Fall 2017 Symposium Abstracts

ABSTRACT

Updating Gas-phase Chemical Mechanisms for Better Prediction of Secondary Organic Aerosols (SOA) From Biomass Burning

by

Isaac Kwadjo Afreh

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside
Dr. Kelley Barsanti, Chairperson

Biomass burning significantly impacts climate and air quality by emitting tons of particulate matter (PM) and trace gases into the atmosphere. These trace gases, specifically non-methane organic compounds (NMOCs), undergo photochemical oxidation to form secondary PM, more commonly known as secondary organic aerosol (SOA). PM in the atmosphere is known to have effects on visibility, radiative climate forcing, cloud droplet formation, and public health. Even though a large fraction of biomass burning PM may be secondary, measurement and modeling based estimates however vary widely. Therefore, there is a great need for climate and air quality models that more accurately estimate the quantity of SOA formed from biomass burning emissions. These air quality models will help support appropriate management and mitigation measures.

Air quality models rely on a gas-phase chemical mechanism to represent emissions of NMOCs and their subsequent chemistry. To enhance computational efficiency, most gas-phase mechanisms adopt simplification strategies whereby individual NMOCs are lumped into surrogate species, largely based on the reactivity of the organic compounds. Though such mechanisms are routinely used for modeling SOA, the lumping approaches have not been optimized to best represent the NMOCs that form SOA. For example, a compound that is known to form SOA may be represented by a surrogate species (based on reactivity with OH) that is not treated as an SOA precursor. The goal of this work is to develop lumping schemes to better represent the wide range of NMOCs emitted from biomass burning that are the most likely to form SOA by considering important factors such as reactivity and SOA formation potential of NMOCs. Simulations from the Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) model as well as experimental data will be used to estimate gas-phase reactivity and SOA potential of individual NMOCs. This research is critical and timely given that in California and other regions of the US wildfires are anticipated to increase in intensity and frequency due to ongoing climate change.

ABSTRACT OF THE DISSERTATION

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
by
Christian Alcaraz

Doctor of Philosophy, Department of Chemical and Environmental Engineering
Bourns College of Engineering
University of California, Riverside
Dr. Charles E. Wyman, Chairperson

Christian Alcaraz[1, 2], Rajeev Kumar[2], Phillip N. Christopher[2], Charles E. Wyman[1, 2]

[1]Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California, Riverside, Riverside, CA
[2]Center for Environmental Research and Technology (CE-CERT), Bourns College of Engineering, University of California, Riverside, Riverside, CA

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, and 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 about 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 converted into fructose before catalytic dehydrogenation to HMF. The presentation will consist of steps taken towards a combined approach to produce fructose from corn stover by investigating pretreatment results from CELF on corn stover and biological saccharification using Clostridium thermocellum cellulosomes.

Michael Bentel
3rd year Graduate Student
Dr. Jinyong Liu's Lab

Title:

Advanced Reduction Process as an Effective Treatment Technology for Emerging Per- and Polyfluoroalkyl Substances In Water

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) with differing chain lengths have been extensively used in a diverse scope of applications. They have contaminated drinking water sources worldwide. PFASs have been proven to be highly recalcitrant and persistent in the environment and living organisms. To address this global challenge, we have developed an innovative and effective treatment system using hydrated electrons for the defluorination of a series of PFASs in water. Hydrated electrons are generated through ultraviolet irradiation onto aqueous sulfite (SO_3^{2-}) at pH 9.2 and 25°C. They readily cleave the highly recalcitrant C-F bonds to yield fluoride (F-). Reaction mechanisms have been probed by conducting experiments with representative PFASs used in aqueous film forming foams (AFFF) and with variable short-chain model structures. This work highlights the effectiveness of hydrated electrons on treating PFAS contaminants in water, and demonstrates its promising application potential in practical water treatment systems.

Role of Particle Chemistry on Filtration Mechanisms of Water Treatment- Food Grade and Industrial Grade TiO2

Presented by: Chen Chen

The removal of food and industrial grade titanium dioxide (TiO2) particles through drinking water filtration was assessed via direct visualization of an in situ 2-D micromodel. The goal of this research was to determine whether variances in surface composition, aggregation size, and ionic strength, result in different transport and deposition processes in porous media, impacting the removal of particles from the environment. Food and industrial grade TiO2 particles were characterized by measuring their hydrodynamic diameter, zeta potential, and zero point of charge before introduction into the 2-D micromodel. The removal efficiency as a function of position on the collector surface was calculated from direct visualization measurements. Notably, food grade TiO2, had a lower removal efficiency when compared with industrial grade TiO2. The difference in removal efficiency between the two particles could be attributed to the higher stability of the zeta potential of the food grade particles, which lead to a reduced aggregate size when compared to the industrial grade particles. This removal trend was most pronounced in the rear stagnation point, due to the high contribution of hydrodynamic forces. It could be inferred from the results presented herein that particle removal strategies should be based on particle aggregation size, surface charge, surface composition, and crystal structure.

Understanding Reduction Kinetics of Aqueous Vanadium(V) and Transformation Products Using Electrochemical Techniques

Gongde Chen

Advisor: Haizhou Liu

Vanadium(V) is an emerging contaminant in the most recent EPA's candidate contaminant list (CCL4). The redox chemistry of vanadium controls its occurrence in the aquatic environment, but the impact of vanadium(V) speciation on its redox properties remains largely unknown. This study developed electrochemical techniques with a rotating ring disk electrode to examine the reduction kinetics of four pH-dependent vanadium(V) species and the stability of their reduction products in the presence and absence of phosphate. Results showed that the reduction of VO_2^+, $H_xV_4O_{12+x}^{(4-x)-}$ (V4) and HVO_4^{2-} proceeded via a one-electron transfer, while the reduction of $Na_xH_yV_{10}O_{28}^{(6-x-y)-}$ (V10) underwent a two-electron transfer process. Koutecky-Levich and Tafel analyses showed that the intrinsic reduction rate constants followed the order of V10 > VO_2^+ > V4 > HVO_4^{2-}. Ring electrode collection efficiency indicated that the reduction product of V10 was stable, while those of VO_2^+, HVO_4^{2-} and V4 had half-lives between milliseconds and seconds. With relative molar concentrations of phosphate to vanadium(V) varying from 0 to 1, phosphate accelerated the reduction rate constants of V10 and V4, and enhanced the stability of the reduction products of VO_2^+, V4 and HVO_4^{2-}. This study suggests that phosphate complexation can significantly impact the efficiency of reductive vanadium(V) removal in water treatment.

2017 CEE Symposium

Title:

Spectroscopic signatures and reactivity of CO adsorbed to atomically dispersed Pt atoms, Pt oxide clusters, and metallic Pt clusters on anatase TiO2

Author: Leo DeRita

Abstract:

Due to their wide use in industrial catalysis, significant efforts have been placed into developing synthetic protocols to reduce the metal nanoparticle size of oxide-supported precious metals due to their expense. Maximally efficient usage of the precious metal is enabled through the controlled production of atomically dispersed metal atoms on the oxide support. However, significant challenges associated with the synthesis and characterization have led to a variety of conclusions regarding the reactivity of dispersed metal atoms on oxide supports. Here we present the case of CO Oxidation over atomically dispersed Pt atoms on anatase TiO2 synthesized by extremely low metal loadings (<0.05 wt %), and high surface area TiO2, to ensure the production of isolated Pt species. Catalysts were prepared through strong electrostatic adsorption (SEA) wet impregnation at various weight loadings (0.025-0.25%) to control the abundance of atomically dispersed atoms and compared against typical catalyst preparations (1 wt %, dry impregnation) providing a range of samples with exclusively isolated Pt, exclusively Pt nanoparticles, and a mixture of both. The catalysts were rigorously characterized using HAADF-STEM and CO probe molecule IR spectroscopy to differentiate Pt oxide clusters, atomically dispersed Pt atoms and metallic Pt particles. The synthesis approaches outlined describe key parameters for production of isolated Pt on metal oxide supports including surface loading, pH, and weight loading.Multiple IR signatures have been identified to characterize isolated metal species in an unambiguous site-specific manner. Following rigorous IR characterization, steady state CO oxidation reaction measurements showed the isolated Pt atoms on anatase TiO2 exhibit higher activity than reduced Pt clusters on a per gram Pt basis and comparable activity on a turnover basis.

Consolidated bioprocessing of advanced poplar lines at the optimum hydrothermal pretreatment conditions identified for BESC standard poplar

Rachna Dhir[1,2,3], Rajeev Kumar[1,2,3], Charles M. Cai1,[2] and Charles Wyman[1,2,3]

(1) Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California Riverside, Riverside, CA, USA, (2) CE-CERT, Bourns College of Engineering, University of California Riverside, and (3)BioEnergy Science Center, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Abstract

Hydrothermal pretreatment is a low cost, catalyst-free, organic solvent-free method for disrupting the highly recalcitrant structure of lignocellulosic biomass in order to improve the accessibility cellulose to hydrolysis by microbes or enzymes. In this study, we combined hydrothermal pretreatment with consolidated bioprocessing (CBP) as an integrated method for producing ethanol from biomass. CBP uses specialized microbes that can produce cellulolytic enzymes on their own so that supplementation of expensive fungal cellulases is not needed. First, reaction conditions were optimized to maximize total cellulose consumption from hydrothermal pretreatment of a native poplar wood (BESC standard) and advanced transgenic poplar lines provided by Oak Ridge National Laboratory (ORNL). Then, advanced CBP organism Clostridium thermocellum was used to solubilize and consume the available glucan from the poplar lines. Through a range of pretreatment conditions, we have optimized the glucose yields during pretreatment and CBP as (Stage 1+2) as 83.1% and xylose yields from pretreatment and CBP (Stage 1+2) as 98.3%, whereas, the combined total sugar yield from glucose and xylose Stage (1+2) at these conditions were estimated at 88.6%, at the end of 7 days. Identified hydrothermal pretreatment conditions with highest glucose and xylose yields further applied to various advanced varieties of poplar. The application of pretreatment accelerated the glucan content of advanced varieties post pretreatment. These pretreated poplar varieties will be subsequently subjected to CBP for comparing their performance to BESC standard poplar.

Application of low-cost particulate matter sensors to measure fugitive dust at the fence-line of a waste processing facility

Brandon Feenstra, David Cocker

Abstract

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 (25 by 25 km), stationary sources of air pollution 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 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 were deployed at the fence-line of the facility. The OPC-N2 reported PM mass concentrations for three PM size fractions (i.e., PM10, PM2.5, and PM1.0), while the gateway allowed the nodes to transmit data to a central cellular communication gateway. The waste transfer 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, and exceptional events. The results of the sensor network 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. Real-time monitoring data can provide both the facility and the community stakeholders with valuable information to better understand local air quality conditions.

UCR 2017 Symposium Abstract

Title:

Support Effects on Ethanol Dehydrogenation over Cu Catalysts
Presented by: Sergei Hanukovich

Abstract:

Ethanol (EtOH) dehydrogenation to acetaldehyde (Acet-H) has been widely studied over oxide-supported Cu catalysts as a reaction pathway that can provide a sustainable alternative to the current industrial process that uses ethylene as a feedstock for fuel. The rates and selectivity for Acet-H formation have been shown to be dependent on Cu particle size, reaction conditions, and the catalyst support. Specifically, it has been argued that Acet-H production occurs exclusively over Cu0 sites, whereas other products such as diethyl ether, ethylene, and ethyl acetate form over the support or metal-support interface. Here, we will discuss how the nature of the oxide support influences Acet-H formation on Cu0 sites. A combination of N2O titration experiments, CO probe molecule IR, in-situ IR, and reactivity measurements under strict kinetic control are used to provide mechanistic insights into the support effects on Acet-H production with a specific focus on comparative turnover frequency measurements, mechanistic interrogation, and stability analysis.

ABSTRACT FOR CEE SYMPOSIUM 2017

Unraveling Excitation Energy Transfer Mechanisms in Plasmonic Nanoantennas

By

Niranjan Vasant Ilawe

PhD Candidate, 4th Year Student

Graduate Program in Chemical and Environmental Engineering

University of California, Riverside, September 2017

Dr. Bryan M. Wong, Advisor

Plasmonic systems composed of nanoparticle arrays have fascinated researchers over the last couple decades, prompting comprehensive studies on plasmon-mediated excitation energy transfer (EET) processes. A theoretical understanding of these processes is crucial not only for the development of nanoscale photonic circuitry, but also for the design of highly efficient energy-guiding nanoantennas. Although theoretical methods based on Forsters resonance energy transfer (FRET) have been successfully applied to single donor/acceptor systems, these methods in their standard form fail for large multi-donor/acceptor assemblies in complex configurations. While ab-initio quantum-mechanical methods like density functional theory (DFT) go beyond the simple point-dipole and spectral overlap approximations of FRET, they are computationally intensive and limited to a few hundred atoms. Here, we describe our use of the density functional tight binding (DFTB) approach and its real-time time-dependent counterpart, RT-TDDFTB, to probe in detail the EET dynamics of plasmonic nanoantenna systems without recourse to the point-dipole or spectral overlap approximations. The computational efficiency of DFTB is due to additional integral approximations arising from the tight-binding approach, resulting in a linear scaling computational cost. In particular, we discuss the results obtained by the RT-TDDFTB calculations for a large plasmonic nanoantenna composed of 220 sodium atoms. We reveal a complex interplay of many-body interactions that govern the EET mechanism in the plasmonic nanoantenna that go beyond the single donor/acceptor interactions considered in traditional theories. We attribute these effects in part to the exceedingly long-range electrodynamic couplings, which are a result of the coherent nature of oscillating electrons in plasmonic nanoparticles. We also corroborate our findings via an analytical two-level system that captures many of the intricacies of the full quantum dynamical method. Most importantly, our time-domain studies provide an intuitive approach to probe in microscopic detail the real-time electron dynamics in large plasmonic nanoantennas.

Effects of Antiscalants on Precipitation of Calcium Salts in Brackish Water Desalination Concentrate

Tushar Jain, Dr. Haizhou Liu

University of California Riverside

Department of Chemical and Environmental Engineering

Alternative water sources such as desalination of brackish groundwater has become increasingly important with increasing population and impacts of climate change. The complex chemical composition of the brine and the lack of understanding of the antiscalants' scale inhibiting properties makes it difficult to develop a screening method to achieve scale-free flow of water. This study looks at understanding the effects of antiscalants such as nitrilotri(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid) and diethylenetriaminepentakis (methylphosphonic acid) on precipitation of commonly found scaling salts such as hydroxylapatite, gypsum and calcite. Furthermore, precipitation kinetics and crystallization mechanism have been proposed in this study. The extent of precipitation is measured in the form of turbidity of the system using a HACH 2100-N turbidimeter. The kinetics of precipitation was examined by fitting a Michaelis Menten type model. The order of sensitivity of antiscalant towards the rate of precipitation was NTMP > EDTMP > DTPMP. The order of effectiveness of antiscalants in terms of its inhibition capacity was DTPMP > EDTMP > NTMP.

Study of metal-oxide nanostructure as a photoelectrode in organic-inorganic solar cell devices

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, DSSCs and PSCs 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 TiO2 or ZnO that absorbs light in the ultra violet (UV) region, but cannot absorb visible (Vis) 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 expands the absorption range of organic-inorganic solar cell devices and improves their performance.

In this work, ZnO-CuO core-shell and ZnO-CuO backbone-branch nanostructure have been successfully synthesized and used for the photoelectrode in organic-inorganic solar cells. ZnO nanorods are synthesized via chemical vapor deposition. CuO shell and branches are synthesized on ZnO nanorods by thermal oxidation and sol-gel method, respectively. In order to understand the effect of adding CuO layer, the performance of the DSSCs using ZnO nanorods and ZnO-CuO core-shell structure is tested and compared. The morphology, optical properties, and crystallinity of the synthesized materials are characterized by scanning electron microscope, UV-Vis-NIR spectrophotometer, and X-ray diffraction (XRD) respectively.

Carbonization of LiFePO4 Cathode: Optimized Porosity and Carbon Additives

Jiyong Kim
Advisor: Dr. Martinez-Morales

Lithium iron phosphate (LiFePO4, LFP) is a well-proven chemical, driving technology for battery energy storage applications due to its high theoretical capacity (170 $\llbracket mAh \cdot g \rrbracket^{\wedge}(-1)$), lower cost, longer cycle life, better safety, and more environmental friendliness in comparison to other traditional cathode materials like lithium cobalt oxide (LiCoO2) and lithium manganese oxide (LiMn2O4). However, the key limitation of LFP has been its low intrinsic electronic conductivity (~ $\llbracket 10 \rrbracket^{\wedge}(-9) S \cdot \llbracket cm \rrbracket^{\wedge}(-1)$) at room temperature. Several methods have been used to enhance electronic conductivity, such as carbon coating, super-valence ion doping on the Li-site, and nano-networking of electronic conductive metal-rich phosphides.

Based on a numerical study on the selecting of conductive additives for LFP cathodes, it was determined that the best conductivity in each cathode was achieved by the combination of 30% active material, 7.5% graphite, 10.15% carbon black, and 12.35% polyvinylidene fluoride (PVDF) by volume, to achieve 40% porosity. In this work, we used polyvinyl chloride (PVC) to create pores in the cathode. The LFP cathode was prepared in a slurry composed of lithium iron phosphate powder as the active material, carbon black and graphite as conductive additives, PVDF as a binder, and N-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was deposited on the aluminum substrate using the doctor blade method. The cathode was heated at 300°C to evaporate PVC and create a matrix of pores. The cathode's morphology was characterized by a scanning electron microscope (SEM). An image analysis program was then used to calculate the pore volume. Coin-cells were assembled with various percent of porosity in a glove box. Cycling testing was performed using an Arbin tester.

Plasmonic Nanowire Optical Probe for Near Field Scanning Microscopy

By
Sanggon Kim
Department of Chemical and Environmental Engineering
University of California, Riverside

Prof. Ruoxue Yan (CEE)

Keywords: Near-field scanning optical microscopy, diffraction limit, surface plasmon, nanowire waveguide, Raman enhancement.

Abstract

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 58% in these probes, which corresponds to 106 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 107 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 MoS2 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.

Effect of micro- and macro-accessibility of cellulose on Clostridium thermocellum consolidated bioprocessing

Ninad Kothari1, 2, 3, Charles Cai1, 2, Rajeev Kumar2, 3, and Charles E. Wyman1, 2, 3

1Dept. of Chemical and Environmental Engineering, Bourns College of Engineering, University of California Riverside (UCR), Riverside, CA, USA.
2Center for Environmental Research and Technology (CE-CERT), Bourns College of Engineering, University of California Riverside, Riverside, CA, USA.
3BioEnergy Science Center (BESC), Oak Ridge National Laboratory (ORNL), Oak Ridge, TN, USA.

Lignocellulosic biomass is the only known sustainable resource that is low enough in cost and available in sufficient quantity to support production of liquid transportation fuels, such as, bioethanol, at a scale that could significantly reduce the almost total petroleum dependence of the transportation sector. The conventional approach for ethanol production from lignocellulosic biomass involves the following operations: size reduction, thermochemical pretreatment, enzyme production, enzymatic cellulose hydrolysis, fermentation, and product recovery. The use of fungal cellulolytic enzymes to deconstruct cellulose from lignocellulosic biomass is expensive because of the high doses of enzymes needed to achieve economically viable ethanol yields. Alternatively, consolidated bioprocessing (CBP) simplifies bioprocessing of lignocellulosic biomass by using cellulolytic microbes, such as Clostridium thermocellum, that eliminate the need for adding expensive enzyme and directly converting biomass into fuel ethanol. Cellulose accessibility to fungal enzymes or C. thermocellum cellulosomes for hydrolysis can be divided into micro- and macro-accessibility. Macro-accessibility of cellulose is mostly affected by the presence of hemicellulose and lignin in the complex cell wall structure of biomass, whereas, micro-accessibility is affected by the properties of cellulose itself, such as its crystallinity, type, and chain length. Clostridium thermocellum can achieve only up to ~48% glucan conversion of unpretreated, milled switchgrass in 7 days. Therefore, thermochemical pretreatment of biomass may be required to increase cellulose macro-accessibility and enhance biological conversion to achieve higher, economically feasible product yields. Therefore, in this work, we compared and evaluated how changes in removal and disruption of hemicellulose and K-lignin from raw switchgrass by hydrothermal, dilute acid, dilute alkali, and novel co-solvent enhanced lignocellulosic fractionation (CELF) pretreatments impact CBP deconstruction of switchgrass by C. thermocellum. Further, once cellulose is made macro-accessible to C. thermocellum cellulosomes, the micro-accessibility of cellulose can affect deconstruction. To determine whether cellulose micro-accessibility affects metabolites production by C. thermocellum, we applied CBP to model cellulosic substrates including, Avicel PH-101, α-cellulose, Sigmacell 50, cellulose from cotton linter, and milled Whatman 1 filter paper. These substrates were chosen because of their differences in cellulose crystallinity and degree of polymerization and resulting differences in cellulose micro-accessibility. The results revealed that C. thermocellum CBP is affected by macro-accessibility of cellulose but not affected by its micro-accessibility. Therefore, pretreatment of lignocellulosic biomass is essential to render cellulose more macro-accessible for enhanced biological deconstruction of the biomass and higher product yields.

Bioinspired design of multi-functional hybrid catalysts for synthetic organic chemistry

Louis Lancaster, Ian Wheeldon
Department of Chemical and Environmental Engineering, University of California, Riverside

Abstract:
Selective alcohol oxidation can be a powerful tools that would be useful in areas of energy conversion, environmental remediation, and synthetic organic chemistry, making it an area of major concern for researchers. The utility of such tools has been unrealized in most industrial settings due to the inherent risks these reactions carry when scaled to industrial relevant quantities. Aerobic oxidations in particular provide all the necessary ingredients for chemical fires. In addition, the methods currently used for oxidation reactions involve organic solvents and highly toxic compounds, the environmental consequences of which are compounded by the poor atom efficiency of these reaction methods.

To address these concerns, we designed a catalytic system that selectively oxidizes aliphatic alcohols and glycols under ambient aqueous conditions. The first bifunctional catalyst was assembled using an organic electrocatalyst, TEMPO , and an alcohol dehydrogenase isolated from Pyrococus furiosus, AdhD. These catalysts were selected for their selectivity towards primary and secondary alcohols respectively. The covalent attachment of these components was confirmed by mass analysis and chemical reactivity assays. The attached catalysts had reduced reaction velocities of 10-15% when compared to the unmodified catalysts. The enhancement to TEMPOs TON that is realized by its immobilization to an enzyme outweighs the reduced catalytic rates.

Generation of functional monoclonal antibodies targeting G protein-coupled receptors

Kibaek Lee
Advisor: Xin Ge

As important signaling molecules located on cell membranes, G protein-coupled receptors (GPCR) represent one of the largest therapeutic targets – estimated that 40-50% drugs on market act on GPCRs. With inherent high specificity and high affinity in addition to low toxicity and long in vivo half-life, monoclonal antibodies have become very attractive therapeutic agents targeting GPCRs. However, generation of antibody agonists / antagonists against GPCRs is extremely challenging for at least three reasons: (1) GPCRs are difficult to be produced; (2) The druggable hotspots of GPCRs cannot be readily accessed by normal antibody designs; (3) A function-based but not binding-based selection method is required. My thesis focuses on developing novel technologies to address these challenges for facile discovery and engineering biologics agonists targeting GPCR. More specifically, we plan to establish mammalian GPCR signaling pathways in yeast cells, apply novel antibody library deign, and develop yeast periplasmic expression system. Our target is glucagon-like peptide-1 receptor (GLP-1R), a well-established target for the treatment of type 2 diabetes. Our progress on these efforts will be discussed in my presentation. Successfully establishing these techniques will lay the groundwork for the discover of antibody drugs for many other GPCRs of biomedical importance.

Tandem catalysis with yolk-shell nanostructures

by

Seung-jin Lee

Doctor of Philosophy, Graduate Program in Chemical Engineering University of California, Riverside
Prof. F. Zaera, Chairperson

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@TiO2 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 TiO2-APTES-boc-proline surface groups, for the promotion of a coupling reaction of benzaldehyde and acetone to benzylideneacetone. For the characterization of the Au@TiO2 and amine catalysts, TEM, IR, and 29Si, 13C and 1H 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/TiO2 and amine catalysts can be located inside and outside of yolk@shell nanoarchitecture, respectively, since they are both based on TiO2. 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.

Impurity Effects on Charging Mechanism and Energy Storage of Nanoporous Supercapacitors

Kun Liu

Department of Chemical and Environmental Engineering,
University of California, Riverside

Room-temperature ionic liquids (RTILs) have been widely used as electrolytes to enhance the capacitive performance of electrochemical capacitors also known as supercapacitors. Whereas impurities are ubiquitous in RTILs (e.g., water, alkali salts, and organic solvents), little is known about their influences on the electrochemical behavior of electrochemical devices. In this work, we investigate different impurities in RTILs within the micropores of carbon electrodes via the classical density functional theory (CDFT). We find that under certain conditions impurities can significantly change the charging behavior of electric double layers and the shape of differential capacitance curves even at very low concentrations. More interestingly, an impurity with a strong affinity to the nanopore can increase the energy density beyond a critical charging potential. Our theoretical predictions provide further understanding of how impurity in RTILs affects the performance of supercapacitors.

Developing the thermotolerant yeast Kluyveromyces marxianus as a microbial host for volatile ester biosynthesis

Ann-Kathrin Löbs, Ronja Engel, Cory Schwartz, and Ian Wheeldon Chemical and
Environmental Engineering, UC Riverside

The yeast Kluyveromyces marxianus is a promising candidate for chemicals biosynthesis. It has rapid growth kinetics at temperatures upwards of 45 °C and can produce short and medium chain volatile esters and ethanol at high rates. Of particular interest is its capacity to produce ethyl acetate at rates upwards of 2 g/L/hr in aerated cultures. Both ethanol and ethyl acetate production rely on the activity of alcohol dehydrogenases to oxidize acetaldehyde to ethanol, which serves a substrate for ethyl acetate production. Little is known about the ester production pathways in K. marxianus. Preliminary results suggest the presence of alcohol dehydrogenase (Adh) and alcohol acetyltransferase (AATase) activity, and the absence of significant reverse esterase activity. In this work, we design a hybrid-synthetic RNA polymerase III promoter to create a CRISPR-Cas9 genome editing systems for K. marxianus. This system was used to construct a disruption library of ADH and AATase genes to study their function in volatile metabolite production. Eat1 disruption resulted in a significant decrease in ethyl acetate production identifying Eat as a crucial enzyme for acetate biosynthesis in K. marxianus. ADH2 disruption resulted in reduced ethanol production along with accumulation of acetaldehyde suggesting an importance of Adh2 in ethanol production. These findings serve as starting point for metabolic engineering approaches towards ethyl acetate and longer chain esters production.

Protease inhibitory mAbs isolated by genetic selection

Tyler Lopez, Aaron Ramirez, Zahid Mustafa, Chris Benitez, Xin Ge*

Controlling many physiological signaling pathways, proteases are one of the most important families of drug targets. Because small compound inhibitors often fail to deliver required selectivity, monoclonal antibodies merge as effective protease inhibitors. However, traditional Ab screening methods rely on binding assays without control on their inhibition functions. In this study, we developed a genetic selection approach to isolate functional mAbs inhibiting a panel of proteases of interest:matrix metalloproteinase-9 (MMP-9, in neuropathic pains), beta-secretase 1 (BACE1, an aspartic protease in Alzheimer), cathepsin K (a cysteine protease in osteoporosis), and Alp2 (a serine protease in aspergillosis). Particularly, mAb B3B12 inhibited BACE-1 with 26 nM potency, and mAb L13, an anti-MMP9 inhibitor (potency = 20 nM), exhibited significant pain attenuation effects in paclitaxel mouse model. Overall, highly potent mAb inhibitors with exclusive selectivity have been discovered for proteases of biomedical importance with the potentials to deliver desired therapeutic efficacy.

Effect of nutrient availability and water chemistry on attachment of produce-associated pathogens and potential surrogates

Holly Mayton
Advisor: Dr. Sharon Walker

Pathogenic microbial contamination of fresh produce causes significant foodborne illness outbreaks in the U.S. and around the world. Recent trends towards more sustainable food production has led to increased usage of manures and recycled irrigation water, which may increase opportunity for bacteria to come in contact with food. Bacterial survival, proliferation, and resulting foodborne illness outbreaks begin with adhesion to a surface, followed by persistence in the face of washing. Thus, understanding pathogens' characteristics and attachment mechanisms under a variety of conditions has become a research priority in food safety. However, a growing body of literature suggests that current indicator organisms used to assess sanitation processes are not sufficient representatives of relevant pathogens. Thus, bacterial attachment to spinach leaf surfaces in a parallel plate flow cell was studied using E. coli O157:H7, Salmonella Typhimurium, and two environmental E. coli isolates suspended in 10 mM KCl, CaCl2, and artificial groundwater (AGW) to determine the influence of water chemistry on adhesion in dynamic flow conditions. In addition, the bacteria were grown in either nutrient-rich or nutrient-deprived environments (Luria Burtani or M9 minimal media) to determine the role of growth conditions on attachment trends. Attachment mass transfer rate coefficients generally increased with solution valence for the two pathogens and increased when bacteria were grown in low nutrient conditions, with E. coli O157:H7 adhering more than Salmonella. Physiochemical characterization of cell surfaces show that electrophoretic mobility, hydrophobicity, and surface charge density varied with solution chemistry, but EPS production and composition has the most influence on microbial adhesion to spinach leaves. Higher total EPS production and lower sugar-to-protein ratios (by mass) were correlated with increased attachment, especially in the more complex chemistry and valence of AGW. Of the two environmental E. coli strains, E. coli B01 produced a lower sugar-to-protein ratio and showed greater attachment when grown in minimal media, while E. coli B05 produced a higher ratio and attached less. Results suggest that these isolates represent potential candidates for non-pathogen bacteria surrogates in testing food safety systems for washing and handling leafy greens.

Including Secondary Organic Aerosol of Particulate Matter into the EPA's MOVES Model

Ayla Moretti
Advisors: Dr. David Cocker & Dr. Matthew Barth

EPA's MOtor Vehicle Emission Simulator (MOVES), is an emission modeling system estimating emissions from mobile sources (vehicles) for criteria air pollutants, greenhouse gases and air toxics. Currently the EPA's MOVES model only accounts for primary particulate matter that is emitted from a tailpipe, which is only a small fraction of the particulate that is emitted. This research will be looking at adding all particulate matter (PM), both primary and secondary, that is emitted from a vehicle's tailpipe, including secondary organic aerosols (SOA). Having both primary and secondary particulate matter in the EPA's MOVES model will allow for more accurate emission estimates as the basis for: human exposure modeling, local and regional air quality modeling, regulatory impact assessments, and trend analysis.

ABSTRACT

Enhanced Nitrogen Removal Using Chabazite in a Hybrid Biological Process

By

Stephen Robert Opot
Chemical and Environmental Engineering
University of California, Riverside, August 2017
Dr. Mark R. Matsumoto, P.I.

Excess nutrients, particularly nitrogen, from wastewater discharged into waterways often lead to eutrophication, hypoxia, and oceanic red tide that threaten public and environmental health. Anaerobic Ammonium Oxidation (Anammox) is a relatively new treatment approach used to remove nitrogen wastewater. Compared to the conventional multi-stage nitrification-denitrification nitrogen (N) removal process, the Anammox process utilizes less energy and eliminates the need for organic carbon additives in wastewater treatment plants. However, the process has encountered a number of pragmatic challenges that has impeded its widespread adoption as a practical treatment alternative. Foremost among these challenges is the very slow growth rate of the Anammox bacteria, which necessitates a long start-up time before high nitrogen removal efficiencies can be obtained on a steady-state basis. Attempts to reduce start-up time are challenged by inadequate seed biomass and bacteria washout during operation. As such, efforts are needed to promote faster bacterial growth and system retention. One approach is to amend bioreactors with materials that have beneficial surface and chemical properties that are capable of concentrating growth factors (e.g., ammonium, NH_4^+), while enabling selective colonization of Anammox bacteria on the materials' surfaces. This strategy could reduce start-up time and biomass wasting.

With evidence of higher cation exchange capacity (CEC) and better ammonium ion exchange (IX) rate than natural clinoptilolites (zeolite, group 7); chabazite material (zeolite, group 4) could be a better alternative to enhance Anammox culture development. Therefore, it is proposed to amend an Anammox SBR with chabazite particles to accelerate the startup period. However, depending on the exchangeable ion associated with the chabazite, there may be cation inhibition released during NH_4^+ IX. As such, the study also seeks to investigate the effect of chabazite sub-species (-Ca & -K), target cation (NH_4^+), and competing cation (i.e. K^+) on ammonium oxidation rate. To date, chabazite (AZ-UB) material has been characterized, lab-scale hybrid Anammox-SBRs developed, and molecular tools applied to detect, quantified, and identified the Anammox bacteria specie in the hybrid systems. Comparative studies have also been conducted to determine the differential effect of chabazite on ammonium oxidation rate and bacteria population.

CO-SOLVENT PRETRATMENT OF BIOMASS ACHIEVES HIGH LIGNIN REMOVAL AND PREVENTS LIGNIN REDEPOSITION

Abhishek S. Patri, Charles Cai, Rajeev Kumar, and Charles E. Wyman*
Department of Chemical and Environmental Engineering and
Center for Environmental Research and Technology (CE-CERT)
1084 Columbia Avenue
University of California, Riverside
Riverside, California 92507
BioEnergy Science Center (BESC), Oak Ridge National Laboratory (ORNL), Oak Ridge, TN
*cewyman@engr.ucr.edu

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 investigated molecular principles responsible for co-solvent assisted delignification of biomass to achieve high enzymatic hydrolysis yields.

Health Effects Investigation of Nebulizing Alternaria Extracts and Nanosilica Particulate Matter using a Mouse Chamber

Xinze Peng

A whole-body exposure chamber is established and characterized for studying the exposure of mice to multiple air contaminants. This design is a result of a collaboration between the UC Riverside School of Medicine, CE-CERT, and plant/botany sciences. Alternaria, which is known as a common fungus to Southern California that has been shown to increase the risk of developing asthma when inhaled chronically, was used as a bioactive material for a five-day health study. Alternaria extracts diluted in water were nebulized into the chamber to generate a particle size distribution with a mode of 100 nm. Preliminary data using mice indicates an increase in both lung inflammation (e.g., elevated eosinophil levels) and brain inflammation (e.g., TLR2 induction) following a continuous five-day exposure. Silica Nanospheres in water solution were also nebulized into the chamber to generate a size distribution with a mode of 100 nm to serve as comparison study of non-bioactive nanoparticles. The research purpose of this study is to determine whether the health effects were caused by bioactive materials or by simple inhalation of nanoparticles.

Effects of hydroperoxyl-radical-to-NO ratio on SOA formation from aromatic hydrocarbons in a controlled reactivity urban atmosphere

Weihan Peng

Secondary Organic Aerosol (SOA) formation from hydrocarbon precursors is typically predicted by using either two-product model or volatile basis set (VBS). Both models use two sets of aerosol yield parameters, low NOx and high NOx, which are estimated from environmental chamber studies. Given the fact that NO has significant effects on SOA, two scenarios of NO conditions are not sufficient to accurately represent the sensitivity of SOA to different NO levels. Thus, this work explores aerosol yield potential with a better resolution of NO concentration. Absolute NO condition or NO/VOC ratio is typically used as the index of oxidation level in environmental chamber; however, the relative level of NO to HO2 largely impacts SOA formation. The reactions of RO2 with both NO and HO2 are two important pathways of SOA formation with the gas-phase products from the RO2+HO2 pathway generally have lower volatility than that from RO2+NO reaction for aromatic hydrocarbon system. The ratio of NO to HO2 controls the branching ratio of these two reactions and thus determines secondary gas-phase products and their ability to partition to aerosol-phase. This work, instead of performing traditional single precursor chamber study, investigates the effects of NO and HO2 on SOA formation from m-xylene and 1, 2, 4 - TrimethylBenzene in a controlled reactivity system by adding a surrogate reactive organic gas mixture. All aromatic experiments were conducted in 90 m3 UCR/CECERT dual environmental reactors. HO2 is predicted using the SAPRC chemical mechanism. The correlation between SOA yield and HO2/NO is presented along with bulk SOA chemical composition via HR-ToF-AMS as a function of HO2/NO.

Fabrication, characterization and applications of 2D material heterostructures

Tung Pham, Jhoann Lopez

Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521

Abstract

In this work, we present fabrication, characterization and applications of 2D heterostructures assembled by single-layer graphene and single-layer MoS2. A vertically stacked MoS2-graphene heterostructure exhibited an n-doping effect while a graphene-electrode MoS2-based field effect transistor (FET) displayed a p-type behavior with a high on/off current ratio and increased charge mobility. These characteristics are attributed to the difference in the work-functions between a n-type (electron-rich) semiconductor such as MoS2 and as-prepared significantly p-doped (electron-depleted) graphene, resulting in a significant transfer of electrons from MoS2 to graphene. This leads to shifting of the charge neutrality point (Vnp) by as much as 30 V in the FET transfer characteristics (Id v/s Vg). The interaction between the individual MoS2 and graphene layers is further confirmed by quenching of photoluminescence intensity in MoS2-graphene heterostructure by 50% as compared to single-layer MoS2 and shifting of peaks in Raman spectroscopy. Compared to gold-electrode MoS2-based FETs, graphene-electrode MoS2-based FETs demonstrated almost 100-fold higher on/off current ratio and a FET mobility of as high as 265 cm2V-1s-1. These fabricated MoS2-graphene heterostructure devices have shown high sensitivity to acetone vapor at concentration of as low as 4% of saturated vapor at room temperature and more rapid response with improved signal to noise ratio compared to graphene-based and MoS2-based devices, respectively.

2017 CEE SYMPOSIUM ABSTRACT

Nanoparticle Enhanced Surface Plasmon Resonance (SPR) at Lipid Bilayer Interfaces for Biosensing Applications

by

Nor Akmaliza Rais

PhD Student, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, Aug 2017
Dr. Jason (Quan) Cheng, Chairperson

Biosensors are devices that take advantage of specific biomolecular interactions for the detection of a target analyte. The bimolecular element can be an enzyme, DNA, antibody, tissue, or whole cell, which generates a signal upon interaction with an analyte. The signal is then measured and quantified via a specific transducer. Biosensors are commonly categorized on the transduction mechanism such as electrochemical, mass-based, thermal and optical. Surface plasmon resonance (SPR) is an optical spectroscopy capable of detecting binding events on a gold surface based on a local change in refractive index and has huge potential in clinical analysis for its simplicity, sensitive, real-time and label-free analysis. SPR is therefore suited to the detection of many biomolecules relating to clinical diagnostics such as DNA, viruses, peptides, therapeutic drugs and other small organic molecules. However, small molecules will have only a minimal change in refractive index, which makes the output SPR signal insignificant, thus the need for signal amplification. In this study, gold nanoparticles are used to enhance the SPR signal due to their increased mass compared to small molecules. Preliminary results using a DNA based model system shows that gold nanoparticles significantly enhance SPR signal. The detection of small molecules and other analytes will be carried out using a novel lipid bilayer interface which mimics the cell membrane and is able to specifically host different receptors. The effect of gold nanoparticles with different shapes and sizes on the SPR signal will be studied and combined with the lipid bilayer interface as a novel surface chemistry for biosensors. As a prove-of-concept, SPR measurement of a model protein system in lipid bilayer-cavitand surface was carried out. In the study, a recognition of antibody was done using a trimethylammonium derivative specifically bind into the cavitand and the result shows promising lipid bilayer surface for SPR immunoassay.

Secondary Aerosol Forming Potential of Gasoline Direct Injection Vehicles with Varying After-Treatment Technologies

Patrick Roth, proth002@ucr.edu, Jiacheng Yang, jyang055@ucr.edu, Diep Vu, dvu3@ford.com, Tom Durbin, durbin@cert.ucr.edu, Georgios Karavalakis, gkaraval@cert.ucr.edu, and Akua Asa-Awuku, asaawuku@umd.edu

Gasoline Direct Injection (GDI) technology has become the preferred standard to Port Fuel Injection (PFI) engines in the US and European markets due to its improved fuel economy. However, GDI vehicles may have difficulty meeting the new two phase LEV III PM Standard set at 3 mg/mile by 2017, and 1 mg/mile by 2025. The use of gasoline particulate filters (GPF), as seen in Europe, can help GDI vehicles meet future PM emissions standards.

In addition to PM, vehicle emissions are an important source of VOCs, NOx, NH3 and CO which through a variety of complex oxidation reactions, can contribute to secondary aerosol and ozone formation in the atmosphere. The focus of this work was to evaluate how the addition of PM emission control systems affects the secondary aerosol formation potential of new technology GDI vehicles over realistic driving cycles.

For this study, the SOA and ozone forming potential from two GDI vehicles (with and without a GPF filter, both in triplicate) were generated over a cold start, LA-92 driving cycle. The exhaust was measured to certification standards, and subsequently collected in CE-CERT's 30m3 Mobile Atmospheric Chamber (MACh). The emissions were then photochemically aged for 8-10 hours, and real-time particle and gaseous phase measurements were analyzed.

As expected, the GPF equipped vehicles displayed a considerable decrease in primary PM (~95%) compared to the stock configurations. The composition of the primary aerosol varied with only ~25% of PM mass attributable to BC in the GPF configurations compared to 85% BC in stock configurations. As the gaseous emissions aged and condensed, primary fractal particles (ρ=0.6 g/cm3) quickly transitioned to more dense (ρ=1.4-1.7 g/cm3), spherical particles, composed of ammonium nitrate and organic species. The change in composition and morphology impacted 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 data generated from this work will aid manufacturers and regulatory agencies understand the atmospheric impacts of the increasing market share of GDI equipped vehicles with varying after-treatment technologies.

Novel Catalytic Pathways for CO_2 Utilization

by

Partho Sarothi Roy
PhD Candidate, Chemical and Environmental Engineering
University of California, Riverside
Advisor: Dr. Chan Seung Park, 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. Technology options to convert CO_2 into higher value fuels and chemicals are not commercially viable under most circumstances. Developing commercially viable technologies to convert CO_2 into high value products will improve the project economics of renewable and non-renewable carbon-based energy production. 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.

Development and application of CRISPR-Cas9-based synthetic biology tools for Yarrowia lipolytica
Cory Schwartz
4th year student
PI: Ian Wheeldon

Identification of organisms which natively possess desirable phenotypes and application of advanced engineering techniques to enhance and understand these properties is a valuable approach for strain engineering in synthetic biology and metabolic engineering. To facilitate this, we have adapted CRISPR-Cas9 from Streptococcus pyogenes for genome editing in the oleaginous yeast Yarrowia lipolytica, which is of interest due to its ability to synthesize and accumulate lipids from a wide range of substrates. To overcome low gene disruption efficiencies, we designed synthetic RNA polymerase III promoters for guide RNA expression. The CRISPR-Cas9 system was applied to markerlessly integrate genes into well-characterized genomic loci for standardized pathway engineering, yielding strains that synthesize the carotenoid lycopene. Lycopene production was then increased by comprehensive overexpression of each step in the biosynthetic pathway to alleviate bottlenecks. We further applied the developed CRISPR-Cas9 system for gene expression regulation via CRISPR interference (CRISPRi), which allowed us to enhance homologous recombination by transiently repressing genes involved in nonhomologous end-joining. Finally, we demonstrated the use of the CRISPR-Cas9 system with an activation domain to activate transcription of genes in Y. lipolytica. Together, these applications show the potential of CRISPR-Cas9 to enable advanced genome editing and transcriptional regulation in Y. lipolytica.

High Solids Enzymatic Hydrolysis of CELF Pretreated Poplar at Reduced Enzyme Loading

Priya Sengupta, Charles M. Cai, Rajeev Kumar, and Charles E. Wyman (Advisor)

Increasing global energy demands and rising greenhouse gas emissions have strengthened the need for sustainable energy sources. Lignocellulosic biomass can be converted into biofuels, but its natural recalcitrance to breakdown into sugars for fermentation into ethanol or other products is currently too expensive. Pretreatment is a process step that seeks to improve sugar yields from biomass, thereby offset additional processing costs by achieving much higher sugar yields at reduced loadings of expensive cellulolytic enzymes. Our UCR team recently invented a pretreatment technology called Co-solvent Enhanced Lignocellulosic Fractionation (CELF) that employs tetrahydrofuran (THF) as a water-miscible co-solvent to augment dilute acid processing of biomass into three distinct fractions: 1) solids consisting of ~90% cellulose, 2) a concentrated sugar solution consisting of mostly hemicellulose sugars, and 3) a highly pure lignin powder. The current study is applying CELF to yield high gravity sugar solutions by enzymatic hydrolysis of the cellulose-rich solids through optimizing its operations in conjunction with lower enzyme doses and higher solid loadings.

Room Temperature Gas Sensor Array based on Selenium, Metal Selenide, Se/SWNT, and MSe$_2$/SWNT Hybrid Nanostructures

Saba Seyedmahmoudbaraghani[a], Kyu-Hwan Lee[b], and Nosang V. Myung[a*]

[a]Department of Chemical and Environmental Engineering, University of California Riverside, Riverside, United States
[b]Electrochemistry Department, Korea Institute of Materials Science, Changwon 641-831, Korea

Corresponding author: Nosang V. Myung, E-mail: myung@engr.ucr.edu

Over the past few years, there has been great attention to the detection and control of NO$_2$ released by combustion, plants, and automobiles since it can cause many environmental issues such as formation of acid rain, photochemical smog, and respiratory diseases. Because of this, different types of metal oxide NO$_2$ gas sensors have been developed thus far. Within these sensors, there has been more work on conductometric metal oxide sensors because of their simple circuit design and robust nature. However, for these sensors to have good sensitivity and fast response time, a higher operation temperature is required. Operation at higher temperature has several drawbacks. Increasing the temperature reduces the selectivity due to the interaction other analytes with oxide surface. Also, the power consumption and device complexities are increased while operating at higher temperatures. Thus, developing a gas sensor that can operate at ambient temperature with a good sensitivity, response time, and selectivity will be very beneficial in terms of cost and manufacturability of smart sensor arrays that are vital for environmental monitoring.

There has been extensive interest on fabrication of gas sensors based on one-dimensional nanostructures such as nanowires and nanotubes. Among these nanostructures, carbon nanotubes have attracted more attention due to their unique electrical, physical, mechanical, and chemical properties. These properties will allow the development of devices that are not only simple, reliable, and reproducible, but also are of low cost. Single-walled carbon nanotube-based chemical field effect transistors (ChemFETs) have been used as gas sensors because they show good chemical-doping effects on various gaseous molecules and are sensitive in charge transfer. However, pristine single-walled carbon nanotubes cannot be used as the sensing elements in gas sensor fabrication due to their limitations such as low sensitivity and selectivity, and long response and recovery times. Therefore, there has been a focus on surface functionalization of single-walled carbon nanotubes (SWNTs).

In this work, we demonstrated the construction of ultra-fast NO$_x$ nanosensors at room temperature by utilizing Se, MSe$_2$, Se/SWNT and MSe$_2$/SWNT networks as sensing materials. Se and MSe$_2$ were synthesized by electrodeposition where morphology and composition were tailored by controlling the electrolyte composition, applied potential, and charge density. By controlling the morphology and density of Se and MSe$_2$, hybrid nanostructures displayed an optimized response and recovery time with high sensitivity toward NO$_x$. Selectivity of the nanosensors was also examined by measuring its response toward various gases such as NH$_3$, H$_2$S, and H$_2$O.

Integration of THF Co-solvent Enhanced Lignocellulosic Fractionation (CELF) with
***Clostridium thermocellum* Consolidated Bioprocessing (CBP) for High Yield Conversion of**
Biomass Resources (or Residues) to Biofuel Ethanol
Priyanka Singh
Advisor: Dr. Charles Wyman

Lignocellulosic biomass is a renewable resource and has the potential to replace petroleum derived fuels. However, recalcitrant nature of the biomass necessitates development of robust conversion technologies to enable future biorefineries. Recently, the Aqueous Biomass Processing (ABP) group at UCR developed a novel Co-solvent Enhanced Lignocellulosic Fractionation (CELF) technology that employs tetrahydrofuran (THF) in solution with aqueous dilute sulfuric acid to produce solids that are highly amenable to downstream saccharification with commercial enzymes. CELF also fractionates biomass into its major components of cellulose, hemicellulose, and lignin, thereby providing the opportunity to enhance revenues and profitability. CELF presents the additional advantage of lignin isolation for processing into fuels and chemicals. Organisms that combine enzyme production, their release of sugars (saccharification), and fermentation of those sugars to ethanol in a single unit operation are gaining attention as an additional route to dramatically reduce enzyme costs. The Wyman team has recently explored combining this single organism consolidated bioprocessing (CBP) approach with CELF technology to achieve virtually theoretical sugar release in record times without the need to add enzyme. The ability to rapidly and almost completely breakdown biomass is a major breakthrough for lowering the cost of making transportation fuels from lignocellulosic biomass. This poster will discuss comparing the CELF/CBP combination with various co-fermentation strategies to further streamline the biomass conversion process while maximizing sugar release and achieving high lignin recovery for future valoriazation studies.

Aquatic stability of few-layered black phosphorus: The leading edge of 2-dimensional nanomaterials
S. Drew Story

Few-layered black phosphorus (FLBP) nanomaterials are quickly joining other planar, or 2-dimensional, nanomaterials in a variety of applications due to its remarkable properties, extending beyond the common optical and electronic applications into cancer therapy and other biomedical applications. Due to their propensity to degrade in the presence of oxygen, albeit sometimes a desirable trait, these materials were previously suspended only in organic matrices. Only recently have FLBP nanomaterials been prepared in aqueous solution, and thus, the aquatic stability of these FLBP nanomaterials is not well known. In this study, we performed fundamental colloidal stability experiments to better characterize these novel materials, and our findings show promise for their continued development and the advancement of FLBP applications. Specifically, the influence of aquatic conditions on the electrophoretic mobility and effective diameter, including that of ionic strength, pH, and the presence of biologically relevant protein were explored. The rate of aggregation of the FLBP nanomaterials was also evaluated to determine the critical coagulation concentration of the suspension and identify the diffusion-limited and reaction-limited aggregation regimes. This work serves as the first fundamental study of the aquatic stability of an increasingly emergent nanomaterial and lays the groundwork for continued development of colloidal applications of few-layered black phosphorus.

Unifying Mechanistic Analysis of the Factors Controlling Selectivity in Fructose Dehydration to 5-Hydroxymethylfurfural by Homogeneous Acid Catalysts in Aprotic Solvents

Glen S. Svenningsen[†], Rajeev Kumar, Charles Wyman, and Phillip Christopher[†]

[†]Department of Chemical & Environmental Engineering, University of California, Riverside, Riverside, California 92521, United States

* Corresponding author: Christopher@engr.ucr.edu

ABSTRACT
US interest in biomass as an alternative energy source continues to increase in demand with growing political, economic and environment concerns associated with the consumption of fossil fuels. One potential route for converting cellulosic biomass to fuels is through the dehydration of fructose to produce 5-hydroxymethylfurfural (HMF), followed by the catalytic conversion of HMF to renewable fuels, such as dimethylfuran (DMF). Economically viable production of HMF from fructose requires high selectivities and yields. However, mechanistic aspects of fructose conversion to HMF are still unclear, making the design of catalysts that enable high yield HMF production difficult. Various reports have proposed different factors that control selectivity including the acid type, fructose tautomer distribution, and solvent type. In order to develop detailed insights into the factors that control HMF yields, we executed extensive kinetic analysis using a variety of solvent systems, reaction conditions, acid types and acid concentrations in a high-throughput reactor to determine the mechanism and selectivity controlling factors in fructose dehydration to HMF by homogeneous acid catalysts. Detailed NMR analysis of the relative distribution of fructose tautomers as a function of solvent type and temperature were also executed. Through these studies we propose a mechanism which controls the selectivity to HMF from fructose, by direrelating HMF selectivity with the distribution of furanose and open-chain forms of fructose.

The Implications of Drought and Water Conservation on the Reuse of Municipal Wastewater: Recognizing Impacts and Identifying Mitigation Possibilities

Quynh K. Tran†, David Jassby†, Kurt A. Schwabe‡*
†Chemical and Environmental Engineering, University of California, Riverside, California, USA
‡School of Public Policy, University of California, Riverside, California, USA

Abstract

As water agencies continue to investigate opportunities to increase resilience and local water supply reliability in the face of drought and rising water scarcity, water conservation strategies and the reuse of treated municipal wastewater are garnering significant attention and adoption. Yet a simple water balance thought experiment illustrates that drought, and the conservation strategies that are often enacted in response to it, both likely limit the role reuse may play in improving local water supply reliability. For instance, as a particular drought progresses and agencies enact water conservation measures to cope with drought, influent flows likely decrease while influent pollution concentrations increase, particularly salinity, which adversely affects wastewater treatment plant (WWTP) costs and effluent quality and flow. Consequently, downstream uses of this effluent, whether to maintain streamflow and quality, groundwater recharge, or irrigation may be impacted. This is unfortunate since reuse is often heralded as a drought-proof mechanism to increase resilience. The objectives of this paper are two-fold. First, we illustrate—using a case study from Southern California during its most recent drought— how drought and water conservation strategies combine to reduce influent flow and quality and, subsequently, effluent flow and quality. Second, we use a recently developed regional water reuse decision support model (RWRM) to highlight cost-effective strategies that can be implemented to mitigate the impacts of drought on effluent water quality. While the solutions we identify cannot increase the flow of influent or effluent coming into or out of a treatment plant, they can improve the value of the remaining effluent in a cost-effective manner that takes into account the characteristics of its demand, whether it be for landscaping, golf courses, agricultural irrigation, or surface water augmentation.

Aerosol Formation from Hydroxyl Radical Oxidation of Agricultural Amines and Reduced Sulfur Compounds

Presented by: Paul Vanrooy

Reduced sulfur compounds, from animal waste products, and amines, from cattle exhalation and rumination, are often co-emitted on agricultural land. Reduced sulfur compounds are thought to be important to new particle formation over the oceans. Amines are thought to play an important role in new particle formation around agricultural land. While both of these compound families have been recognized individually, there have been no studies focused on how these agricultural emissions interact to form particles. To begin filling this information gap, experiments were conducted using a 37.5 cubic meter Teflon environmental chamber housed within the Atmospheric Processes Laboratory at UC Riverside. 100ppb of a reduced sulfur compound (dimethylsulfide, dimethyldisulfide, methanethiol, or hydrogen sulfide) was injected into the chamber, followed by 100ppb of an amine (trimethylamine, diethylamine, butylamine, putrescine, ethylenediamine, cadaverine, or ammonia), and finally 1ppm of hydroxyl radical to push photooxidation. A suite of real time gas-phase and particle-phase instruments measured chemical composition and various physical properties of the aerosol. The aerosol yields were substantial and varied depending on the combination of precursors injected. The presence of humidity had a profound impact on aerosol yield. Mass spectra of the aerosol formed from the individual precursors were compared to that from the interaction experiments. There are several important mass-to-charge peaks present in the interaction experiments that are not present in the individual precursor experiments. This novel investigation provides much needed insight into agricultural aerosol formation.

Characterizing Wastewater Behavior of Titanium Dioxide Nanoparticles

Travis Waller, Ian Marcus, and Sharon Walker

Recommended exposure limits are often set for the general contaminant name (i.e. titanium dioxide, TiO_2) without considering that the engineered nature of nanoparticles imparts specific traits for a desired environmental behavior. Engineered traits influence the environmental behavior such that the same *molecular* nanoparticle may behave differently if intended for different environmental matrices, though each may still be released during product lifecycle. TiO_2 represents an environmentally relevant engineered nanoparticle exhibiting different properties in ideal solutions depending on its intended application. This study examined the systemic impact of two types of TiO_2 (food grade and industrial grade) on the microbiome and water quality in dynamic, complex wastewater media (e.g. septic system). Phenotypic, genotypic, and water quality parameters were employed to ascertain the influences of each TiO_2 particle to microbial structure and function, in addition to, determining the extent of perturbation to effluent quality. Water quality results indicate that organic degradation proceeds at a faster rate during industrial grade TiO_2 exposures than that of food grade TiO_2 exposures. Microbiota composition is relatively stable during industrial grade exposures while food grade displays more variability in the dominant genus. Additionally, the presence of denitrifying genes will indicate the microbial community's capacity to mineralize organic compounds.

High-Efficiency Cellulolytic Enzymatic Fuel Cell via Multienzyme Cascade on DNA Scaffold

By:
Sooyoun Yu

PI: Dr. Nosang V. Myung

As fossil fuel is depleting, an alternative source of energy to accommodate the current standard of living is in great demands. Enzymatic fuel cells (EFCs) are studied as one of the promising alternatives, as they are environmentally friendly and flexible in fuel types. EFCs are also attractive because they can operate under mild conditions such as room temperature, atmospheric pressure, and neutral pH. Along with microbial fuel cells (MFCs), EFCs are the only type of fuel cell that can use biologically derived materials
– such as glucose – as fuels. This eliminates many additional steps to prepare the fuel such as pure hydrogen. Early works with EFCs only involved a single enzyme as biocatalyst, usually glucose oxidase (GOx), to convert glucose to electricity via glucose-oxygen redox reactions. This resulted in incomplete oxidation of fuel and thus a lower power density. Recent studies show that the use of multiple enzymes as biocatalysts allow for more complex, naturally available resources as cellulose to be used as fuel. The objective of this project is to build a fully cellulolytic enzymatic fuel cell with a high power density output from complete oxidation of fuel (glucose). This can be achieved by mimicking the structured multi-enzyme scaffold in anaerobic bacteria called cellulosome to develop a biological approach for fuel cell applications via enzyme organization to create multi-enzyme cascade for cellulose hydrolysis and glucose oxidation. DNA templates were used instead of protein scaffolds to immobilize the enzymes, as proteins suffered truncation issues when size was increased to accommodate for multiple enzymes. Cellulases and commercial GOx assembled in a sequential order on DNA templates – as opposed to free in solution – demonstrated increased production rate of hydrogen peroxide, a byproduct of glucose oxidation. Electrodes have a nanofiber structure fabricated by a simple electrospinning process to maximize surface area-to- volume ratio for higher enzyme loading. Fine tuning of the polyacrylonitrile-based solution recipe and optimization of electrospinning conditions increased conductivity for high current density. Ultimately, the multienzyme cascade system on DNA scaffold is bound to nanofiber mat electrode to build a fully cellulolytic EFC. The successful functionalization of working electrode with 2-enzyme system and its demonstration of increased current via chronoamperometry suggested that the substrate channeling effect of site-specifically organized multienzyme cascade could enhance the efficiency in power generation.

Abstract

Epitaxial, ultra-thin Au coating as a barrier for oxidation damages for silver nanowires
Presented by: Yangzhi Zhu

Silver nanowires (AgNWs) hold promise for applications such as transparent and flexible displays, solar cells, chemical/biological sensors, photonic circuits and scanning tunneling microscopies, but their susceptibility to damage from oxidation has limited their commercialization. Here, we develop a room-temperature chemical coating technique to deposit an ultra-thin, epitaxial layer of Au on the AgNWs surface, which shields the AgNWs from oxidation, and thus it could represent a key to realize their commercial potential. Our work has shown that the Ag@Au core-shell nanowires are stable in air for at least 183 days (>6 months) and in physiological buffer solution (PBS) for at least 21 days. The thin Au coating did not introduce significant Au fluorescence in the SERS spectrum, making them feasible for SERS and plasmonic sensing applications. The results also showed that the thin coating does not have adverse effects on the coupling of surface plasmon polariton in AgNW waveguides, and the device performance is stable for at least 21days. AgNW-AFM probes are low-cost alternatives of high-aspect-ratio, high-resolution AFM probes. It was demonstrated that the Ag@Au core-shell nanowires functions similarly to bare-AgNW, with a much longer shelf-life for at least 3weeks in the air. The Ag@Au nanowires with 6nm of Au layers for flexible electronics can greatly enhance their resistance under heated, high-humidity environment (80°C of temperature, 80% of humidity) for at least 2016h (>84 days).