performance under varying controllable parameters that could affect the process. To date, anammox-bacterial consortium has been successfully enriched in 3L bench-scale reactors seeded with non-typical (extremely high N-concentration at 50°C) wastewater achieving 96% nitrogen removal efficiency (NRE) at 50mg N gVSS^{-1} d^{-1} S.A.A. Batch tests have been conducted to assess and define start-up rates. Anammox bacteria have been detected, quantified and identified as *Candidatus Brocadia Sinica* using 16S rDNA sequencing method. As a test case, the effect of alkalinity on the defined anammox startup rate has also been experimentally evaluated.

Investigation of Surfactant Effect on Emulsion Fouling in Ultrafiltration and Nanofiltration Processes

Xiaobo Zhu
Advisor: Dr. David Jassby

Treating oily wastewater that contains well-stabilized oil emulsions is challenging, as conventional oil separation methods cannot remove oil droplets with sizes bellow 10 μm. Membrane based separation processes ensure high permeate quality, but are prone to oil fouling. Surfactants play an important role of producing well-stabilized oil emulsions, but there has been limited work to explore the surfactant effect on emulsified oil droplets fouling in membrane processes. To fundamentally understand the surfactant effect on fouling, we studied the fouling of hexadecane emulsions stabilized by anionic, cationic and nonionic surfactants in a crossflow filtration system. Furthermore, we used ultrafiltration (UF) and nanofiltration (NF) membranes to understand the impact of membrane surface properties on fouling mechanisms. UF filtration experiments revealed that emulsions stabilized with cationic surfactant quickly fouled negatively charged UF membranes due to electrostatic attraction, while anionic and non-ionic surfactants stabilized emulsions experienced less fouling. In NF filtration tests, membranes were fouled exponentially when filtrating all types of surfactants stabilized emulsions. The permeate quality confirms that NF process achieves better permeate quality than UF process because it is efficient at removing surfactants. However, cationic surfactants are able to pass through NF membranes because of their positive charge.

Photocatalytic Removal of Hexavalent Chromium by Highly Reductive TiO_2 Nanocrystals

Gongde Chen
Advisor: Dr. 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 and called for more efficient Cr(VI) treatment. 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 by inexpensive thermal hydrolysis reactions and used as the catalysts for the reduction of Cr (VI) to Cr (III) under UV irradiation. The synthesized TiO_2 photocatalyst exhibited superior Cr(VI) reduction kinetics to P25 TiO_2 in diverse water chemical conditions. Fast elimination of Cr (VI) can be achieved on the time scales of seconds in actual drinking water matrixes. Surface characterization and hydroxyl radical analysis revealed that DEG molecules were chemically bonded on TiO_2 surface and contributed to internal hole-scavenging effect and high electron releasing capacity. This unique feature is able to prevent the introduction of commonly used organic scavengers for holes. The removal of Cr(VI) by reductive TiO_2 exhibited a three-stage kinetics at low catalyst dose: an initial fast-reaction phase, a lag phase that resulted from surface precipitation of $Cr(OH)_{3(s)}$, and a final reaction phase that caused by surface regeneration from oxidation-reduction induced ripening process. The lag phase disappeared in acidic conditions that prevented the formation of $Cr(OH)_{3(s)}$. The catalyst exhibited extremely high electron release capacity that can be reused for multiple cycles of Cr(VI) removal in drinking water treatment. The outcome of this study will lead to the development of a cost-effective and highly efficient chromium removal technology.

Comparison and characterization of biofilm removal by different chemical cleaning solutions for water treatment applications

Caroline Kim
Advisor: Dr. Sharon Walker and Dr. David Jassby

Biofilm formation is a concerning issue for many industrial processes, including water treatment membranes, heat exchangers, and piping networks, as it leads to fouling and poor performance of the system. Combinations of physical and chemical cleaning methods are commonly used to remove the deposited biofilms. However, there is little understanding of the interactions between chemical cleaning agents and the biofilm. Therefore, companies perform a series of iterations to design a chemical cleaning solutions to target specific biofilms in their processes. Numerous studies have considered the interactions between various chemical solutions and biofilm, but still the mechanism is not clearly known. Investigating the interaction between the individual components of the biofilm might help understanding this issue.

A homogeneous layer of a single biofilm component (polysaccharides, proteins, nucleic acids, lipids) will be studied on an ultrafiltration membrane in a transparent flow cell. The interaction of the biofilm components with different cleaning agents (acid, base, surfactant, oxidizer, chelator, heat) will be evaluated by surficial analysis techniques including confocal laser scanning, atomic force, and environmental scanning electron microscopy, as well as streaming potential, and zeta potential analysis.

This project will give insights into the impact of representative cleaning agents on individual biofilm components, the interactions between the collector surface and individual components and ultimately, to design an efficient microbial cleaning strategies for fouled surfaces. The results of this work will help to ensure a safe and sustainable operation of water supply and enhance the performance of membrane-based water treatment processes.

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

Stephen “Drew” Story
Advisor: Dr. Sharon L. Walker

A systematic investigation was performed to confirm the viability of a static light scattering (SLS) technique to characterize aggregate morphology of two-dimensional engineered nanomaterials (2-D ENMs). Aggregation of graphene oxide (GO) and lithiated-molybdenum disulfide (Li-MoS_2) was studied and compared to that of a spherical reference colloid, carboxylate-modified latex nanoparticles. The critical coagulation concentration (CCC) for all dispersions was determined by an analysis of aggregation kinetics using dynamic light scattering, and this elucidated the transition from the reaction-limited aggregation (RLA) regime to diffusion-limited aggregation (DLA). The findings of this study supported the trend predicted by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of an increase in attachment efficiency as the 2-D ENM colloids destabilize. For all nanomaterials, as ionic strength approached the CCC, fractal dimension decreased; whereas, any increase in ionic strength beyond the CCC did not yield significant change in fractal dimension. Across comparable primary particle sizes, and using both carbonaceous (GO) and inorganic (Li-MoS2) 2-D ENMs, this study supports the use of SLS for the measurement of fractal dimension for two-dimensional materials. An additional examination of aggregate morphology in both RLA and DLA regimes is being conducted via cryogenic transmission electron microscopy (cryo-TEM). In this technique, colloidal suspensions are flash frozen before being imaged in their then current aggregation state. This additional characterization may further support the hypothesis that SLS is an acceptable technique to determine fractal dimension of 2-D ENMs.

Investigation of Filtration Mechanisms Involved with Removal of Engineered Nanomaterials from Drinking Water

Chen Chen
Advisor: Dr. Sharon L. Walker

An *in situ*, quantitative experimental system has been designed to assess removal of engineered nanoparticles during drinking water filtration. The focus of this study is the determination of whether differences between food and industrial grade TiO_2, such as particle size and surface composition, resulted in comparable behaviors in porous media. Techniques to prevent the enrichment of the nano and micro scale particles in water responsible for their detrimental effects are presented in addition to guidelines for management of water treatment. Methods include direct visualization of filtration processes with an *in situ* method and 2-D micromodel. Overall removal efficiency has been evaluated, in addition to, the collector grain efficiency as a function of position on the collector surface. Complementary particle characterization was conducted including dynamic light scattering (DLS), zeta potential (ZP) and zero point of charge (ZPC). Modeling (DLVO profiles and COMSOL) is used to simulate the physicochemical interactions and flowrate distribution around the collector. Hydrodynamic forces are shown to be quite impactful as deposition trends vary as a function of size, as well as, the location on the collector due to the relative hydrodynamic force experienced by the particle. This research aids in the elucidation of the fate and transport of engineered nanoparticles in multiple aqueous conditions, to better define their movement, and ultimately, their removal from engineered and natural systems.

Kinetics and Mechanisms of Cr(VI) Formation via the Oxidation of Cr(III) Solid Phases by Chlorine in Drinking Water

Michelle Chebeir
Advisor: Dr. Haizhou Liu

Hexavalent chromium Cr(VI) is being considered for more stringent drinking water standards by regulatory agencies. Cr(VI) can be inadvertently produced via the oxidation of trivalent chromium Cr(III) solids. This study investigated the kinetics and mechanisms of Cr(III) solids oxidation by chlorine in drinking water and associated Cr(VI) formation. Impacts of water chemical parameters such as bromide concentration (0–5 mg/L) were examined. Results showed that the rapid oxidation of Cr(III) solid phases by chlorine was accompanied by Cr(VI) formation and an unexpected production of dissolved oxygen. Analysis of reaction stoichiometry indicated the existence of Cr intermediate species that promoted the autocatalytic decay of chlorine. Bromide, a trace chemical constituent in source waters, exhibited a catalytic effect on Cr(VI) formation due to an electron shuttle mechanism between Cr(III) and chlorine and the bypass of Cr intermediate formation. The kinetics data obtained from this study suggest that the oxidation of Cr(III) solids by chlorine in water distribution systems can contribute to Cr(VI) occurrence in tap water, especially in the presence of a trace level of bromide.

A detailed analysis was also conducted on the occurrence and speciation of Cr in drinking water systems in U.S based on data reported by the U.S. EPA's Unregulated Contaminants Monitoring Program. The data revealed that Cr(VI) levels varied between 0.03 and 97 µg/L in treated drinking water, with higher percentage of occurrence in Southwest regions of U.S. and a positive correlation between higher Cr(VI) levels and the use of groundwater as a drinking water source. Cr(VI) and total Cr showed either an increase or a decrease from the entry point of the distribution system and the exit point of maximum residence time in tap water. The changes in Cr levels suggested complex physicochemical processes in water distribution systems, including oxidation of Cr(III) by residual disinfectants (i.e. chlorine and chloramine) and adsorption of Cr(VI) by corrosion scales.

Phyla Level Inhibition of Human Gut Microbiome during Titanium Dioxide Exposure

Travis Waller
Advisor: Dr. Sharon L. Walker

Extensive usage of engineered nanomaterials (ENMs) results in unexpected consequences due to the release of these particles into human and environmental systems during product lifecycles. Titanium dioxide (TiO_2), frequently used in coatings, pigments, and paints, represents a major fraction of ENMs that reach wastewater treatment facilities making it the focus of many fate and toxicity studies. Anaerobic decomposition in both the human body and wastewater treatment depends on microbial activity making their inhibition a particular concern. Whereas P25 (the most commonly used “industrial grade” form of TiO_2) is typically used in fate and toxicity studies, lifecycle analyses reveal food grade TiO_2 accounts for a larger fraction of the particles present in wastewater streams from anthropogenic inputs. As such, the impacts of food and industrial grade TiO_2 on the composition and phenotype of a human gut microbiota were studied. Findings show an inhibition of an expected natural shift in microbial composition from *Proteobacteria* to *Firmicutes* phyla in the presence of both types of TiO_2 particles, with food grade exposures having a greater effect. Additionally, both TiO_2 exposures resulted in lower values of the colonic pH (< 5) as compared to the control (> 5), with food grade exposures resulting in the largest reduction (~ pH 4). Results of this study indicate that when considering environmental exposure and risk, as well as the design of environmental fate and toxicity studies, intrinsic physical and chemical properties of ENMs may indeed result in significantly different microbial responses within complex systems.

Direct deposition of Carbon Nanotube-polymer composite films on filtration membrane surfaces

Alexander Dudchenko
Advisor: Dr. David Jassby

Application of electrical potential to conductive filtration membranes has shown a great potential for fouling and scaling mitigation. The application of an electrical potential to the conductive membranes has been shown to effectively electrostatically charge the membrane surface, preventing charged foulants from attaching, change ion concentrations and speciation at the surface, and affecting surface pH. Previously, pressure deposition has been utilized to prepare conducting membranes via deposition of carbon nanotubes (CNTs) onto a porous support, followed by a crosslinking step in a polymer matrix. This technique requires the use of ultrafiltration membranes with pores smaller than the CNTs being deposited. These requirements prevented successful deposition of CNT's onto microfiltration (MF) membranes with larger pores, as well as makings it difficult to pressure deposit CNTs onto reverse osmosis (RO) membranes where the required operating pressures can become excessive. Here, we use a spray coating approach to deposit smooth composite and cross-linkable CNT films onto RO and MF membranes. We employ a layer by layer spray deposition approach, where we alternate spraying CNTs and polymer layers that form highly conductive and stable films after crosslinking. We then demonstrate the functionality of these films in membrane distillation, where the CNT film is used as joule heater, and RO where it is used to change surface pH to enhance membrane performance.

Development and application of CRISPR-Cas9-based tools for chemical production in the yeast *Yarrowia lipolytica*

Cory Schwartz
Advisor: Dr. Ian Wheeldon

The yeast *Yarrowia lipolytica* has been the focus of a wide range of metabolic engineering studies due to its native ability to metabolize a wide range of substrates and to accumulate lipids to a high level. While successful engineering of *Y. lipolytica* has been achieved, a lack of advanced genome engineering tools has limited its potential to this point. Most works have relied upon sequential random integrations into the genome with a selectable marker, followed by a Cre-Lox-mediated marker recovery step. A method removing the need for marker recovery after each integration would allow for more rapid strain development and better utilization of *Y. lipolytica's* unique metabolism. In this work, we developed and characterized a set of standardized genomic locations for CRISPR-Cas9-mediated markerless pathway integration, and used them to produce the commercially relevant carotenoid lycopene. Genomic locations for insertion of genes were selected by identifying regions that were unlikely to be important for growth under normal conditions. We then used our previously developed CRISPR-Cas9 system to attempt integration of GFP into each site, and characterized the integration rate into each. Growth of each integrant was also quantified, to ensure that no essential cellular function had been interrupted. Fluorescence from each site was then quantified via flow cytometry, and expression from each site was compared. Two genes, phytoene synthase and phytoene desaturase from *Pantoea ananatis*, were codon optimized and integrated into 2 of the characterized sites, yielding a strain of *Y. lipolytica* capable of synthesizing lycopene. Several upstream genes, designed to increase flux to lycopene, were integrated into 2 other sites, and lycopene production by *Y. lipolytica* was measured.

Identification of Highly Selective MMP-14 Inhibitory Fabs by Deep Sequencing

Tyler Lopez
Advisor: Dr. Xin Ge

Matrix metalloproteinase (MMP)-14 is an important target for cancer treatment due to its critical roles in tumor invasion and metastasis. Previous failures of all compound-based broad-spectrum MMP inhibitors in clinical trails suggest that selectivity is the key for a successful therapy. With high specificity, monoclonal antibodies (mAbs) therefore arise as attractive inhibitors targeting the particular MMP of interest. As a routine screening method, enzyme-linked immunosorbent assays (ELISA) have been applied to paned phage libraries for the isolation of mAbs inhibiting MMP-14. However, because of suboptimal growth conditions and insufficient antibody expression levels commonly associated with monoclonal ELISA, a considerable number of potentially inhibitory clones might not be identified. Taking advantage of next-generation sequencing (NGS), we monitored enrichment profiles of millions of antibody clones along three rounds of phage panning, and identified 23 Fab inhibitors of MMP-14 with inhibition IC_{50} values of 10-4000 nM. Among these inhibitory Fabs, 17 were not found by monoclonal phage ELISA in previous study. Particularly, Fab R2C7 exhibited an inhibition potency of 100 nM with an excellent selectivity to MMP-14 over MMP-9. Inhibition kinetics and epitope mapping suggested that as a competitive inhibitor, R2C7 directly bound to the vicinity of MMP-14 catalytic site. This study demonstrates deep sequencing is a very powerful tool to facilitate the systematic discovery of mAbs with protease inhibition functions.

Design and electrochemical control of biologically inspired catalytic cascades for chemical synthesis

Louis Lancaster
Advisor: Dr. Ian Wheeldon

Catalytic reactions are involved in at least one step of the manufacturing of an estimated 90% of chemical products worldwide. The catalysts used in a typical manufacturing process require extreme operating conditions and high purity reagents to achieve acceptable yields and selectivities, increasing the cost of the product and the environmental impact of the process. Biocatalysts are an attractive substitute for many current catalysts due to their high activities at ambient conditions and the low impact of synthesizing and purifying them. Engineered systems of multiple immobilized catalysts can increase the efficiency of industrial chemical synthesis by eliminating the need for separation processes in between catalytic reaction steps.

The design of catalytic cascades in this work is inspired by nature and the solutions that have evolved to meet the challenges involved with maintaining homeostasis. Elegant architectures have been observed at the molecular level that exploit various mechanisms to control the diffusion of reaction intermediates from one catalytic site to the next. Hybrid catalytic cascades that mimic biological systems have been envisioned for the one-pot synthesis of some commodity chemicals as well as the stepwise electrochemical oxidation of various hydrocarbons for energy conversion.

The design rules elucidated from the reaction pathways of some microorganisms will be utilized to build self-assembling nanostructured hybrid catalytic cascades incorporating organic, electro-, and biocatalysts. A thermostable alcohol dehydrogenase from *P. furiosus,* AdhD, has been crosslinked with a derivative of TEMPO to create a simple 2-step catalytic cascade that can selectively oxidize the primary and/or secondary alcohols of butanediols. TEMPO's unique redox properties can be used to control the reaction kinetics of this simple cascade. We aim to incorporate this initial work into a larger cascade built into the framework of a supramolecular hydrogel that can be controlled using electrochemical methods. The composition of the hydrogel will be adjusted to control the spatial orientation of the attached catalytic active sites and the redox potential of the electrocatalysts in order to optimize the reaction kinetics.

Correlation Between Sizes and Specific Activities of Enzyme Complexes

Long Chen
Advisor: Dr. Xin Ge

Biological catalysis systems often utilize enzyme complexes composed of multiple reaction centers to provide reaction proximity, substrate channeling and synergic effects. One excellent example of such complexes seen in Nature is the cellulosome, a superior machinery used by cellulolytic bacteria with high reaction efficiency. In cellulosome, dozens of cellulases of different functions connect via scaffoldin proteins to form a catalytic entity with MW up to 6 MkD. Inspired by the optimum performance of cellulosome, people constructed mini-cellulosomes usually composed of 3-6 enzymes, but their specific activities cannot match with that of native cellulosomes. We argue it must be evolutionarily beneficial to construct such huge yet quite unique enzyme complexes by consuming considerable amounts of energy and resource. In this study, we built cellulosomes carrying 1-25 cellulases of three types (glycoside hydrolase families 5, 9, and 48) and investigated the correlation between sizes and specific activities of enzyme complexes. This study reveals that higher degree of cellulosome complexity tends to result in more efficient cellulose hydrolysis with plateaued synergic effects after complexity reaches certain degree.

Impurities in a Room-Temperature Ionic Liquid for Supercapacitors:
Friend or Foe?

Kun Liu
Advisor: Dr. Jianzhong Wu

Electrical double-layer capacitors (EDLCs), also known as supercapacitors, have attracted significant attention as promising electrical energy storage systems. In EDLCs, charges are stored electrostatically by the fast reversible adsorption of ions of the electrolyte onto active materials. Recent years have witnessed growing interests in both the fundamentals and applications of EDLCs. A number of strategies have been explored to optimize the device performance in terms of both the energy and power densities. Because the properties of electric double layers (EDL) are sensitive to the ion distributions in the close vicinity of the electrode surfaces, the supercapacitor performance can be easily altered in the presence of impurity. In this work, we study the impurity effects on EDLC performance by using a coarse-grained model of room-temperature ionic liquids (RTILs) and the classical density functional theory (CDFT). The theoretical investigation is focused on the generic features of impurity molecules, such as the molecular size, polarity, self-interaction energy, and binding affinities with the electrode surface and surrounding ions. We identify key parameters controlling both positive and detrimental influences of impurity on ionic distribution as well as the energy storage in porous electrodes. The theoretical predictions provide insights for the impurity behavior at the electrolyte/electrode interface and, more important, useful guidance for formulation of additives to boost supercapacitor performance.

Plasmonic Resonances: A Systematic Analysis of Metal Nanoparticle Systems Using Real-Time Time Dependent Density Functional Tight Binding Method

Niranjan Vasant Ilawe
Advisor: Dr. Bryan M. Wong

Recent advances in the study of local surface plasmon resonances (LSPR) in metallic nanoparticles has led to the emergence of novel applications in chemical and biological sensing, optical transmission, nanophotonic devices, and energy harvesting. Crucial to the advancement of such applications is the theoretical understanding of LSPR with regard to nanoparticle shapes, sizes, compositions, chemical environment and relative arrangements. Classical electrodynamic theories often fail to capture the quantum resonances for particle sizes less than 10 nm, while ab-initio quantum mechanical calculations are computationally costly and currently limited to systems with less than ~100 atoms. The real-time time dependent density functional tight binding (DFTB) formalism 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 (TDDFT) at a fraction of the computational cost.

My project proposes to, (i) Introduce and apply the DFTB formalism to study the optical properties of nanoscale metallic systems, and, (ii) Systematically analyze the parameters (shape, size, composition, environment and relative arrangement) that control the LSPR in metallic nanoparticles using DFTB.

Initial DFTB simulations, applied to spherical sodium nanoparticles reveal a non-monotonic behavior, while icosahedral nanoparticles display a uniform blue shift, of the plasmonic resonances as the particle size decreases. Local field enhancements produced around the sodium nanoparticles, and between nanoparticle dimers, on application of monochromatic laser field, assert the importance of a complete atomistic structural description, often overlooked by classical theories. A further investigation into other metals, geometries and orientations is envisioned. The effect of solvent and chemical environment on the optical properties by including explicitly, solvent and adsorbates on the surface of the metal nanoparticles will be analyzed. Electronic coupling between nanoparticles and the influence of a static electric field on energy transfer will also be studied.

Optimizing ionic liquid mixtures to available electrode materials

Justin Nathaniel Neal
Advisor: Dr. Jianzhong Wu

The supercapacitor currently has large power output, but a small energy density. To broaden its application, ionic liquids are used to expand the operating potential window. Mixtures of these ionic liquids give better stability and fidelity under cycling making for a durable device. The proper electrode material with large surface area provides the supercapacitor the energy density required for a storage device. These materials, however, have varied pore size distributions which can affect the packing, and thus capacitance, of ionic liquids within them. Using classical density functional theory, asymmetric ionic liquids were mixed within slit-pores at varied potential. Using a linear combination of pores, the optimal mixture not only agreed with experimental values, but profited a 30% increase in total energy density.

Solvent Structure of Surface-Supported Amine: a Molecular Dynamics Study

Shijie Sheng
Advisor: Dr. Jianzhong Wu

Amine grafted silica gel is an efficient heterogeneous catalyst in Knoevenagel reaction and draws much attention in green chemistry for applications like heavy metal adsorption and CO_2 fixation. Despite of its successful applications in many fields, the question of how the silica substrate affects the local chemistry environment of tethered amine still remains unknown. In order for a deep understanding, in this work, we investigate the solvent structure of primary amine in aqueous solution and silica supported amine. We perform MD simulations of both pure amines and silica supported amine in aqueous solution. To sample the non-trivial 3D density profile, spherical harmonics expansion method is adopted. Using this method, the 3D density profile is generated for both pure amine and silica supported amine in aqueous solutions. In the simulations, the effect of PH and silica surface ionization rate are also investigated from the solvent structure for a further understanding. In addition, how the silica substrate affects the tethered primary amines of different chain length is also discussed. Further, the change in hydrogen bonding network in the vicinity of N-terminal of primary amine is also investigated for the presence of silica substrate.

Differential Heat of Adsorption and Isosteres

Yun Tian
Advisor: Dr. Jianzhong Wu

Heat of adsorption is a basic thermodynamic property extensively used not only for understanding thermal effects and heat management in industrial gas storage and separation processes but also for development and validation of adsorption models and materials force fields. Despite a long history of theoretical studies and a vast experimental literature, controversies often arise in the thermodynamic analysis of heat effects due to various assumptions used to describe gas adsorption and inconsistency between calorimetric measurements and isosteric heat obtained from various adsorption isotherms. Here we present a rigorous theoretical procedure to predict isosteric heat without any assumption for the adsorbent or operating conditions. By avoiding problematic division between bulk and the adsorbed phases or semi-empirical estimation of the pore volume, the new theoretical procedure enables accurate description of heat effects important for diverse applications of adsorption processes. In this work, a rigorous thermodynamic framework is presented to analyze isosteric heat of adsorption without any unjustified assumptions on the geometry of porous adsorbents or operating conditions. Quantitative relations between the differential heat and various isosteres have been established with the grand-canonical Monte Carlo simulation for gas adsorption in amorphous as well as crystalline porous materials. The inconsistencies and practical issues with conventional methods for the analysis of heat effect have been clarified in the context of the exact results for model systems. By resolving a number of controversies on heat analysis, the theoretical work is expected to have broad impacts on both the fundamentals and industrial applications of adsorption processes.

Electro chemical performance of Magnesium 1-carba closo decaborate($Mg(CB_9H_9)_2$) in Tetraglyme

Rahul Jay
Advisor: Juchen Guo

The need of safe and efficient energy storage devices is something researchers across the world are aiming for at present. Although, Lithium(Li)-ion batteries are currently at the forefront of electrochemical research, there is still wide interest in other chemistries. Magnesium(Mg)-ion is one such chemistry that sparks vast interest in the electrochemical research community. Mg metal is attracting lot of attention as its volumetric capacity of 3832 mAh.cm-3 is higher than Li 2061 mAh.cm-3. Mg is also the 5th most abundant metal in the earth crust which drives down the material cost. Mg unlike Li also demonstrates no dendrite growth during the reversible plating/stripping process which alleviates safety concerns for it to be employed as a negative electrode in batteries. But, the absence of practical electrolyte for Mg-ion chemistry is one of the major challenges faced by researchers in this field. Most of the current electrolytes used rely heavily of chloride-based complexes that hinders accessing of the full potential of the Mg metal. In this presentation we are going to present the electrochemical behavior of a halogen free monocarborane molecule. Magnesium 1-carba closo decaborate (Mg(CB9H9)2 in tetraglyme(G4) demonstrates reversible Mg platting and stripping with coulombic efficiency as high as 89% which was demonstrated by cyclic voltammetry. The electrolyte also demonstrates very high anodic stability between 3.6 and 3.8 V vs Mg which is much higher than chlorine based electrolytes. The conductivity of the electrolyte at different concentrations was measured with a specially designed cell via potentiostatic impedance measurements. 0.45M concentration of the electrolyte was determined to have the highest conductivity. Mg-ion batteries provided an initial discharge capacity of about 93mAh.g-1 but dropped to about 30 mAh.g-1 around cycle 30. Although reversible cycling behavior was observed for the electrolyte we believe the size of the big size of the molecule hinders in efficient intercalation of the ions within the cathode and the future for reversible Mg-ion chemistry would be in thoroughly studying simple structured conventional Mg salts such as Mg(TFSI)2 (Magnesium(II) Bis(trifluoromethanesulfonyl)imide), MgPF6 (Magnesium hexaflourophosphate).

Light-Induced Desorption of CO from cytochrome *c* Via the Activation of the CO-Fe Bond in Heme

Sergei Hanukovich
Advisor: Dr. Phillip Christopher and Dr. Ian Wheeldon

Today, reaction selectivity is thermodynamically limited by system temperature and pressure. However, photocatalysis provides a novel means of controlling single steps in complex reactions, 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. Carbon monoxide (CO) inhalation in large enough quantities is fatal to humans, thus developing methods of alleviating CO poisoning is very important. CO poisoning occurs through the adsorption of CO gas onto an iron (Fe) site of a heme group of an enzyme. Photocatalysis offers a novel and simple technique of breaking this CO-Fe bond.

Although previous work has shown that light photons may be used to desorb CO from an active catalyst such as Pt, to our knowledge, no work has shown a similar ability to desorb CO from a heme group in enzymes. Using a xenon lamp source, we effectively broke the CO-Fe bond from our enzyme of interest, cytochrome *c*, by inducing desorption with light photons at varying wavelengths. A UV-Vis spectrometer was used to monitor the concentration of CO, which showed that the desorption rates trend very well with the relative absorbance spectra of the enzyme. Thus, the wavelengths that the enzyme is best equipped to absorb (414 nm for cytochrome *c*) are also those at which the faster CO desorption kinetics occur. Upcoming studies will be focused on studying light-induced CO desorption from cytochrome P450, an active human enzyme that can adsorb CO at physiologically relevant conditions. We expect to see similar trends to those observed with cytochrome *c,* opening the door to potentially novel pathways for treating CO poisoning.

Giant Raman Response to the Encapsulation of Sulfur in Narrow Diameter Single-Walled Carbon Nanotubes

Guanghui Li
Advisor: Dr. Juchen Guo

Single-walled carbon nanotubes (SWNTs) offer extraordinary physical and chemical properties such as high carrier mobility and current-carrying capacity, unique optoelectronic properties, large surface area, and high electrochemical stability, thus showing great potential for applications in thin-film transistors (TFTs), novel electronic and optoelectronic devices, logic circuits, solar cells, and lithium-sulfur batteries.

Lithium-sulfur batteries based on SWNTs are or current interest because of the high capacity of sulfur as a cathode component for rechargeable batteries when paired with metallic elements such as lithium. The use of carbon-based nanomaterials, including single-walled carbon nanotubes (SWNTs) to encapsulate sulfur provides an interesting approach to the study of the electrochemical lithiation process at the cathode in which there is confinement of the active sulfur species. In addition, SWNTs can provide a conducting pathway for current flow during the charging and recharging processes. Thus it is of the utmost importance to understand the interaction between sulfur and carbon-based materials - particularly as it relates to SWNTs in which there is confinement of the active sulfur species (S@SWNTs). Raman and absorption spectroscopies can be useful tools to study these interactions. In our initial study we discovered a giant Raman response to the encapsulation of sulfur in narrow diameter SWNTs with the appearance of new peaks at 319, 395 and 710 cm^{-1} which originate from the sulfur species within the SWNTs. The encapsulated species also shifts the near-IR interband electronic transitions to lower energy by more than 10%. These effects seem to originate from the van der Waals interaction of the confined sulfur species with the walls of the SWNTs which is not expected to be significant in the case of the previously studied large diameter SWNTs. Our studies in this area will continue on SWNTs of different diameters and with a variety of encapsulated species.

MoS_2−graphene heterostructure based field-effect transistor for sensing of volatile organic compounds

Tung Pham
Advisor: Dr. Ashok Mulchandani

In this work, we investigate the electrical properties of MoS_2−Graphene heterostructure synthesized by physical stacking of single-layer MoS_2 over single-layer graphene grown using chemical vapor deposition (CVD). We fabricate field-effect transistors (FET) using the hybrid material as the channel to overcome the limitations of individual materials, i.e. zero band gap in graphene and low electrical mobility of MoS_2. Due to the difference in the work-functions and MoS_2 being a n-type (electron-rich) semiconductor and as-prepared graphene being significantly p-doped (electron-depleted), there is a significant transfer of electrons from MoS_2 to graphene. This charge transfer leads to shifting of the charge neutrality point (V_{np}) by as much as 30 V in the FET transfer characteristics (I_d v/s V_g). The interaction between the individual MoS_2 and graphene layers is further confirmed by quenching of photoluminescence intensity in MoS_2-graphene hybrid by 50% as compared to single-layer MoS_2 and shifting of peaks in Raman spectroscopy. Additionally, the MoS_2-graphene hybrid shows stability in ambient air with negligible shifting of V_{np}, otherwise observed for graphene-based FET transfer characteristics. Finally, we investigate potential real world applications of MoS_2-graphene FET devices for sensitive and selective detection of volatile organic compounds (VOCs) such as acetone and toluene. We compare the performance of the hybrid material to single-layer MoS_2 and single-layer graphene using chronoamperometric and transfer characteristic measurements. We conclude that for acetone the sensitivity and signal-to-noise ratio for MoS_2-graphene hybrid is much higher compared to single-layer MoS_2 and graphene, while for toluene the response of singe-layer graphene is higher compared to the hybrid or single-layer MoS_2.

In situ coupling exothermic and endothermic magnesiothermic process to synthesize graphite-silicon composites

Zheng Yan
Advisor: Dr. Juchen Guo

Silicon is a promising candidate of anode material for next generation lithium-ion batteries due to the ability of large amount of lithium atom incorporation which can make the capacity reach to 4200mAh/g; also it is inexpensive and abundant in earth. However, particles pulverization, electrode fracture, poor conductivity and forming unstable solid-electrolyte interphase (SEI) during lithium insertion and extraction which has limited mass loading and tap density as well as cycle stability and further hinder commercial applications of silicon. In this work, we used in situ exothermic and endothermic reactions to synthesize graphite coated silicon particles. By creating graphitized carbon shell to overcome conductivity problem and build thin and stable SEI layer on the shell surface. Meanwhile nanosized silicon particles and created void space through magnesiothermic reduction reaction can help alleviate particle pulverization and accommodate volumetric expansion and prevent lithiation-induced strain breaking carbon shell during lithium insertion. In the proposed work, kinetics of magnesiothermic reduction of SiO2-carbon core-shell to graphite coated Si particles will be systematically studied and combine with experiments to find out how to maximum the conversion of Silica to the kinetic preferred product of Silicon instead of thermodynamically preferred silicon carbide. Finally, Silicon based anode material will be investigated for electrochemical performance.

Synthesis, characterization and catalytic performance of binary and ternary molybdenum borides

Hyounmyung Park
Advisor: Dr. Boniface Fokwa

Due to an excessive amount of CO_2 released in the atmosphere from an extensive use of fossil fuels, a demand for an eco-friendly, clean and renewable energy has emerged. Hydrogen is a favorable alternative to fossil fuels, but hydrogen needs to be produced because it does not occur naturally as a gas. One method to produce hydrogen is by splitting water through electrolysis. To attain potent water splitting for a wide range of applications, both active and economical catalysts for the hydrogen evolution reaction (HER) are required. Currently, a few noble metals (e.g. platinum) are the most efficient electrocatalysts for improving the efficiency of HER; however, they are expensive and lack abundance. Therefore, the discovery of active HER electrocatalysts made from earth-abundant and non-noble metal elements initiated a key step in the development of large-scale hydrogen production technology. Recent studies have shown that molybdenum based materials such as molybdenum boride (MoB), molybdenum carbide (Mo_2C) had excellent catalytic properties for HER. Metal borides have high hardness and high melting points and they are stable both acids and bases. Thus, they can become low-cost alternative electrocatalysts for HER.

In this work, we firstly focused on binary system such as Mo_2B, MoB and MoB_2. Metal borides have high melting points so arc melting is an appropriate method for their synthesis, because arc melting is simple and we can quickly reach high temperatures. X-ray powder diffraction was used for phase identification and determination of lattice parameters. HER activity and stability were studied by performing linear sweep voltammetry (LSV) and cyclic voltammetry (CV).

We expect that adding other elements such as iron, cobalt or nickel, the resulting ternary compounds may lead to even better catalytic performance. Future work will focus on ternary systems.

Stretchable Self-healing Conductive Polymer Composite for Electronic Devices Application

Nor Akmaliza Rais
Advisor: Dr. Chao Wang

While flexible organic electronic devices are already prevalent, the need for stretchable and self-healing electronics remain desirable and necessary for many emerging applications; e.g. sensors, solar cells, light-emitting diodes, displays and wearable medical devices. In recent years, there has been intense research into stretchable and self-healing materials, however the lack of high bulk conductivity becomes the shortcoming that limits their potential in electronic application. Currently, a void remains for combining all the properties without compromising the electrical and mechanical functionalities of the device, before and after it stretched and self-healed. Here, we introduce an “all-polymers” system composed of Fluoroelastomer and a conductive polymer Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) which shows stretchable and self-healable properties. After the preparation of composite material, the bulk properties are electrically and mechanically evaluated, as well as its self-healing performance. The electrical conductivity can be tuned by varying the amount of PEDOT:PSS and can reach values as high as 0.25 S cm^{-1}. From tensile testing, it was found that with increasing PEDOT:PSS loading, the Young’s Modulus and Yield Stress increases. The effect of PEDOT:PSS loading is more pronounced when it cause significant decrease in elastic recovery and early breakage during elongation test. The prepared composites exhibit Young’s Modulus in the range of 0.5 to 3.0 MPa and Stretchability as high as 140%. When fractured and put back together, the material is self-healable after curing at 60ºC for at least 3 hours, however no firm result was obtained to conclude the percentage of conductivity restoration. When strain is applied, the conductivity decreases exponentially before the material break. In conclusion, the results demonstrate PEDOT:PSS as a promising conductive filler in a stretchable self-healing “all-polymer” composite system. However the full potential of PEDOT:PSS was not achieved when PEDOT:PSS and the elastomer were used in the polymer composite. Further developments are still needed to understand the arrangement of PEDOT:PSS filler networks within the elastomer matrix for better electron pathways therefore higher conductivity > 1 S cm^{-1}, and to optimize the composite formulation to achieve mechanical and self-healing capability suitable for electronic application.

Understanding and Exploiting Photochemically Induced Phase Change in Monolayer Molybdenum Disulfide

Peter Byrley
Advisor: Dr. Ruoxue Yan

With the ever increasing demand for low cost optical and electronic devices for a variety of industries, world research has directed itself toward the discovery of useful alternatives to traditional silicon based technology. Semiconducting transition metal dichalcogenides (TMDs), especially MoS_2, are a good choice for use in nanoelectronic devices including field effect transistors because of their direct band gap in the visible range, low subthreshold swing, and excellent on/off ratios. However, they are limited by their variable electron mobility and high contact resistance between the semiconducting 2D channel material and the contact metal electrodes.

TMDs can exist in different solid phase structures ranging from the metastable metallic 1T MoS_2 phase to the thermodynamically stable semiconducting 2H MoS_2 phase. Phase-engineering in monolayer TMDs would enable the fabrication of high-quality heterophase structures with the potential to improve carrier mobility and contact. Such phase transitions have been demonstrated recently with the organolithium chemical method, which is a highly hazardous procedure.

The research objective of this study is to investigate photochemically induced 2H to 1T phase transformation in monolayer MoS_2 and the impact of this novel phase-engineering mechanism on its electrical properties. The central hypothesis is that the controllable partial transition from a semiconducting 2H to metallic 1T phase can be realized in monolayer MoS_2 through photo-reduction in the presence of hole scavenging chemicals. Preliminary results have demonstrated likelihood of phase transition using this method.

Study of charge transfer phenomena of cocatalyst-loaded light-absorbers for producing hydrogen from water

Yibo Jiang
Advisor: Dr. Phillip N. Christopher

Photocatalytic watersplitting is an environmentally friendly approach to harvest oxygen and hydrogen from water via solar irradiation. Over the past four decades, a great variety of photocatalyst designs have been created for hydrogen production. Cocatalyst loading is one of the most effective approaches to enhance the photocatalytic activities. Conventionally, it is believed that cocatalysts facilitate charge separation once upon the photo-excitation of electron and hole pairs. Yet, the details of charge transfer direction, kinetics, and the resulted photocatalytic phenomena still remain opaque for particulate photocatalyst systems. Gallium zinc oxynitride (GaNZnO as abbreviation) is among a few n-type visible-light absorbers that have demonstrated the ability to perform overall watersplitting reaction. Previous results have shown variable photocatalytic activities largely affected by cocatalyst types (metals versus metal oxides). In this study, GaNZnO along with the loaded cocatalysts, is investigated via a variety of techniques, including sacrificial reagent aided half-reaction kinetics analysis, microscopy, and infra-red spectroscopy. The analyses of the kinetics data are interpreted with characterization results from microscopy and spectroscopy, which are expected to provide more insights of charge transfer phenomena near the cocatalyst | light absorber interface.

Application of Organometallic Chemistry to the Electrical Inter-connection of Graphene Nanoplatelets

Mingguang Chen
Advisor: Dr. Robert C. Haddon and Dr. Ruoxue Yan

The formation of bis-hexahapto bonds between graphitic surfaces can electronically interconnect the surfaces of carbon materials containing the polybenzenoid ring system and increase the conductivity without introducing a strong perturbation to the in-plane electronic structure. In this paper, we report the use of organometallic chemistry to interconnect the surfaces of small scale graphene nanoplatelets by using a variety of metals and photo-chemically activated organometallic reagents.

Investigation of Rechargeable Batteries Based on Multivalent Metal Anodes

Linxiao Geng
Advisor: Dr. Juchen Guo

Among the rechargeable batteries beyond lithium chemistry, the ones based on aluminum (Al) are particularly promising: Al not only is the most abundant metal in the earth's crust but also has attractive capacity due to its trivalency. However, lacking of cathode materials has greatly hindered the development of aluminum ion battery. For the first time, we demonstrated chevrel phase Mo_6S_8 as intercalation type cathode material for aluminum ion battery. Mo_6S_8 shows unambiguous electrochemical activity for reversible Al intercalation and extraction with good cycle stability. In addition to the electrochemical analysis, XRD investigations provide the crystallographic information on the Al intercalated Mo_6S_8. We conclude that the theoretical formula of fully Al intercalated Mo_6S_8 is Al_2Mo6S_8 with Al occupying two different sites in the Mo_6S_8 crystal lattice. From the practical aspect, the theoretical material-level specific energy of a battery with Al anode and Mo_6S_8 cathode is approximately 90W h kg^{-1} (assuming 0.5 V nominal voltage), which can be an attractive alternative for large-scale energy storage technologies. Besides chevrel phase Mo_6S_8, we will also present the synthesis of nano sized layered TiS_2 and cubic Ti_2S_4 as well investigation of their electrochemical properties as cathode materials for ionic liquid based rechargeable aluminum ion battery at both room temperature and 50 °C. The proposed titanium sulfide cathode materials showed decent reversible capacity and a higher working potential. More importantly, it further validates the feasibility of finding transition metal sulfide cathode materials for rechargeable aluminum ion battery.

Plasmonic Nanowire Optical Probe for Near Field Scanning Microscopy

Sanggon Kim
Advisor: Dr. Ruoxue Yan

Near-field 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. In particular, by combining Raman spectroscopy with scanning probe microscopy, NSOM-Raman, also termed Tip-Enhanced Raman Spectroscopy (TERS), offers surface chemical mapping capability at the resolution of an AFM. However, conventional NSOM probes suffer from either low optical transmission (~10^{-6}) or low contrast, both of which significantly limit the sensitivity, speed of image construction, as well as probe lifespan due to the high illumination power necessary to obtain decent signal-to-noise ratio. We have developed a novel NSOM-Raman probe design based on adiabatic plasmonic nanofocusing to create a nanoconfined light source on a sharp metal tip with high optical transmission, resolution and contrast. 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 aperture NSOM probes to allow high-speed scanning. In addition to the high transmission, this probe also demonstrated a 10^7 Raman contrast between the near field signal and far-field background due to the localized illumination and large electric field enhancement at the tip of the nanowire, which is 10 times higher than commercial TERS tip. Theoretical modeling has predicted a sub-5 nm Raman mapping resolution. Experimentally, we have successfully integrated the probe with a commercial NSOM system and have recently demonstrated subwavelength photoluminescence mapping of MoS_2 monolayer, which is an important step towards nanoscale chemical mapping. This new probe design also allows for higher device reliability, which is another major limitation for conventional NSOM probes. My future work will be focused on the full development of nanoscale chemical mapping system using the plasmonic nanowire probe for the characterizations of materials, catalysis, and biological systems.

Analyzing Pt Structure Sensitivity in Single Atoms to Fully Coordinated Surfaces through Site-Specific IR Spectroscopy

Leo DeRita
Advisor: Dr. Phillip Christopher

There is a heavy focus on understanding the structure sensitivity of Pt catalysts from the limit of well-coordinated Pt atoms in terraces on large particles, down to single Pt atoms coordinated directly to oxide supports for the CO oxidation and water gas shift reactions. The latter has been of particular interest since advances in x-ray based spectroscopy and transmission electron microscopy. These provide ensemble measurements of structural features of supported Pt catalysts that are used to correlate the reactivity of various active sites on different supports.

An alternate approach to characterization and analysis of the structure sensitivity is the employment of *site-specific* CO probe molecule FTIR spectroscopy to identify the reactivity of various Pt active site geometries on supported Pt catalysts, which overcomes shortcomings of characterization techniques that rely on ensemble measurements. A caveat to the use of FTIR is its reliance on the unequivocal assignment of spectral features, which can vary as a function of support composition.

Here we will present results of rigorous FTIR-based analysis of molecular adsorption, temperature programmed studies, and oxidation reactions for Pt catalysts on titanium dioxide supports prepared through conventional dry impregnation and strong electrostatic adsorption (SEA) wet impregnation techniques with weight loadings ranging from ultra-low to more typical (0.025 - 2%). The reactivity and coordination of adsorbed CO on these Pt sites varies greatly with weight loading. With IR Probe Molecule spectroscopy, we can differentiate in-situ changes in where and how the adsorbates bind, providing mechanistic insight. We can further couple this with kinetic studies of typical catalytic reactions such as CO Oxidation to directly compare the efficiency of these catalysts and find the optimal combinations to drive these reactions in a cost efficient manner. This work will soon be extended to additional supports of varying reducibility, which plays a dynamic role in the stability and coordination of the adsorbates.

Solid State Lithiation-delithiation of Sulphur in Sub-nano Confinement

Chengyin Fu
Advisor: Dr. Juchen Guo

Rechargeable lithium–sulphur (Li–S) batteries continue to be one of the most promising technologies for electrochemical energy storage. In order to dramatically improve the performance of these Li–S systems, we require a detailed understanding of the interactions between lithium and sulphur in these complex, heterogeneous electrochemical environments. Due to the high electrical resistivity of sulfur, it is essential to incorporate sulphur into conductive hosts, of which the majority are carbonaceous materials. The rationale for using carbonaceous hosts, particularly porous carbon materials, is rooted from the well-known polysulfide shuttle reaction induced by the dissolution of lithium polysulfides (Li_2S_n) into electrolytes. 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, which is distinctly different from conventional Li–S reactions, 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.

Engineering and characterization of edge defects in graphene nanoribbons for enhanced sensitivity

Pankaj Ramnani
Advisor: Dr. Ashok Mulchandani

Large area graphene is a zero band gap semimetal with the valence and conduction bands intersecting at the K points in the Brillouin zone. Band gap engineering of graphene by lateral confinement of charge carriers into pseudo one-dimensional nanostructures like graphene nanoribbons (GNRs) and nanomesh has been demonstrated both experimentally and theoretically. The most commonly used methods for patterning graphene, including electron-beam lithography (EBL), nano-imprint lithography (NIL) and block co-polymer lithography (BCP) use an etch mask to selectively protect a certain region of graphene and the exposed graphene region is removed using O_2 plasma. However, the GNRs fabricated using these methods typically have a high degree of edge roughness and edge functionalization of the C atoms which introduces doping and significantly alters the charge carrier mobility and band gap of graphene. In this work, large-grain single-layer graphene films were grown using chemical vapor deposition (CVD). GNRs with widths varying from 30 – 200 nm were patterned using electron-beam lithography (EBL) and O_2 plasma treatment. We use Raman spectroscopy and x-ray photoelectron spectroscopy (XPS) for detailed characterization of the GNR edges. Thermal annealing and electrochemical reduction was used to partially repair the edge defects created by the O_2 plasma treatment. The electrical properties of GNRs, such as charge carrier mobility, extent of doping and band gap were characterized by fabricating field-effect transistors (FETs). Finally, we demonstrate the enhanced sensitivity of the GNR-FET devices by investigating their performance as a gas sensor for pollutant gases including NH_3 and NO_2.

Low Severity CELF Pretreatment of Corn Stover for the Development of Novel Simultaneous Saccharification and Isomerization (SSI) technology for Catalytic Conversion into Drop-In Fuels

Christian Alcaraz
Advisor: Dr. Charles E. 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” biofuels, i.e., hydrocarbons that are compatible with the existing fuel infrastructure. Corn stover has received attention as a sustainable feedstock for conversion into biofuels because of its abundance in the United States. The lignocellulosic matrix of corn stover cell walls is comprised primarily of three biopolymers: cellulose, hemicellulose, and lignin. Cellulose is the most abundant and well protected of the three biopolymers, and biological processes can realize the high glucose yields from cellulose essential to commercial viability. However, for biocatalysts to access cellulose, the lignocellulosic matrix must be disrupted through pretreatment, a balancing act between applying sufficiently severe reaction conditions to enhance sugar release and mild enough conditions to limit sugar degradation. The Wyman laboratory developed a new pretreatment called Co-solvent Enhanced Lignocellulosic Fractionation (CELF) that can remove up to 90% of lignin while recovering most sugars from hemicellulose in solution, thus leaving glucan highly vulnerable to hydrolysis with high yields at low enzyme loadings. Biological saccharification of cellulose to glucose by *Clostridium thermocellum* cellulosomes can be utilized as a first step in SFP production. Next, since SFP yields are higher from fructose than glucose, the resulting glucose solution will be enzymatically isomerized into fructose before catalytic dehydration to HMF. As a start towards this project, corn stover pretreatments need to be optimized such that maximum glucan is released during the biological saccharification step but minimized during prior pretreatment. With this in mind, low severity CELF pretreatment was applied to corn stover at 0.5wt% sulfuric acid, 50% THF in water solution (v/v), and 10 wt% solids loading in a 1 L stirred tank Hastelloy Parr reactor that was rapidly heated by a sand bath and equipped with a double-stacked pitch blade impeller for 10, 20, 30, and 40 minutes. The compositions of the solids and liquids were analyzed using Laboratory Analytical Procedures (LAP) developed by the National Renewable Energy Laboratory (NREL). A mass balance conducted at shorter times showed solid glucan retention approaching 96%.

Commented [CW1]: Should be doing this on mass basis as I have said countless times

Synthesis of CuO nanodot structures via thermal oxidation process as photoelectrode for organic-inorganic solar cells

Kichang Jung
Advisor: Dr. Martinez-Morales

Organic-inorganic solar cells, including dye-sensitized solar cells (DSSCs), and perovskite solar cells (PSCs) have shown promise as alternate technologies to Si-based solar panels, due to their cost effectiveness, simple fabrication, and wide application. Generally, organic-inorganic solar cells consist of a photoelectrode (that acts as an electron transport layer), an absorption layer, a hole-transport material, and a counter electrode. The photoelectrode is made from a transparent metal-oxide material such as TiO_2 or ZnO that absorbs light in the ultra violet (UV) region, but cannot absorb visible or near-infrared (NIR) light, due to their wide band gap energy (3.2 ~3.4 eV). Furthermore, in these devices the absorption layer is made out of a dye or perovskite material that can absorb visible light, but cannot absorb NIR light. This results in 46% of the solar spectrum being untapped.

Due to its narrow band gap energy (~ 1.2 eV), CuO absorbs light around 1000 nm. In the generic organic-inorganic solar cell devices, NIR light cannot be captured by the metal oxide material, or the organic-inorganic absorption layer. Therefore, a secondary layer (i.e. CuO nanostructure) can be explored as a secondary absorption layer to develop a more effective photoelectrode material that increases the absorption range of organic-inorganic solar cell devices and their performance.

In this work, CuO has been synthesized on FTO glass by thermal oxidation. The thickness of a seed layer deposited by E-beam evaporator is 100 nm. Our results confirm the successful synthesis of CuO nanodots structures via this method. The thermal oxidation process is optimized under various temperature conditions, open environment, and 1hour reaction time. X-ray diffraction(XRD) results show that a composition of Cu-Oxide compounds is obtained depending on the process temperatures. SEM analysis shows Cu-O compound morphology. Especially, nanodot structures are found at the 250 and 275 ^{o}C. In order to analyze optical properties of CuO, UV-Vis-NIR spectrophotometer is used. To determine crystallinity, crystal structure and grain size, XRD spectrometer is used. The grain size is calculated by Scherrer's equation using parameters from the XRD results. In future work, the synthesized CuO nanodot structures will be applied as a photoelectrode for organic-inorganic solar cell devices.

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

Ninad D Kothari
Advisor: Dr. Charles E Wyman

Almost all liquid fuels are derived from finite petroleum resources that contribute significantly to climate change. Ethanol is a high octane, cleaner burning fuel option that can be made from lignocellulosic biomass. It also offers a low carbon footprint and the potential to be further upgraded into other drop-in fuels, such as butanol, jet fuel, gasoline, and diesel. However, ethanol production from lignocellulosic biomass is a complex process that involves numerous operations including size reduction, pretreatment, enzyme production, enzymatic hydrolysis, fermentation, and product recovery. A simplified, integrated bioprocessing alternative is consolidated bioprocessing (CBP), which directly converts polysaccharides in lignocellulosic biomass into ethanol. A leading CBP option utilizes the thermophilic anaerobe *Clostridium thermocellum* to produce its own enzyme consortium for hydrolyzing polysaccharide chains in lignocellulosic biomass into fermentable sugars. The organism then metabolizes the sugars, producing ethanol and other by-products. Although it's been recently shown that *C.thermocellum* can effectively solubilize some select feedstocks/species, pretreatment of lignocellulosic biomass may still be required to achieve high sugar yields from *C. thermocellum* biomass deconstruction. However, different pretreatment technologies produce solids with varying compositional characteristics, making a uniform process optimization difficult. This study, therefore, compared the effects of lignin or hemicellulose removal from switchgrass lignocellulosic biomass (Stage 1) and subsequent sugar release by *C. thermocellum* (Stage 2). The objective was to identify pretreatment conditions that give the highest possible total sugar release (Stage 1 + Stage 2) for each pretreatment technology. The pretreatment technologies considered in this work are: hydrothermal, dilute alkali, dilute acid, and co-solvent enhanced lignocellulosic fraction (CELF). The resulting washed solids obtained after pretreatment were then subjected to *C. thermocellum* CBP at 5 g/L glucan loading. The results showed that lignin removal from switchgrass had a more positive impact on biological deconstruction by *C. thermocellum* than hemicellulose removal. Moreover, removal of lignin and hemicellulose simultaneously by CELF pretreatments showed 100% sugar release from switchgrass when combined with CBP.

A High-Throughput Investigation on the Production of 5-Hydroxymethylfurfural from Fructose

Glen S. Svenningsen
Advisor: Dr. Charles E. Wyman

5-Hydroxymethylfurfural (HMF) derived from renewable biomass sugars has received large interest in industry and academia, as a viable production source for plastics and commodity chemicals. The highest yields and selectivity of HMF have been primarily reported from aprotic co-solvent mixtures, such as dimethyl sulfoxide (DMSO). However, there is still little understanding of what particular factors influence the production of HMF. We employ a high-throughput investigation of HMF production in aqueous and DMSO co-solvent mixtures, utilizing a 96 well hastelloy reactor. We report the effects of atmosphere, water content, reaction time, temperature, acidity, and acid type on fructose dehydration to HMF in DMSO mixtures. Fructose dehydration in DMSO mixtures was also compared to several additional dipolar aprotic, aqueous mixtures including N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and dimethylacetamide (DMA). It was found that fructose conversion rates and HMF selectivity increased with the polarity index of the solvent. Having the highest polarity, DMSO demonstrated the highest HMF selectivity (80.3%) followed by NMP (76.2%), DMA (73.7%), and DMF (70.8%) at 120oC for 10 mins. Moreover, we found that acid type has no influence on selectivity and the addition of water in aprotic systems raises HMF selectivity at higher temperatures (>120oC). These results suggest that solvent and environmental conditions play a critical role in dictating selectivity and rate. We propose a mechanistic scheme for fructose dehydration to HMF, under deaerated conditions, emphasizing an intrinsic equilibrium step between HMF and humin production and illustrate which factors increase HMF production and selectivity.

Sugar Yields from Solids and Liquids Following Co-Solvent Enhanced Lignocellulosic Fractionation (CELF) of Switchgrass

Abhishek S. Patri
Advisor: Charles E. Wyman

Over the decades, numerous environmental and political concerns have motivated research into sustainable, domestic sources of fuels to replace those derived from petroleum. Lignocellulosic biomass represents the most abundant renewable resource and provides the only known platform which could sustainably produce liquid fuels on a large scale and at low cost. Due to its complex and recalcitrant structure, raw biomass hinders biological conversion of polysaccharides, thus necessitating pretreatment to deconstruct the plant by allowing cellulose and hemicellulose to be more accessible to enzymes for release of fermentable sugars. Several pretreatment methods, including hydrothermal and dilute acid approaches, have been developed to improve enzyme accessibility, but each is limited by the high loadings of expensive enzymes required after pretreatment. Recently, we developed a novel pretreatment called Co-solvent Enhanced Lignocellulosic Fractionation (CELF) that applies aqueous tetrahydrofuran (THF) with dilute sulfuric acid to remove a large portion of the lignin in biomass, while simultaneously achieving high yields of five carbon sugars from hemicellulose during pretreatment and of six carbon sugars from glucan using very low enzyme dosages (Nguyen et al., *ChemSusChem*, 2015). In this study, we first applied CELF to switchgrass to determine conditions for maximum sugar release from the combined operations of pretreatment and enzymatic hydrolysis. We then evaluated total ethanol yields from anaerobic fermentation of the pretreatment liquor by a genetically engineered yeast strain that ferments both pentose and hexose sugars.

Comparing sugar titers and ethanol yields from fed batch fermentation of CELF and DA pretreated Poplar solids at high glucan loadings

Rachna Dhir
Advisor: Dr. Charles E. Wyman

Biological conversion of lignocellulosic biomass to liquid fuels reduces greenhouse gas emissions and addresses other economic and strategic challenges. However, costs are high due to high enzyme loadings and capital costs, particularly at glucan loadings over 10% needed to realize economically attractive ethanol concentrations. Because solids concentrations above about 10% cannot be readily mixed in batch fermentations, a fed batch strategy was applied to establish maximum carbohydrate conversions from enzymatic hydrolysis of THF Co-Solvent Enhanced Lignocellulosic Fractionation (CELF) and dilute acid pretreated poplar wood. At 15, 18 and 20% glucan loadings, glucose concentrations of 63, 70, and 75g/l were achieved in only 2 days from CELF pretreated solids while concentrations from hydrolysis of dilute acid solids were only 45, 53, and 60g/l, respectively.

Establishment and Characterization of a Mouse Chamber for Investigating Health Effects

Xinze (Eric) Peng
Advisor: Dr. David Cocker

Recently we completed a new chamber for studying the exposure of mice to multiple air contaminants. The chamber can simultaneously control for multiple VOCs, particulate size and mass concentrations (synthetic or directly from source), active soils and/or pollens. The design is a result of a collaboration between the UC Riverside School of Medicine, CE-CERT, and plant/botany sciences. The system provides for controlled and well characterized whole animal exposures (typical duration of 1-2 weeks) where dosage is by inhalation of the air pollutants. Uniform dispersion and exposure stability of each class of air pollutants was characterized. Stability, range, and characterization of the system are summarized along with generation of air pollutants by the test subjects.

Novel Catalytic Pathways for CO_2 Utilization

Partho Sarothi Roy
Advisor: Dr. Chan Seung Park and Dr. Phillip N. Christopher

Renewable energy production processes have achieved significant technological and commercial maturity over the past two decades. However, most of this progress is related to power generation while technologies to produce commercially viable and fungible transportation fuels have lagged behind. Transportation sector poses unique challenges due to requirements including high energy density, compatibility with existing infrastructure, and high volumes of fuel consumption across the world. Technologies to produce carbon based renewable fuels such as Renewable Natural Gas (RNG) are needed to address these challenges.

Most renewable carbon based fuel gases including syngas from biomass gasification and biogas contain significant quantities of CO_2. Even if cost effective CO_2 separation methods are available, it is highly unlikely that renewable fuels will be economically competitive against fossil fuels. Converting the CO_2 along with methane into syngas is an attractive option since it can potentially improve the utilization of distributed renewable carbon resources while creating additional revenue streams. The overall objective of this dissertation is to develop novel catalytic pathways that can lead to cost effective and efficient technologies for renewable energy generation, with a particular emphasis on CO_2 utilization.

Biogas conversion using the bi-reforming reaction (steam and CO_2 reforming of CH_4) pathway in a compact and cost effective heat exchanger platform (HEP) type reactor can be the solution for utilization of the distributed resource. The process needs to be studied using the Aspen plus simulation package and experimentally over a [Pd-Rh/($CeZrO_2$/Al_2O_3)]/metal foam reforming catalyst with the goal of producing a high H_2 syngas. The bi-reforming reaction by controlled stoichiometric ratio of the reactants can produce a syngas with a 2:1 ratio followed by methanol synthesis. Methanation of renewable H_2 using CO_2 is an important pathway that can convert excess renewable electricity into a high value fuel. The proposed pathways will be studied to produce high value chemical products with reduced carbon intensity compared to existing methods.

Secondary Aerosol Formation from Agricultural Amines and Reduced Sulfur Compounds

Paul Van Rooy
Advisor: Dr. David Cocker

Gas phase amines and reduced sulfur compounds are often co-emitted from agricultural processes. Amines have been recently recognized as potentially major sources of agricultural aerosol formation, while the reduced sulfur compounds are largely ignored. There is a severe lack of knowledge and understanding regarding the interactions that take place between these co-emitted pollutants to form aerosol. As part of a collaboration between UC Riverside, Western Kentucky University, and Claremont colleges, environmental chamber experiments were conducted in order to investigate secondary organic aerosol formation and properties from these sources. Trimethylamine (TMA) was injected into the environmental chamber along with a reduced sulfur compound (dimethylsulfide, dimethyldisulfide, methanethiol, or hydrogen sulfide) and the hydroxyl radical for oxidation. The aerosol yields and characteristics from the oxidation of the combination of precursor were much different than aerosol from either the amine or sulfur compound alone. The amine and the sulfurs interacted quickly to form a substantial concentration of aerosol, much greater than the hydroxyl radical oxidation of the individual components. For example, dimethyldisulfide and TMA with the hydroxyl radical formed nearly 150 micrograms per cubic meter of aerosol after three hours, while separately they formed no more than 20 micrograms per cubic meter. Bulk aerosol composition varied with reduced sulfur compound used. TMA with dimethyldisulfide showed large sulfate peaks. Other combinations (e.g. TMA and methanethiol) showed peaks at high mass-to-charge ratios, consistent with oligomer formation. This novel investigation provides important information on agricultural aerosol formation. Knowledge gained through this study may be useful in regional air quality models as well as particulate matter regulations, specifically for large agricultural operations.

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

Patrick Roth
Advisor: Dr. Akua Asa-Awuku

Vehicle emissions are an important source of VOCs, NOx, CO, and PM, which can contribute to SOA and ozone formation. Previous work has characterized the physical and chemical properties of aged emissions from vehicles operating over realistic driving conditions. However, these studies focused on older technology vehicles, such as Port Fuel Injection (PFI) vehicles, with less attention on newer technology gasoline direct injection (GDI) vehicles.

GDI technology has become the preferred standard to PFI engines in the US and European markets due to its increased specific output and improved fuel economy. However, GDI vehicles will have difficulty meeting the 3 mg/mile LEVIII PM Standard (2017) due to increased PM emissions; whereas PFI vehicles generally emit below 1 mg/mile. As a result, manufacturers may begin electing to utilize gasoline particulate filters (GPF) to meet the LEVIII PM Standard.

For this study, the SOA forming potential from the emissions generated from five GDI vehicles (one with GPF filter) were investigated over the LA-92 driving cycle in triplicate. The exhaust was collected in CE-CERT's 30m^3 Mobile Atmospheric Chamber (MACh). The emissions were then photochemically aged and real-time particle and gaseous phase measurements were analyzed.

As the gaseous emissions aged and condensed, the fractal, primary particles (BC) quickly transitioned to more dense, spherical particles. The change in composition and morphology impacts both volatility and hygroscopicity measurements. Aged emission masses were found to exceed the primary masses with varying ratios of inorganic ammonium nitrate and secondary organic material (HR-TOF AMS). The vehicle equipped with the GPF filter displayed a considerable decrease in primary PM along with differences in the physical and chemical compositions of aged emissions. The data generated from this work will aid manufacturers and regulatory agencies understand the impacts of the increasing market share of GDI engines.

Effect of Exhaust Gas Cleaning System on Gases and Particles Emissions from an Ocean Going Vessel

Jiacheng Yang
Advisor: Dr. David Cocker

Ocean going vessels (OGVs) are a significant source of particulate matter (PM), sulfur oxides (SOx), and nitrogen oxides (NOx) emissions in the world. The high levels of SOx and PM emissions associated with OGVs are mostly because the use of heavy fuel oil (HFO) with high levels of sulfur in marine diesel engines. In October 2008, the International Maritime Organization (IMO) adopted the revised MARPOL Annex VI that requires the global Sulfur cap to be reduced from current 3.50% to 0.50% effective from January 2020, with the limits applicable in the emission control areas (ECAs) for SOx and PM educed to 0.10% effect from January 2015.

In order to meet this standard, the ship needs to operate with marine gasoline oil (MGO), or switch to LNG engine, and or operate with an exhaust gas cleaning system (EGCS) to remove the SOx to meet the standard. Due to the high cost of operating the MGO or switching to an LNG engine, a retrofit EGCS seems to be a more potential solution for meeting the MARPOL VI and ECAs standard.

This study was done on an OGV that routinely operates in the North America ECAs. Emissions tests were done on a Mitsui B&W 7L70 16.6MW main engine and a Wartsila 6R32D Auxiliary engines, including the measurement of SOx, NOx, PM, carbon monoxide (CO), and carbon dioxide (CO_2) emissions, as well as black carbon (BC) using three different methods (light absorption, light absorption-photoacoustic and thermal optical). The results indicate the marine scrubber system has an efficiency of over 95% in removing SOx. The scrubber system was also able to remove 9% of PM2.5, 11% of CO, and approximately 30% of BC emissions. The EGCS did not have a significant effect on NOx and CO_2 emissions.

Does Aerosol Chemistry Affect Droplet Kinetics?

Emmanuel Fofie
Advisor: Dr. Akua Asa-Awuku

Cloud droplet size influences particle scattering, the optical depth, and global cloud radiative forcing. In this study, we explore the droplet growth of simple inorganic salts (sodium chloride and ammonium sulfate) and organic acids such as succinic, malonic and oxalic acid. We also explore the droplet growth of activated complex aerosol from secondary organic aerosol (SOA) generated from seeded and un-seeded chamber experiments.

A DMT CCN counter with an enhanced resolution optical particle counter measures droplet sizes. The bin sizes are decreased two-fold and calibrated. The UC Riverside environmental chamber generated secondary organic aerosol from the ozonolysis of tricyclic sesquiterpenes and internally mixed, organic coated aerosols; dicarboxylic acids condense onto an $(NH_4)_2SO_4$ core.

Aerosol activate, form cloud condensation nuclei (CCN) and their droplet growth is characterized according to their mass accommodation coefficient and mixing states. A coupled analysis of laboratory CCN experiments and droplet growth modelling, Continuous Flow Streamwise Thermal Gradient CCN (CFSTGC) model, explores the effects of chemical composition on the droplet sizes when characterized by the hygroscopicity and the mass accommodation of water.

Results indicate that the final droplet sizes of activated inorganic salts and organic acids have different thermodynamic water uptake (hygroscopicity) but similar droplet kinetics. The hygroscopicities of pure and mixed compounds range from 0.1 to 1.2 and estimated mass accommodation coefficients can range over an order of magnitude (0.1 to 1.) Hence the observed kinetics of these compounds may not be divergent enough to result in a statistically significant difference in final droplet sizes. The more complex SOA ozonolysis show quantifiable differences in activated droplet sizes. The average hygroscopicity is ~0.1 and the estimated accommodation coefficient increases from 0.05 to 0.15.

We discuss reasons why the differences in aerosol systems can have such a vast influence on droplet sizes.

In-Use NOX Emissions from 2012+ Technology Heavy-Duty Diesel Vehicles

Yu (Jade) Jiang
Advisor: Dr. David R. Cocker

Characterization of in-use emissions from on-road heavy-duty trucks is an important element of developing accurate emissions inventory estimates. The goal of this work was to obtain emissions data on 2010 model year and later Class 8 diesel trucks equipped with the newest emission control strategies, with a special emphasis on data that can be used to improve estimates of “zero-mile” emission rates (ZMRs). We tested five heavy-duty Class 8 diesel trucks equipped with DPFs for PM emissions and SCR systems for NO_x emissions. The vehicles tested ranged in model year from 2012 to 2015, with 4 of the 5 engines being 2014 or newer. The vehicle matrix included 2 Cummins engines, and one engine each from Detroit Diesel Corporation (DDC), Volvo, and Navistar. The engines/vehicles were certified to a 0.2 g/bhr-hp or a lower certification limit, with the exception of one engine that was certified to a 0.35 g/bhr-hp standard. Each vehicle was tested on UCR’s heavy-duty chassis dynamometer over the four phases of ARB’s Heavy Heavy-Duty Diesel Truck (HHDDT) cycle and the Urban Dynamometer Driving Schedule (UDDS).

The results of this study are summarized below.

- NOx emissions varied depending on the test cycle and the test truck. The Volvo truck appears to be an outlier with noticeably higher NOx emissions. Thus, NOx results for the Volvo truck are discussed separately from the results for the Cummins #1, Cummins #2, DDC and Navistar engine-powered trucks.
- For the Cummins #1, Cummins #2, DDC and Navistar trucks, NOx emissions over the UDDS cycle (the cycle most relevant to ZMRs) ranged from 0.495 to 1.363 g/mi (0.136 to 0.387 g/bhp-hr). On a bhp-hr basis, those emission levels are comparable to the level to which the engines were certified, with some trucks being below and other being above the 0.20/0.35 NOx g/bhp-hr level. NOx emissions over the Transient cycle were slightly higher than over the UDDS, with emission rates ranging from 0.803 to 3.252 g/mi (0.194 to 0.762 g/bhp-hr).
- For the Cummins #1, Cummins #2, DDC and Navistar trucks, the lowest emissions were found over the two Cruise cycles. For the HHDDT-S, NOx emissions ranged from 0.067 to 0.249 g/mi (0.023 to 0.078 g/bhp-hr). For the Cruise, NOx emissions ranged from 0.068 to 0.471 g/mi (0.030 to 0.225 g/bhp-hr).
- For the Cummins #1, Cummins #2, DDC and Navistar trucks, the highest NOx emissions were seen over the Creep cycle, which showed NOx emission ranging from 2.131 to 9.468 g/mi (0.910 to 3.613 g/bhp-hr). The higher NOx emissions for the Creep cycle can be attributed to the fact that the cycle is composed of short, low-speed accelerations between periods of idle that include lower loads and temperatures, and that cover a very short distance (0.124 miles). Such stop-and-go type of driving tends to create high emissions when evaluated on a per-mile or per unit of work done basis.

Understanding Ultrafine Particulate Emissions & Dispersion from Wastewater Treatment Processes and Their Impact on Regional Air Quality and Health

Pedro Piqueras
Advisor: Dr. 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.

In this study we present particle concentration and size distribution measurements from Orange County Sanitation District aerated basins and we compare them to filter samples collected from ambient air. In addition, we have used EPA’s model AMS/EPA Regulatory Model (AERMOD) to establish a relationship between basin coverage, source emission and dispersion. Three different scenarios were modeled with annual, monthly and daily meteorological data. The scenarios that were taken into consideration were complete open basins, partially covered basins and mainly covered basins.

Results suggest that aerobic processes generate particles through bubble bursting which are currently being dispersed in areas surrounding WWTPs. In OCSD’s case, the aerosols emitted from the aerated basins are reaching neighborhoods and public spaces such as school and parks. It was also determined that partial coverage of the basins does not substantially reduce the particle concentration emitted; therefore a full coverage of the basins is advised. The relationship presented in this study can be used in the future to determine the emission rates from other wastewater treatment facilities if area and airflow are known.

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.

Secondary Organic Aerosol (SOA) and Ozone Formation from Photo-Oxidation of Unburned Whole Gasoline and Diesel

Weihua Li
Advisor: Dr. David Cocker

Direct evaporation from unburnt gasoline and diesel fuels is an established source of ozone and SOA forming hydrocarbon precursors. As new control technologies continue to decrease primary OA and gas-phase vehicle emissions, whole fuel evaporation becomes a more significant source of ambient aerosol formation. Therefore, determining the SOA forming potential of whole gasoline and diesel vapor is of significant interest. While SOA formation from some gasoline components such as aromatics have been individually studied under controlled conditions, there are only a few studies on how these complex mixtures behave in the atmosphere. Given changes in fuel formulations over time, it is important to revisit whole gasoline as an important SOA precursor, especially in light of increased knowledge on the impact of reactivity on aerosol formation and improved atmospheric chambers and instrumentation. Multiple photo-oxidation experiments with the presence of NO_x were conducted in the UCR CE-CERT dual 90m^3 smog chambers to investigate SOA and ozone formation from three different types of unburned fuels: commercial gasoline, commercial diesel, and reference fuels. Additionally, the fuels were also added to a surrogate mixture to best mimic the reactivity of an urban atmosphere. Liquid gasoline and diesel samples were collected at service stations during winter 2016 in Riverside, California and characterized by using gas-chromatography methods. Data will be presented comparing the aerosol formation from the different whole fuels in the presence of NO_X and also in the controlled reactivity system. SOA bulk chemical composition characteristics in the different systems were identified by the HR-ToF-AMS. Physical properties of the resulting aerosol, such as density and volatility will also be presented. The goal of this work was to investigate the influence of fuel composition on SOA formation and properties and ozone formation.

Gas Phase Vapors Play a Critical Role in Cloud Condensation Nuclei Activation

Ashley Erin 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. 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-hygroscopicity. However, this calculation assumes that the hygroscopicity of particles stays constant for a given precursor gas.

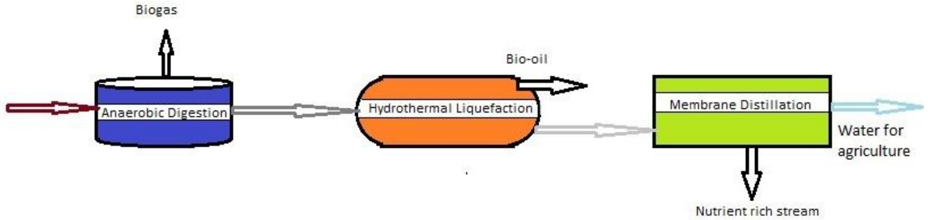
In the experiments presented, the CCN activity of secondary organic aerosol (SOA) from the photooxidation of two biogenic compounds, isoprene and longifolene were studied. Experiments were carried out in the UCR CE-CERT Environmental Chamber. A TSI SMPS ran in parallel with a Droplet Measurement Technologies Cloud Condensation Nuclei Counter (CCNC) was used to observe the hygroscopicity of resulting SOA, and an Agilent GC-FID quantified the gas-phase decay of the precursors. The gas phase decay of precursors was then related to the CCN/CN ratio rather than the size distribution to test if gas phase precursors play a direct role in CCN activation, and the extent to which the precursors influence CCN activation.

POSTER PRESENTERS

Sustainable use of dairy farm anaerobic digestate: from environmental pollutant to new source of water, energy, and nutrients

Unnati Rao
Advisor: Dr. Sharon Walker and Dr. David Jassby

Every year, the United States produces close to 200 million cubic meters of anaerobic digestate from liquid dairy waste effluent. The objective of this project is to study the integration of two process to extract energy, nutrients and water for agriculture from this digestate. Hydrothermal liquefaction (HTL) will be used for energy recovery and membrane distillation (MD) will separate the residual organic matter and nutrients from the HTL effluent. The effluent from the HTL process will be at an elevated temperature, and this residual heat can be used for MD, which requires the feed to be heated.



Anaerobic digestion is the most common method for treating liquid manure. However, this technique only converts about 40-50% of the biomass into biogas. HTL is carried out under high temperature and pressure and its products are in two phases. The HTL process produces an oily phase bio-crude oil that can be refined and processed into conventional liquid fuels, and an aqueous phase, rich in nutrients and some micro-pollutants. MD is a membrane-based water treatment process that relies on a temperature gradient across the membrane and the vapor pressure difference acts as the driving force. The separation relies on the transport of water vapor across a hydrophobic membrane - this ensures that the permeate stream is of a high quality. Since the feed stream into the MD system consists of organic matter, the membrane is susceptible to fouling. This makes the use of anti-fouling membranes crucial for this project. Electrically conducting membranes have been shown to prevent fouling. Carbon nanotubes (CNTs) are used to make the membrane electrically conductive. The output of the MD system would include two streams - a purified water stream and a nutrient rich stream that can be used as a high-strength fertilizer.

This project will enable dairy waste products to be used as a resource rather than a waste, by separating valuable energy and nutrients from the aqueous stream. The goal of the project is to determine optimum operating conditions and materials to maximize recovery of valuable products while minimizing fouling and energy use.

Direct expression of active human tissue inhibitor of metalloproteinases by periplasmic secretion in *Escherichia coli*

Kibaek Lee
Advisor: Dr. Xin Ge

Matrix metalloproteinases (MMPs) play a pivotal role in remodeling of extracellular matrix that are implicated in morphogenesis, wound healing, tissue repair. Tissue inhibitor of metalloproteinases (TIMPs) regulate the activity of these multifunctional MMPs. Since unregulated MMP activities are related to numerous diseases such as arthritis, cancer, and atherosclerosis, TIMPs have potential therapeutic worth. Ordinarily, to study their roles, TIMPs have been expressed in baculovirus-infected insect cells, mammalian cells as well as the cytoplasm of *Escherichia coli* (*E. coli*). However, these methods are costly, time-consuming, and inefficient in yield with heterogeneous products. In this study, direct production of active TIMPs from periplasmic space of *E. coli* was described. Western blot analysis showed that molecular chaperon disulfide isomerase (DsbC) enhanced the expression levels of TIMPs. Using BL21(DE3) as the host further reduced the amount of unwanted truncation. High expression levels of N-TIMP-1, -2, and TIMP-2 were archived and 0.2-1.4 mg purified TIMPs were typically yielded from per litter of culture medium. Periplasmically produced N-TIMP-1, 2 and TIMP-2 exhibited excellent inhibition activities towards MMP-1/2/7/14. In 2D and 3D cell based bioassays, recombinant N-TIMP-1, -2 regulated cancer cell morphogenesis and migration. In addition, N-TIMP-2 can also be utilized to evaluate the binding efficiencies and binding sites of antibodies on MMP-14. All above results indicated that periplasmic expression is an excellent strategy to produce active TIMPs with therapeutic potentials targeting MMPs.

Stability and Synthesis of Isolated Rhodium Metal Site Catalyst

Chithra Asokan
Advisor: Dr. Phillip Christopher

Recently, there has been significant interest in identifying and implementing the unique reactivity of atomically dispersed active precious metal sites on oxide supports. Finding a process to synthesize highly dispersed active metal atoms in high concentration, while remaining stable against agglomeration under reaction conditions, is a difficult endeavor. This study examines at a fundamental level how interactions between the supporting oxide material and the active precious metal can be engineered to control the stability and activity of isolated Rhodium atoms. Insights from this work will be used to design catalysts specifically to maximize utilization of rhodium single atoms for NOX reduction to create a cost efficient catalyst in catalytic convertors.

The procedure of Strong Electrostatic Adsorption (SEA) has been examined as a potential method of creating highly dispersed metal atoms on an oxide surface. The theory behind this procedure states that adsorption of anionic or cationic species on oxide surfaces is fundamentally related to the surface charge of the oxide and the charge of the ion. Generally, oppositely charged ions (counter-ions) are adsorbed and co-ions are repelled from any charged surface. Inductively coupled plasma mass spectrometry (ICP-MS) is used to examine how varying the pH of the support affects uptake of the precious metal. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Chemisorption are used to characterize optimum isolation and dispersion of single metal atoms while analyzing variables of support, precursor, surface loading, and rhodium weight percent.

The mechanism of single atom adsorption has also been studied via density functional theory calculations. Specifically, stable single Rh atom adsorption on the prevalent 101 anatase titanium dioxide surface is examined. Adsorption of carbon monoxide, hydrogen, and water to the single rhodium atom are observed to compare to experimental characterization techniques. The basis of potential NO reduction reaction pathways is also considered.

Tandem catalysis with yolk-shell nanostructures

Seungjin Lee
Advisor: Dr. Nosang Myung

Tandem catalysis is an interesting goal where multiple catalysts act on a single molecule to yield a product via a sequence of staged catalytic steps. Specifically, the reactant first reacts with catalyst A and turns to an intermediate, and then, a product is produced from the intermediate upon reaction with catalyst B. This ‘one-pot’ tandem reaction is highly attractive in terms of reducing product loss from isolation, purification of intermediates, and time. In this research, Au@TiO_2 yolk-shell catalysts are bring designed for the oxidation of benzyl alcohol to benzylaldehyde, and an amine functionality is being added via the formation of TiO_2-APTES-boc-proline surface groups, for the promotion of a coupling reaction of benzaldehyde and acetone to benzylideneacetone. For the characterization of the Au@TiO_2 and amine catalysts, TEM, IR, and ^{29}Si, ^{13}C and ^{1}H solid-state NMR are employed together with acid-base titrations which are used to calculate the surface concentration of the active sites on the titania. For our further studies, as a strategy to place different kinds of catalysts on a single surface, yolk@shell nanostructures are going to be fabricated, which have lower density, larger surface area, and higher loading capacity. Thus, benzyl alcohol can be made to react in one pot to benzylideneacetone in the yolk@shell tandem catalysts. Specifically, the Au/TiO_2 and amine catalysts can be located inside and outside of yolk@shell nanoarchitecture, respectively, since they are both based on TiO_2. However, although two catalysts can be placed in the same surface, the reaction conditions for the catalysts may be largely different. Thus, in order to find optimal conditions for the reactions, each catalyst is going to be executed under different reaction conditions such as temperature and concentration until finding the common conditions where both can be operated together.

Template-Free Synthesis of Selenium Nanowires

Saba SeyedMahmoudBaraghani
Advisor: Nosang Myung

During past few years, one-dimensional nanostructures such as nanotubes and nanowires have drown much attention due to their possible application in nanodevices. This is due to their enhanced performance which results from their high surface-volume ratio. Selenium is known to be an important elemental semiconductor which has been widely studied because of the exhibition of so many appealing properties such as high photoconductivity and low photomelting temperature, high piezoelectric, thermoelectricity, and non-linear optical responses. Together with the properties of semi- conductors, gas sensors have been devised for use in various applications, including electronic noses, clinical assaying, explosive detection, and work place hazard monitoring. Gas sensors typically operate at very high temperatures. Unlike other semiconducting gas sensors, trigonal-selenium nanowire gas sensors have the ability to operate at room temperature without the need of heating to high temperatures.

There has been extensive research on Selenium nanowires and nanorods among all Se nanostructures. Se nanowires can be fabricated by using solution-phase method, chemical vapor deposition method, and electrodeposition. The electrodeposition technique is more promising due its simplicity, cost-effectiveness, and low growth temperature. In the method of electrodeposition, trigonal selenium nanowires has been reported to be fabricated using some kind of template.

In the present work, we are looking forward to fabricating one-dimensional trigonal Selenium nanowires using electrodeposition without the aid of a template. The morphology is controlled as a function of applied potential, temperature, and concentration of selenium dioxide (SeO_2) in the electrolytes. The temperature-dependent annealing will also be performed. The morphology and crystallinity of the Se nanostructures are characterized by Raman spectra, TEM, SEM, and XRD. The electrodeposition of trigonal Selenium nanostructures is demonstrated based on an analysis of linear sweep voltammetry and pH-Eh (pourbaix) diagram.

Development and Characterization of Cellulolytic Enzymatic Fuel Cell via Incorporation of Multienzyme Cascade Scaffold on DNA

Sooyoun Yu
Advisor: Dr. Nosang Myung

As fossil fuel is depleting, an alternative source of energy to accommodate the current standard of living is of great research interest. Out of many methods that have been studied, fuel cells have been shown to be both environmentally friendly and flexible in fuel types, including hydrogen and alcohols. Enzymatic fuel cells (EFCs), more specifically, use isolated enzymes to catalyze redox reactions. In addition to its mild operating conditions and use of renewable biocatalysts, EFC is attractive as it consumes biologically derived materials as fuel. This study examined the feasibility and benefits of development of cellulolytic biofuel cells by mimicking the structured multi-enzyme scaffold in anaerobic bacteria called cellulosome to completely break down cellulose to glucose, which was then oxidized to generate current. Three cellulases of different cutting mechanism of cellulose, and cellulose binding domain (CBD) were expressed in *E.Coli*. The four proteins were purified using elastin-like peptide (ELP) and conjugated to DNA using a HaloTag fusion partner. SDS-PAGE and native gel were used to confirm correct purification and conjugation, respectively. Proteins and an oxidoreductase (glucose oxidase, GOx) were site-specifically immobilized on a DNA scaffold in an appropriate order for efficient cellulose hydrolysis and glucose oxidation. Absorbance at 340 and 575 nm was measured to quantify the resulting concentration of glucose and reducing sugar, respectively. Specific molar production rate of immobilized multienzyme scaffold was calculated then compared with that of free enzymes. With confirmed benefit of immobilizing cellulases and GOx, cellulolytic biofuel cell can be assembled by binding an end of the DNA scaffold to an electrode. Electrochemical analytical methods such as cyclic and linear sweep voltammetry, chronoamperometry and electrochemical impedance spectroscopy can be performed to determine the surface coverage of enzymes and power and current density of the EFC.

Epitaxial, ultra-thin Au coating as a barrier for oxidation damages for silver nanowires

Yangzhi Zhu
Advisor: Dr. Ruoxue Yan

Silver nanowires hold promise for applications such as transparent and flexible displays, solar cells, chemical/biological sensors, photonic circuits and scanning probe microscopies, but their susceptibility to damage from oxidation has limited their commercialization. We have developed a room-temperature chemical coating technique to deposit an ultra-thin, epitaxial layer of Au on the AgNW surface, which shields the AgNWs from oxidation and could represent a key to realizing their commercial potential. Our preliminary result has shown that the Ag@Au core-shell nanowires are stable in air and in physiological buffer solution for at least 6 weeks. The thin Au coating did not introduce significant Au fluorescence in the SERS spectrum, making them feasible for SERS and plasmonic sensing applications. Preliminary tests also showed that the Au coating does not have adverse effects on the propagation and coupling of surface plasmon polariton in Ag Nanowire waveguides, and the device performance is stable for weeks. AgNW-AFM probes are low-cost alternatives of high-aspect-ratio, high-resolution AFM probes. It was demonstrated that the Ag@Au core-shell nanowire functions similarly to bare-AgNW, with a much longer shelf-life for at least 4 weeks in the air. The electrical stability of the Ag@Au nanowires for flexible electronics is underway.

Co-solvent enhanced fractionation and catalytic conversion of lignocellulosic biomass to furanic fuel precursors.

Aakash Parikh
Advisor: Dr. Charles E. Wyman

A great amount of research has been conducted in the past couple of decades on lignocellulosic biomass as replacement for fossil fuels for production of transportation fuel and platform chemicals. Sugar degradation products such as furfural (FF) and 5-hydroxymethyl furfural (HMF) are one of the most promising alternatives to petroleum based chemicals. The overall aim of the project is to capitalize on high yields of FF and HMF obtained from hardwood poplar using tetrahydrofuran (THF), a highly tunable solvent, and convert them catalytically into fungible fuel blend stocks (furans and alcohols). Furthermore, due to high delignification capability of THF, valorization of lignin into bio-oil or cyclohexyl alkanes would also increase process revenue. A heterogeneous catalyst system is being developed for simultaneous transformation of both FF and HMF to alcoholic and/or hydrocarbon fuels. Along with this, two different methods, precipitation by dilution and boiling, to effectively extract lignin from the process without affecting its structure, are being compared. The critical data and yields from the laboratory data generated for the experiments are employed in ASPEN PLUS to identify cost reducing opportunities.

Application of Low-cost Air Quality Sensors to Measure Fugitive Dust Emissions from a Waste Collection and Processing Facility

Brandon James Feenstra
Advisor: Dr. Akua Asa-Awuku

With the emergence of low-cost air sensing technology, novel applications and case studies are being developed that increase the spatial and temporal resolution of current air monitoring networks. While air quality is typically measured at a regional level, stationary sources can significantly contribute to the overall air pollution impacts at a local level. An air quality sampling campaign was designed to monitor fugitive dust emissions from a waste collection and processing facility in Southern California. A network of nine solar-powered sensor nodes equipped with an Optical Particulate Counter (model OPC-N2, Alphasense, UK) and a 900 MHz mesh network gateway was deployed at the fence-line of the facility in June 2016. The OPC-N2 reports PM mass concentration measurements for three PM size fractions (i.e., PM_{10}, $PM_{2.5}$, and $PM_{1.0}$), while the gateway allows the nodes to transmit data to a central cellular gateway. The waste facility is located in close proximity to and upwind of an elementary school and residential housing. Results of the air monitoring campaign will show how fugitive dust emissions from the facility relate to meteorological data, facility activities (e.g. truck traffic), and exceptional events (e.g. road construction). Real-time monitoring data can provide both the facility and the community stakeholders with valuable information to better understand local air quality conditions. Over the next 12 months, the facility plans to invest millions of dollars in renovation expenses to implement advanced air control technologies designed to reduce dust emissions. The results of the sensor network will provide valuable real-time PM measurements pre, post, and during the renovation process with the opportunity of quantifying the costs and benefits of specific emissions control strategies.

Development of Model Framework for Predicting the Impacts of Fire Emissions on Air Quality

Isaac Kwadjo Afreh
Advisor: Dr. Kelley Barsanti

Wildfires have significant impacts on climate and air quality. With the frequent occurrence of wildfires in the western US and Canada, regulatory agencies urgently need accurate models of the impacts of fires to implement appropriate control and mitigation measures. Atmospheric models, used for predictions of the air quality and climate impacts of fires, represent the emissions of non-methane organic compounds (NMOCs) and their subsequent chemistry. Such models rely on a gas-phase chemical mechanism to represent the reactions of NMOCs with oxidants to form pollutants and short-term climate forcers; for example, ozone and secondary organic aerosol (SOA). SOA is a significant component of fine particulate matter (PM2.5), which has long been linked to radiative climate forcing and adverse health impacts. To enhance computational efficiency, individual NMOCs emitted by fires (represented in fire emission inventories) are lumped into surrogate species that are specific to a given gas-phase chemical mechanism. Gas-phase mechanisms are generally categorized into two main groups, namely condensed (lumped) and semi-explicit mechanisms. However, lumping strategies in the most widely used condensed gas-phase mechanisms - such as SAPRC and MOZART - are largely based on the reactivity of an organic compound with the hydroxyl radical (OH). As currently implemented, this approach severely limits the representation of the physical properties of the individual compounds, beyond their reactivity with OH; and therefore, severely limits the accuracy of such models, particularly for predictions of SOA. In this work, lumping schemes for gas-phase mechanisms will be developed to better represent the relevant properties of individual compounds emitted by fires. In addition to OH reactivity, important factors that are not considered in current mechanisms, such as solubility and SOA formation potential of NMOCs, will be considered. The updated model framework will improve the accuracy of predicted SOA formation from NMOCs emitted from fires. Ultimately, this research will lead to the improved atmospheric models that are needed for predicting and evaluating the impacts of wildfire emissions on air quality and climate.

Effects of Select Low Vapor Pressure –Volatile Organic Compounds (LVP-VOCs) on Atmospheric Photochemical Reactions

Weihan Peng
Advisor: Dr. David Cocker

Volatile Organic Compounds (VOCs) play an important role in atmospheric photochemical oxidation, which results in the formation of Secondary Organic Aerosol(SOA) and ground-level ozone. Low Vapor Pressure Volatile Organic Compounds(LVP-VOCs) is a type of VOC defined as a chemical “compound” or “mixture” contains at least one carbon atom and has a vapor pressure less than 0.1 mm Hg or a boiling point greater than 216 °C. It’s an essential component in consumer products, like caulk remover, laundry detergent and paint stripper. According to CARB, LVP-VOCs currently receive exemption from the VOC limits because of their relative lower vapor pressure and higher boiling point. However, recent study indicates that LVP-VOCs may have greater impacts on atmosphere that previous understood. Therefore, more qualitative and quantitative analysis of the availability of LVP-VOCs to atmospheric photochemical reactions should be conducted to provide more information on LVP-VOCs regulation.

This research characterized the role of LVP-VOCs in atmospheric photochemical reactions with respect to the formation of SOA and ozone specifically. All experiments were conducted by using the advanced environmental chamber facility at University of California, Riverside (UCR) College of Engineering – Center for Environmental Research and Technology (CE-CERT) to investigate atmospheric reactivity, ozone and SOA formation. Two large Teflon® bags were used to assure high volume to surface ratio and therefore low particle wall loss. SOA properties such as density, volatility and hygroscopisity, along with both gas and particle phase chemical composition were studied.

Radial Differential Mobility Analyzer

Sushmit Sadanand Poojary
Advisor: Dr. David Cocker

An RDMA (Radial Differential mobility analyzer) is an instrument which can be used to classify aerosol particles by size. In contrast to how a DMA works, in an RDMA, aerosol particles flow radially towards the center of negatively charged parallel disks. It can classify particles over a size range of 3-200 nm. The main difference between a RDMA and a conventional cylindrical DMA is geometry. The RDMA is specifically designed to measure ultrafine aerosol particles. It can achieve a high transmission efficiency of 0.85 to 0.90 in the particle size range of 3-10 nm and it has a considerably shorter residence time as compared to a conventional cylindrical DMA. The RDMA has a relatively simpler design which requires a smaller number of precision parts. It is compact, relatively light in weight and low in cost.