Graduate Student Poster Presentations
1st floor, Center for the Arts, UB North Campus
Wednesday October 21, 2009
2:30 - 4:30 p.m.

Presenting research on:

- Bioengineering
  - Cell Adhesion
  - Cell and Tissue Bioengineering
  - Gene Therapy
  - Protein Engineering
  - Transport Processes in Biological Systems
- Molecular and Multiscale Modeling
  - Applied Computational Quantum Chemistry
  - Surface Thermodynamics
  - Property Estimation and Prediction
  - Diffusion in Metals
- Nanoscale Materials Science and Engineering
  - Advanced Power Sources
  - Controlled Crystallization
  - Heterogeneous Catalysis
  - Nanoparticle Modeling, Synthesis and Characterization
  - Polymers for Drug Delivery
  - Self-Assembly

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All Ph.D. students are fully supported as research or teaching assistants. Additional fellowships sponsored by the State University of New York, the National Science Foundation, Praxair, Inc., and other organizations are available to exceptionally well-qualified applicants.
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1. Design and Optimization of Triple Promoter Lentiviral shRNA Vector

Stella Alimperti, Jun Tian, and Stelios T. Andreadis

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260.

Cell array is a technique that gives the opportunity of studying not only a single gene but a cluster of genes that participate in stem cell differentiation. Also, dynamic measurement in arrays could give an extra advantage of continuously monitoring the up- or down regulation of genes. However, dynamic measurement of gene silencing requires a specific design for shRNA lentiviral vector. We design and optimize a shRNA lentiviral vector in order to monitor the silencing of gene which is regulated under specific promoter. According to this design, we need to combine three different promoters: constitutive promoter CMV of one marker gene (e.g. DsRed) that is used to measure transduction efficiency, the tissue specific promoter of interest (e.g. SMAa) driving expression of second marker (e.g. EGFP) and the H1 promoter driving the shRNA sequences designed to knock down genes included in the TGFbeta pathway (e.g. SMAD2, SMAD4). Initially, we can knock down the EGFP gene and we can measure the hPGK promoter activity by using flow cytometer. Afterwards, we create an array and we can measure the fluorescence intensity under the microscopy. Our results show that transduced cells exhibits low levels of GFI because of the silencing. As expected, the level of red fluorescence intensity (RFI) depends on the titer of virus. However, the normalized response (GFI/RFI) is independent of the virus titer strongly suggesting that RFI must be used to normalize gene expression. Hence, this shRNA vector can be applied in developing a lentiviral stem cell library.

Key Words: cell array, siRNA, tissue specific promoter, fluorescence intensity.


Juhee Han,1 Daniel D. Swartz,2 and Stelios T. Andreadis1

1Department of Chemical and Biological Engineering, and 2Women and Children’s Hospital of Buffalo, University at Buffalo, The State University of New York, Buffalo, New York.

We demonstrated that functional smooth muscle cells can be derived from bone marrow using smooth muscle alpha actin promoter (P_SmαA). These bone marrow derived smooth muscle cells (BM-SMC) have high potential as an autologous cell source for vascular tissue engineering. However, recently we examined the effect of organismal aging on the properties of neonatal and adult BM-SMC and their tissue engineering vascular constructs. Our results showed that the proliferation potential and contractile function of BM-SMC declined with donor age. These results are currently extended to obtain a gene expression profile of BM-SMC as a function of animal age using DNA microarray and determine potential strategies to reverse these aging effects in adult BM-SMC. Our preliminary data showed that either expressed in low level for Nanog or absent for Oct4 transcripts in neonatal BM-SMC while neither of them is expressed in adult BM-SMC. These two are key transcription factors in maintaining the stem cell phenotype of embryonic stem cells as well as mesenchymal stem cells. Therefore, we proposed that overexpression of these transcription factors, alone or in combination may be used to increase self-renewal and differentiation potential of adult BM-SMC. To this end we used lentiviral vectors encoding Nanog or Oct4 in bone marrow derived mesencymal stem cell (BM-MSC) from adult and neonatal ovine animals. Ultimately these efforts may enhance the potential of bone marrow derived mesenchymal stem cells for treatment of cardiovascular disease which is more prevalent in the elderly.

Key Words: Bone marrow, Mesenchymal stem cell, Nanog, Oct4, Self-renewal, Myogenic differentiation.
3. **Alpha-Catenin Is Necessary for JNK-Mediated Regulation of Adherens Junctions**

**Meng Horng Lee and Stelios T. Andreadis**

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260.

Recently, we discovered that c-Jun N-terminal kinase (JNK) phosphorylates beta-catenin and regulates formation of adherens junctions, which is accompanied by actin bundle reorganization in several epithelial cell lines and primary cells. In this paper we report that alpha-catenin is necessary for JNK-mediated regulation of adherens junctions. Indeed, immunoprecipitation experiments showed that inhibition of JNK kinase activity by chemical or genetic (siRNA) means significantly reduced the amount of alpha-catenin that was bound to beta-catenin. In addition, knocking down alpha-catenin in A431 cells using siRNA inhibited formation of adherens junctions and actin reorganization by JNK. Similar results were obtained with ME180 cells lacking alpha-catenin and the effect was completely reversible as introduction of alpha-catenin rendered ME180 cells sensitive to JNK. Using gain-of-function and mass spectrometry experiments we are currently investigating which domain(s) of alpha-catenin and which other possible binding partner(s) may be important in JNK-mediated formation of adherens junctions. Our results suggest that JNK acts as a switch that regulates adherens junctions by controlling binding of alpha-catenin to beta-catenin. These findings may have wide implications in cell-cell communications during tissue development, epithelial-to-mesenchymal transition and cancer metastasis.

*Key Words: JNK, alpha-catenin, adherens junctions*

4. **Conjugation of Transforming Growth Factor-beta1 to Fibrin Hydrogel for Tissue Engineering**

**Maoshih Liang and Stelios T. Andreadis**

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Transforming Growth Factor-beta1 (TGF-beta1) is an important cytokine which participates in various physiological processes. This cytokines is synthesized, secreted, and stored in extracellular matrices (ECMs) as a 100kDa latent structure which contains two non-covalently associated parts: latency-associated peptide (LAP) and matured TGF-beta1. After being activated, matured TGF-beta1 releases from LAP and triggers physiological cascade through receptors on the cell surface. Previous researches show that covalent conjugation of TGF-beta1 onto cell seeded tissue engineered scaffolds can help increase ECMs deposition and strengthen material mechanical properties. However, without artificial polymers’ help, TGF-beta cannot covalently embedded inside fibrin gel which is the scaffold used in our group and will lose 50% within one day at low fibrin concentration. In this poster, we propose a method to covalently conjugate matured TGF-beta1 onto fibrin gel by expression and purification of fusion TGF-beta1. Proliferation inhibition of mink lung epithelial cells and luciferase assay show that fusion TGF-beta1 still possesses reasonable bioactivity. Furthermore, immunoprecipitation proves that this fusion TGF-beta1 can readily conjugate to fibrinogen with the help of active Factor XIII. At last, TGF-beta1 release experiment reveals almost no fusion TGF-beta1 released from 1mg/mL fibrin after fibrin polymerization. In sum, this method provides a feasible way to fabricate fibrin gel with covalently liked TGF-beta1 which can be used for tissue engineering.

*Key Words: transforming growth factor-beta1, fusion protein, fibrin, protein delivery, tissue engineering*
5. Fibrin-Conjugated Pseudotyped Lentivirus for Cell-Controlled and Spatially Localized Gene Delivery: Implications for Lentiviral Microarrays

Roshan M. Padmashali and Stelios T. Andreadis

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Recently, we reported that fibrin hydrogels can be used for effective pDNA encapsulation and gene delivery. Here we report our recent efforts to immobilize lentivirus in fibrin gels to achieve gene transfer in a cell-controlled and spatially arranged manner. Transduction efficiency on fibrin gels was comparable to conventional methods but cellular toxicity was significantly diminished. Gene transfer was strongly dependent on matrix degradation by target cells but a significant fraction of lentiviral particles diffused out of the gel over time. To eliminate viral diffusion we engineered lentiviral particles that bind covalently to fibrin during polymerization. To this end, we engineered fusion proteins between the viral envelope glycoprotein (VSV-G), peptide domains that are recognized by factor XIII and protease cleavage sites that are recognized by plasmin. All modified variants exhibited similar transduction efficiency with the wild type and bound to fibrin hydrogels in a factor XIII dose dependent manner. As a result diffusion of virus from the gels decreased dramatically even for fibrin gels with low fibrinogen concentration. When the modified lentivirus preparations were spotted in an array format, gene transfer was strictly confined to virus-containing fibrin spots with no cross-contamination between neighboring sites suggesting that this transduction system may be ideal for generation of lentiviral microarrays for high throughput studies.

Key Words: lentivirus, factor XIII, VSV-G, fibrin

6. Functional and Mechanical Robust Vascular Constructs from Hair Follicle Derived Stem Cells and Small Intestinal Submucosa

Hao-Fan Peng,1 Daniel D. Swartz,2 and Stelios T. Andreadis1

1Department of Chemical and Biological Engineering, and 2Women and Children’s Hospital of Buffalo, University at Buffalo, The State University of New York, Buffalo, New York.

Our laboratory recently demonstrated a new source of smooth muscle cells derived from hair follicle stem cells. Hair follicle smooth muscle progenitor cells (HF-SMPCs) demonstrated high proliferation potential, contractile function and great ability for matrix remodeling. In this study, we aimed at engineering vascular constructs composed of hair follicle smooth muscle cells and vascular endothelial cells on small intestine submucosa (SIS). Hair follicle smooth muscle cells migrated into SIS under physiological strain (10%) by two weeks after seeding. They aligned in the direction of force, infiltrated the SIS and expressed smooth muscle cells specific markers such as alpha-actin, calponin and myosin heavy chain. HF-SMPCs secreted collagen and elastin the two major extracellular matrix molecules of native vessels. Notably, the vascular reactivity and mechanical strength of these constructs were similar to those of native arteries. We further co-culture HF-SMPCs with endothelial cells in the lumen of cylindrical constructs. Endothelial cells easily attached and formed a homogeneous layer on the surface of SIS. These vascular constructs exhibited endothelium-dependent and endothelium-independent response to several vasoagonists, suggesting that both hair follicle smooth muscle cells and endothelial cells are functional. Taken together, our data demonstrated that hair follicle is an easily accessible source of proliferative and functional cells for engineering mechanically strong, biologically functional vascular constructs with potential for arterial implantation.

Key Words: hair follicle stem cell, blood vessel engineering
Novel Bioreactor Approach to Mechanical Preconditioning of Tissue Engineered Arterial Constructs

Evan Schlaich,1 Hao Fan Peng,2 Daniel D. Swartz,3 and Stelios T. Andreadis2

1NYS Center of Excellence in Bioinformatics and Life Sciences, 2Department of Chemical and Biological Engineering, and 3Women and Children’s Hospital of Buffalo, University at Buffalo, The State University of New York, Buffalo, New York.

Our laboratory recently demonstrated that fibrin-based tissue engineered vessels (TEVs) can be used as an alternative cardiovascular treatment within the venous system. These constructs, although applicable in the venous system, lack the mechanical integrity required for implantation within the arterial system. This necessitates the need for alternative methodologies. The modified approach our group employed utilized the use of decellularized small intestine submucosa (SIS) seeded with bone marrow derived endothelial and hair follicle derived smooth muscle stem cells. As well, we aimed to improve the function of our TEVs by mechanically stimulating the cells on and within the construct using a novel bioreactor. In preconditioning the constructs to a physiological level, we hoped to achieve better cell function and improved tissue development. The bioreactor, which is fully autoclaveable and placed entirely in an incubator, provided the stem cells a habitat that mimics in vivo conditions. The advantage of this system is that it allowed for direct instantaneous manipulation of flow conditions and pressures ex vivo that would not otherwise be feasible peri-operatively. Originally, the bioreactor produced conditions near that of the venous system, due to low shear stress and overall resistance. Modifications were made to achieve a flow rate analogous to arterial conditions while maintaining physiological pressures. With these alterations, arterial pressure (120/80mmHg), shear stress (10-15 dynes/cm2), distension (10%), and distension frequency (1Hz) within the constructs were achieved. The computer-assisted bioreactor allowed for the gradual ramping and pulsation of fluid flow to enhance cell alignment, morphology, proliferation, and migration changes. We have shown through the optimization and application of this bioreactor the development of a non-thrombogenic endothelial monolayer within our constructs, as evidenced by SEM and immunostaining. As such, we have demonstrated that TEV preconditioning promotes improved vascular remodeling and suggests a new paradigm in cardiovascular tissue engineering.

Key Words: bioreactor, vascular tissue engineering, preconditioning, endothelial, smooth muscle
8. Microarray of Lentiviral Reporter Vectors for High-Throughput and Real-Time Dynamic Gene Expression Profiling

Jun Tian, Stella Alimperti, and Stelios T. Andreadis

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260.

Quantification of gene expression dynamics is limited due to the destructive, expensive and laborious nature of current gene expression profiling techniques such as qRT-PCR and cDNA microarrays. Here we developed scalable live-cell microarrays to measure gene expression dynamics in real time and in a high-throughput manner. To this end, we generated dual-promoter lentiviral vectors that were designed to provide independent and high level gene expression. Each lentivirus harbored a transcriptional regulatory element e.g. NF-κB or promoter e.g. IL-8p encoding for destabilized green fluorescence protein and a constitutive promoter driving red fluorescence protein for signal normalization. Lentivirus preparations were immobilized in a microarray format using a robotic spotter to generate the LentiVirus microArray (LVA). Target cells were transduced with immobilized lentivirus and after treatment with TNF-α, IL-1 or IFN-γ transcriptional activity was interrogated in real-time using fluorescence microscopy. In contrast to standard methods, our experiments provided rich dynamic information over a period of several days. Data normalization by red fluorescence intensity eliminated errors due to spot-to-spot variability in transduction efficiency or changes in cell proliferation upon cytokine treatment. These results were confirmed by flow cytometry. Finally, contrary to transfection arrays, the LVA can monitor gene expression in primary cells and stem cells thereby providing a useful tool for deciphering gene regulatory networks of complex biological processes.

Key Words: microarray, gene expression profiling, lentivirus, real-time measurement, high throughput screening

9. Silencing of Fatty Acid Synthase 2 to Improve Flavonoid Production in Saccharomyces Cerevisiae

Namita Bhan, Zachary L. Fowler, and Mattheos A. G. Koffas

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Fatty acid synthase 2 (FAS2) is the alpha subunit of the hexameric fatty acid synthase complex that catalyzes the synthesis of long-chain saturated fatty acids. FAS2 carries out the beta-ketoacyl reduction and beta-ketoacyl synthesis that are the primary consumers of malonyl-CoA, the major metabolite required for flavonoid production. We propose that down-regulating expression of FAS2 using antisense RNA will increase the availability of intracellular malonyl-CoA thereby increase recombinant flavanone production. In this work we selected seven different target fragments of approximately 500 base-pairs targeting the FAS2 mRNA. Each fragment was cloned in the reverse direction under a galactose-inducible promoter and transformed into Saccharomyces cerevisiae harboring the genes for flavanone production; namely 4-coumaroyl-CoA ligase, chalcone synthase and chalcone isomerase. Quantification of silencing effect was done by on target qRT-PCR and production of flavanones in batch fermentations.

Key Words: flavonoids, malonyl-CoA, antisense RNA
10. Building an Anthocyanin Library for Inhibition Studies of Human Pancreatic Alpha-Amylase

Hila Dvora and Mattheos A. G. Koffas

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260.

Diabetes affects nearly 8% of the United States population, with over 90% of these cases being type II diabetes. This condition is caused by cells’ inability to efficiently utilize insulin for glucose uptake from the blood. One current treatment involves inhibition of the enzymes responsible for carbohydrates digestion. This reduces the rate of increase of postprandial blood glucose level. Previous studies suggest that flavonoids in general and anthocyanins in particular could act as digestive enzyme inhibitors. Investigations of the effect of structure on inhibition have identified that hydroxylation of the 4’-carbon of the flavonoid B-ring is one of the most important structural features for inhibition. However, since plant extracts are typically used for such studies, it is yet unclear how non-natural diversification of functionality at that position might affect inhibition. It is also unclear how the identity of the sugar group at the 3-carbon of the anthocyanin might affect inhibition. Through mutasynthesis of a library of natural and non-natural anthocyanins with diverse functionality at the 4’-carbon and diversity of the 3-carbon sugar group, the effects of these structural features on inhibition can be studied against human pancreatic alpha-amylase. This library will be created by combining organic synthesis and metabolic engineering strategies in E. coli. These compounds will then be tested for inhibition against human pancreatic alpha-amylase in order to elucidate the effect of structure on inhibition.

Key Words: anthocyanins, flavonoids, metabolic engineering, mutasynthesis, Escherichia coli, diabetes, natural colorants

11. Development of Efficient Production Platform of Novel Antimicrobial Agents by Malonyl-CoA Overproduction and also Studying the Antimicrobial Efficacy

Karan Prakash Shah and Mattheos A. G. Koffas

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Genetically tractable microorganisms, such as Escherichia coli, serve as ideal platform for recombinant protein expression and heterologous biosynthesis of a variety of small molecules with varying health benefits. However, in many cases protein activities and biosynthetic efficiency are greatly limited by precursor and co-factor availabilities in the recombinant host. Malonyl-CoA is a critical metabolite for the biosynthesis of numerous fine chemicals of industrial significance including fatty acids, flavonoids and polyketides to name a few. In the present work we alter intracellular levels of Malonyl-CoA by deleting and/or over expressing fatty acid synthesis pathways and regulators. These selected targets should lead to inhibition of Malonyl-CoA consumption in the biosynthetic pathway. To assess the impact of the genetic modifications, the plant-derived pathway for biosynthesis of flavanones, the primary flavonoid, was introduced on co-replicable vectors to then examine flavanone production by shake flask fermentation.

We are also interested in testing the anti-microbial properties by determining Minimum Inhibitory Concentration (MIC) values of various novel flavonoid compounds synthesized chemically. From literature, it is known that flavonoid compounds have antibiotic properties and are used by plants to fight microbial infections. We are synthesizing various non-natural flavonoid compounds with substituent halogens at different positions in the structure. We aim to synthesize compounds with high antibiotic activity, either by themselves or in combination with efflux pump inhibitors similar to that of potent antibiotics.

Key Words: malonyl-CoA, fatty acid, antimicrobial, MIC
12. Using Polyphenol Melanization as a Screen for Resveratrol Overproducers in *Escherichia coli*

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Lack of pigment in resveratrol producing microorganisms prevents the application of current high-throughput screening methods to identify overproducing strains. In this work, we first investigated if resveratrol can retard microbial growth as a medium-throughput screening method with no significant results. Laccase activity in the haploid yeast *Cryptococcus neoformans* has been attributed to the formation of melanin outside the cell wall becoming part of a defensive polysaccharide capsule. Laccase activity is a major cause of virulence in humans via the melanization of dopamine. Interestingly, we show here that *C. neoformans* has the ability to create melanin-like pigmentation from various flavonoid molecules across a range of flavonoid classes and specifically prefers those with 3′,4′-dihydroxylations. Using this information, we then set out to create a high-throughput in vivo screening method for resveratrol production in *Escherichia coli* based on laccase melanin formation. First, we explored the feasibility of expressing a laccase from *Bacillus subtilis*, BsCotA, in *E. coli* and the ability of resveratrol to inhibit laccase ability by reducing pigmentation. Secondly, we will co-express BsCotA with the two genes, 4-coumaroyl-CoA ligase and stilbene synthase (STS), required for recombinant resveratrol production in *E. coli*. By introducing a library of STSs, identification of highly active STS proteins can be performed by visual inspection of colony-color loss.

*Key Words:* resveratrol, laccase, flavonoids, melanin
13. **Biosynthesis of Novel Isoflavonoids in *Saccharomyces cerevisiae* with Altered Estrogen Receptor Binding Activity**

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Isoflavonoids are plant secondary metabolites synthesized primarily in leguminous plant as plant defense response and to establish the symbiotic relationship between the plant and rhizobial bacteria. In human, isoflavonoids have been demonstrated to possess a huge array of pharmacological potentials and health benefits particularly in the area of heart disease and cancer. However, minute quantities of these polyphenols produced in their native plants complicate the effort to assess their potentials. The overall goal of this project is to construct a versatile system in microorganism to efficiently convert both natural and synthetic flavanones into their corresponding high-value isoflavones. The challenge of embedding plant isoflavone biosynthetic pathway lies in the expression of the initial enzyme, isoflavone synthase (IFS). This type II P450 enzyme requires attachment to an intracellular membrane and a reversible association with a second membrane-bound enzyme, namely cytochrome P450 reductase (CPR). The final dehydration step leads to the fabrication of isoflavones can be catalyzed by a third cytoplasmic protein, 2-hydroxyisoflavanone dehydratase (HID) even though the reaction can occur spontaneously. Co-expression of this three enzymes system in *S. cerevisiae* made possible the production of natural and unnatural isoflavones in practical quantities; hence allows the study of the binding affinity as well as the structure-activity interaction of each isoflavone analogs with human estrogen receptor α and β. Phytoestrogenic character of each isoflavones analogs can be evaluated and compared to estradiol.

*Key Words*: isoflavonoids, isoflavone synthase, 2-hydroxyisoflavanone dehydratase, cytochrome P450 reductase, ERα and ERβ
14. Engineering Central Metabolic Pathway of *Escherichia coli* BL 21* for Enhanced Flavanone Production

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Flavanone compounds represent an abundant source of bioactive substances that have found wide applications in pharmaceuticals and nutraceuticals. Metabolic engineering has emerged as a powerful platform in synthesizing natural products and shown tremendous advantages over chemical synthesis or solvent extraction method. In this project, synthetic pathway for production of flavanone was constructed by heterologously expressing plant 4-cl (4-coumarate CoA ligase), chs (Chalcone synthetase) and chi (chalcone isomerise) gene in *E. Coli*. To further enhance flavanone production, a minimal set of genetic interventions were proposed by OptFlux framework developed in Maranas’ group. These include: (1) upregulation of glycolytic pathway to enhance the pool of malonyl-CoA by overexpression of gapd (glyceraldehydes-3-phosphate dehydrogenase), pgk (phosphoglycerate kinase), pdh (pyruvate dehydrogenase) and acc (acetyl-CoA carboxylase) gene; (2) downregulation of TCA pathway to decrease the drainage of acetyl-CoA by knockout of mdh (malate dehydrogenase), fumABC (fumarase A, B, C) and acnAB (aconitase A, B) gene; and (3) elimination of competing pathway to reduce the formation of byproducts (propionate and succinate) by deletion of scpC (propanoyl-CoA: succinate CoA-transferase) and sucCD (succinyl-CoA synthetase C, D) gene. By this combinatorial approach, the engineered *E. Coli* was expected to achieve the high production of flavanone.

*Key Words*: flavanone, *E. Coli*, metabolic engineering, central metabolic pathway
15. **Theoretical Identification and Experimental Validation of α2,3 Sialyltransferases Critical in Mediating Human Leukocyte Binding**

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Sialyl Lewis-X (sLeX) type carbohydrate structures, found at the N-terminus of the leukocyte cell surface receptor P-selectin Glycoprotein Ligand-1 (PSGL-1) binds E/P-selectin expressed on activated endothelial cells. This molecular interaction regulates cell adhesion at sites of inflammation. Studies of enzymes/glycosyltransferases involved in glycosylation of PSGL-1 largely focus on mouse models and only partial information is available on the precise human enzymes involved in this important post-translational modification. To address this aspect, a biochemical reaction network model was developed. To validate aspects of the theory, experiments were also designed with focus on the role of specific human α2,3 sialyltransferases (ST3Gal-I, -II, -IV, and –VI) in regulating selectin-ligand formation. Efficient shRNA perturbing ST3Gals were identified using cells stably expressing a ST3Gal-GFP construct for each gene. The effect of gene silencing on cell surface sLeX expression, P-selectin-IgG binding under static conditions, and leukocyte-platelet adhesion under fluid shear was measured in HL-60 leukocytic cells. Consistent with model predictions, knockdown in expression and activity of ST3Gal-I and –II, both alone and in tandem, resulted in an up-regulation of P-selectin mediated adhesion in both static and shear assays. Knocking-down ST3Gal-IV and –VI down-regulated P-selectin mediated adhesion. Overall, the study couples theory and experiments to quantify the contributions of α2,3 sialyltransferases in regulating sLeX formation and cell adhesion in human leukocytes.

*Key Words*: PSGL-1, O-linked Glycosylation, shRNA, α2,3 sialyltransferases, glycosylation network modeling

16. **von Willebrand Factor Self Association Is Essential for Fluid Shear Mediated Platelet Activation**

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At the site of vascular injury, von Willebrand factor (VWF) A1 domain bridges platelet receptor GpIbα to exposed collagen that results in the events leading to thrombus formation. The fluid shear enhances the binding of VWF to platelet GpIbα and under high shear stress conditions platelets are activated by a process termed as “shear induced platelet activation (SIPAct)”. Fluid shear was applied on human platelets from platelet rich plasma (PRP) using a cone and plate viscometer and the binding of VWF-488 (Alexa-488 conjugated plasma VWF (pVWF)) was measured using flow cytometry. We observed augmented binding of VWF-488 and increased activation of platelets by the addition of unlabeled pVWF. This was efficiently blocked by anti-GpIbα and not by anti-GpIIb/IIIa antibodies, which indicated that VWF may self associate under fluid shear and bind to platelets resulting in platelet activation. To address this hypothesis, we expressed functional full length recombinant VWF (rVWF) and VWF that lack A1 domain (ΔA1-VWF) in Chinese Hamster Ovary (CHO) cells. ΔA1-488 (Alexa-488 conjugated ΔA1-VWF) binding to the platelet was augmented by addition of unlabeled pVWF. ΔA1-488 was used as a tool to detect VWF self association in whole blood. This observation was further supported by experiments with VWF immobilized polystyrene beads or beads conjugated to anti-GpIbα antibody, where application of fluid shear resulted in enhanced platelet binding and activation under low shear conditions. These results indicate that binding of self associated VWF may induce mechanotranduction at the platelet GpIbα-axis which may result in SIPAct.

*Key Words*: von Willebrand Factor, VWF, thrombosis, platelet activation, GpIbα, fluid shear
17. Robust, Rapid and Cost-Effective Assays for Determining ADAMTS13 Activity in Human Plasma

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Thrombus formation is initiated at the vascular injury site due to the interaction between Von Willebrand Factor (VWF) multimers (that bind to the injured subendothelium) and platelets in the blood stream. The thrombus size is regulated by ‘a disintegrin and metalloprotease with thrombospondin type 1 motif 13’ (ADAMTS13) as it cleaves VWF at its A2 domain under conditions of high shear. If ADAMTS13 is nonfunctional either because of mutations in its gene or because of autoantibodies that inhibit its action, VWF multimers won’t be cleaved effectively, leading to the formation of platelet-rich microthrombi in blood vessels. This condition is termed as Thrombotic Thrombocytopenic Purpura (TTP). Current assays used for measuring ADAMTS13 activity in plasma suffer from issues like low sensitivity, long turnaround times, high cost, etc. We are seeking to develop robust, rapid and cost-effective assays. We made fusion proteins of human recombinant VWF-A2 domain with fluorescent proteins in Rosetta-gami 2 strain of E. coli that would enable us to perform direct cleavage assays of ADAMTS13 in cytoflowmetry and fluorometry. These functional assays would be used as diagnostic tools for measuring ADAMTS13 activity in plasma, and hence as indicators of TTP. Silver stained gels clearly show the cleavage of the fusion proteins into two fragments. Subsequently, ADAMTS13 would be screened against biological molecules to determine its potential inhibitors, which would lead to better understanding of acquired TTP.

Key Words: Von Willebrand Factor, ADAMTS13, TTP, thrombocytopenia, VWF-A2 domain, direct cleavage assay.

18. Study of Site Specific Glycosylation on PSGL-1 Regulating Inflammation

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During the initial tethering step of leukocyte recruitment, leukocyte surface protein P-selectin glycoprotein ligand-1 (PSGL-1) binds to selectins on the inflamed endothelium. Specific methods to modulate glycan structures on PSGL-1 can yield therapies for inflammatory diseases. To quantitatively measure changes in PSGL-1 glycan structure associated with various treatments, a recombinant PSGL-1 protein-probe (PSGL-1pp) was developed and stably expressed on two mammalian cell lines, CHO and HL-60, using lentivirus. PSGL-1pp has a unique O-linked glycosylation site at threonine-57 near the N-terminus of PSGL-1, which participates in selectin recognition and cell adhesion under fluid flow. Following the glycan site is a poly-histidine tag for purification and a proteolytic cleavage site used to release PSGL-1pp. Results demonstrate that PSGL-1pp released by protease can be readily captured and detected using cytometry-bead assays. Site-specific glycosylation was detected by flow cytometry using HECA-452 and CSLEX-1, monoclonal antibodies recognizing the sialyl Lewis-X carbohydrate epitope. To amend the PSGL-1pp design for suitable mass spectrometry (MS) analysis: 1) three amino acids RGR were added between the N-terminal peptide and the histidine tag to reduce the peptide size; 2) the Ser/Thr/Pro-rich domain was replaced with human Fc-tail to enable sequence coverage of the protein. The peptide of interest was observed following tryptic digestion and peptide separation using C-18 reverse phase nano-LC and analyzed using LTQ-Orbitrap XL (FT-MS) with protein expressed in an E.coli system. MS analysis for mammalian proteins to study their glycosylation structure is currently underway. Overall, combining recombinant protein expression with flow cytometry and MS may be useful to detect and quantify changes in site-specific glycosylation that regulate human inflammatory diseases.

Key Words: PSGL-1, glycosylation, sialyl Lewis X
19. Domain Level Interactions within Blood Protein Von Willebrand Factor

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The blood protein Von Willebrand factor (VWF) regulates thrombosis and hemostasis. By binding platelets in blood and collagen exposed on the denuded endothelium, VWF forms a molecular bridge that recruits platelets to sites of vascular injury. VWF function is regulated by applied hydrodynamic forces. While it does not bind platelets spontaneously, application of shear stress > 60 dyn/cm² enhances VWF-A1 domain recognition of platelet-GP Ibα. Fluid shear thus alters domain-level interactions that stabilize native protein conformation. To determine the 3D arrangement of domains within VWF, recombinant dimeric VWF was crosslinked using the homobifunctional linker (BS3). Crosslinked protein was digested with Glu-C in either normal or O¹⁸ labeled water. Peptide fragments were subjected to nano-LC separation followed by tandem mass-spectrometry on a LTQ Orbitrap hybrid FTMS. A program implementing cross-correlation and probability based scoring was developed to analyze and rank tandem MS data. Program code was validated against two commercial software, SEQUEST and MASCOT. Analysis of cross-linked VWF MS data revealed potential intra-molecular interactions within VWF. Prominently, specific peptides in the D’D3 domain were observed to lie in proximity to amino acids in the A1 domain that contribute to platelet-GpIbα recognition and Von Willebrand Disease Type IIb. Functional studies partially validate MS findings. Together, the data suggests that the increased affinity of VWF for platelets under shear may be due to the release of weak shielding of A1 domain by the D’D3 domain.

Key Words: Von Willebrand factor, thrombosis, hemostasis, fluid shear, platelets, mass-spectrometry

20. Targeting Important α(1,3)Fucosyltransferases in Human Leukocyte Recruitment

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Leukocyte recruitment consists of an adhesion cascade through which a leukocyte undergoes capture, rolling, firm adhesion, and endothelial transmigration to where it can exert its effects at the point of inflammation. This adhesion cascade is mediated by recognition of specific glycan structures on leukocyte cell-surface receptors by selectins expressed on endothelial cells activated by an inflammatory event. A terminal fucose is added to the most important of these carbohydrate structures in leukocyte adhesion, the sialyl Lewis X (sLeX) structure, by α(1,3)fucosyltransferases (FucT). Previous FucT studies have been carried out with mouse FucT knockouts, but to date there are few studies performed in a human cell line or with FucT-silenced normal mature cells. The goal of this project is to quantify the effect of silencing various FucTs in a human promyelocytic system via both static and dynamic functional assays and eventually in vivo experimentation. To accomplish this, commercially available shRNA sequences were first screened in CHO cells engineered to contain a FucT-GFP fusion protein by quantifying the change in fluorescence post-silencing. A DsRed reporter was then incorporated into the best silencing vectors to quantify transduction efficiency. From this point, static and shear-based functional assays will be executed with these DsRed shRNA vectors in HL-60 leukocytic cells to determine the relative importance of each FucT in leukocyte recruitment. Advancing the knowledge of glycan function in leukocyte recruitment may eventually suggest new therapeutic strategies in the treatment of immune and inflammatory-related diseases.

Key Words: α(1,3)fucosyltransferase, sialyl Lewis X, sLeX, leukocyte recruitment
21. Study of Platelet Thrombus Formation Using Microfluidic Devices

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Platelet adhesion, activation and thrombus formation are central features of hemostasis. Platelets are also key players of various cardiovascular disease pathogenesis. Normal hemostasis occurs at the sites of vascular injury, at abnormally high fluid shear rates. Following denudation of the endothelium, one of the first steps of the coagulation cascade involves the binding of the plasma glycoprotein Von Willebrand factor (VWF) to the exposed subendothelium. Platelet recruitment on the wall occurs via the reversible interaction between platelet receptor GPIBa and the VWF A1 domain. The adherent platelets change shape and form tethers to bind other platelets and plasma protein fibrinogen to form initial hemostatic plug, via activation by various agonists (Thrombin, ADP, Thromboxane A2, Collagen, Epinephrine) released or expressed at the injured endothelium. Mural thrombus formation at regular circulation conditions can result in heart attack or stroke. Whole blood perfusion study in a parallel plate flow chamber has been a powerful tool in understanding the initiation and propagation of platelet thrombus formation at pathological shear conditions. Such a flow chamber assay, however, required several milliliters of blood for a single run. To overcome this limitation, we have designed a microfluidic device that can be used to study the mechanism and dynamics of thrombus formation with only microliter quantities of blood. These devices can be applied to evaluate the effects of various agonists in platelet activation and thrombus formation. Microfluidic devices can also help us study small animal models of thrombosis ex vivo with minimal animal sacrifice.

Key words: platelet, thrombus, microfluidics, VWF

22. Glycosyltransferase Assays for Leukocytes, Cancer Cells and Stem Cells

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Glycomics is an emerging research area. It aims to integrate large scale experimental data sets and computational techniques to better understand the structure, chemistry and roles of carbohydrates in guiding glycan formation. This in turn regulates diverse processes including cell adhesion, bacterial/viral interaction with host cells and cancer metastasis. The glycan structures are formed by catalytic action of glycosyltransferases enzymes on protein, lipid and small molecule scaffolds. The levels of these enzymes in the Golgi are a key feature regulating glycan structures. We have developed a method to monitor these enzyme activities in a simple fashion. Particular emphasis is placed on studies of enzymes mediating the O-linked glycosylation pathway in human cells like sialyltransferase, fucosyltransferase and galactosyltransferase. Reactions are performed in small volumes with an array of carbohydrate substrates, followed by the rapid, tandem separation of product from unreacted radioactive sugar-nucleotide. The development of this method overcomes complex and time-consuming washing and separation steps which pose limitations on traditional methods. We can thus quantify and compare different enzyme levels in a given cell system. In case of cancer cells system we observed large differences in different breast cancer cell lines for these enzyme. In case of stem cells we observed quantitative differences as the stem cells are allowed to differentiate. The fucosyltransferases are down regulated while sialyltransferases and galactosyltransferases are upregulated. The assays were used to study the reversibility of recombinant sialyltransferase. So, this is a versatile method that can be applied to any cell system to get insight into the glycosylation pattern in the system.

Key Words: glycosylation, glycosyltransferase assays, cancer cells, leukocytes, stem cells
Engineering Specificity at the Dimer Interface of Streptavidin

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Streptavidin is composed by four identical subunits and binds biotin with the dissociate constant ($K_d$) around $10^{-14}$ M, which is one of the strongest protein-ligand interactions. However, the applications of the protein are limited because of its tetravalent biotin-binding ability. To engineer the novel streptavidin with a reduced valency, we decided to engineer the residues that are at the interface between two subunits. By re-designing the hydrogen-bond network and van der Waals contacts at the interface using molecular dynamics (MD), we will engineer novel streptavidin heterodimers or orthogonal homodimers. These heterodimer and homodimers can then be combined to engineer streptavidin tetrampers with various subunit stoichiometry, including $a_3b$ and $a_2b_2$. We can also design streptavidin molecules with specific biotin-binding orientation by engineering the dimer-dimer interface residues. In our preliminary studies, we mutated the residues 74 and 76, which are located at the center of the interface and are involved in intermolecular hydrogen bonds. When the protein is purified from bacteria or displayed on the yeast surface, the engineered streptavidin shows the subunit specificity as predicted by MD, demonstrating that computation can be used to predictably change the quaternary structure of streptavidin.

Key Words: streptavidin, orthogonal homodimer, heterodimer, molecular dynamics, yeast surface display

Figure 1. The native dimer interface of streptavidin. The residues in stick are involved in intimate intermolecular hydrogen binding and side chain packing.
24. Disulfide Trapping of Transient Protein Complexes on the Yeast Surface

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Protein-protein interactions are complex, and form the basis of the quaternary structure of multimeric proteins, which mediate essentially all biological processes. To date, different biochemical and biophysical techniques are employed to analyze these interactions, however they are labor intensive, and have low sensitivity. Moreover, most of the protein-protein interactions are transient in nature, which are difficult to study on yeast or phage surface because of prolonged induction time. To overcome these limitations, we developed a technique by combining high throughput yeast display and disulfide trapping which we refer as Stabilization and Trapping of Unstable Complexes by Engineered Disulfide (STUCKED) that can be used to study the formation of protein complex based on simple fluorescence labeling. To show its applicability to a broad spectrum of protein complexes with the subunit dissociation constant $K_d$ ranging from 0.5 to 20 µM, we show that three different quaternary structures, including the antibody variable domain (Fv), the IL-8 dimer, and the p53-MDM2 complex, can be displayed on the yeast surface by introducing an interchain disulfide between the subunits. All three systems are efficiently displayed on the yeast surface, showing that the constraint imposed by disulfide bonds can stabilize protein complex structures. We also demonstrate that a disulfide formation is very specific between the subunits, as mutations that decrease the affinity of subunit interaction also reduce the display efficiency. The displayed complexes exhibit functional characteristics that are expected of wild proteins, and most of the disulfide stabilized complexes are formed within the secretory pathway during the export to the yeast surface. Thus, this technique will enable the efficient analysis of weak interactions and can also provide valuable quantitative information of binding affinity in the future.

**Key words:** disulfide trapping, quaternary structure, yeast surface display, protein-protein interaction

![Figure 1](image)

**Figure 1.** Schematics of STUCKED. An unstable protein complex can be expressed on the yeast surface by crosslinking two co-expressed subunits.
25. **Engineering of Monomeric Streptavidin**

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Streptavidin is a homotetrameric protein which binds its ligand, biotin, with extremely high affinity. The high binding constant for this interaction ($K_a \approx 10^{-14}$) has made the streptavidin/biotin system one of the strongest non-covalent interactions known in nature and has become the basis of a number of studies aimed at determining what particular intermolecular interactions give rise to the tight binding. If this strong binding can be understood, it should help in probing other systems where similar interactions are important. In particular, the design of new drugs and ligands for proteins and nucleic acids will benefit from having a detailed understanding of the interactions involved. Strong streptavidin-biotin bond can be used to purify or detect various biomolecules and attach these biomolecules to one another or onto a solid support. The aim of this project is to engineer a monomeric streptavidin from the wild-type tetrameric streptavidin, while maintaining its high binding constant. However, upon the breaking of tetramer into monomer, the short loop between the first 2 strands has caused the solvent molecules to enter biotin binding pocket of the molecule, and thus, destabilizing the molecule and disrupting the binding of biotin to the molecule. Therefore, we decided to extent this short loop by adding additional residues, so that the longer loop would form a barrier to protect the binding pocket and prevent solvent molecules from entering the binding pocket. The association between the engineered monomer and biotin is monitored with molecular dynamics simulation and several biochemical assays will be used to characterize the monomeric streptavidin.

*Key Words: streptavidin, quaternary structure*

![Figure 1](image.png)

**Figure 1.** Streptavidin tetramer will be engineered to a monomer without losing the high binding affinity.
26. Directed Differentiation of Human Embryonic Stem Cells to Cardiomyocytes for Heart Failure

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Heart failure which results in fibrotic scar formation and impairs cardiac function is the number one cause of death. Transplantation of heart muscle cells differentiated from stem cells give scientists a novel way to reserve the damaged heart besides heart transplantation. But the present differentiation protocols are involved Fetal Bovine Serum (FBS) which could potentially transmit pathogens from animal source and also generates a highly heterogeneous differentiated cell population with low percentage of cardiomyocytes. So we developed this new protocol with less concentration of FBS and higher yield percentage of cardiomyocytes.

The whole differentiation process was divided into 4 stages (mesendoderm, mesoderm, early cardiac and mater cardiac stage) and different grow factors with different concentrations were added at different stages. The differentiated cells were analyzed by stage specific markers by RT-PCR and immunostaining at different stages. The finally differentiated cardiomyocytes were characterized by qPCR, immunostaining and flow cytometry which confirmed the expression of cardiac markers, such as atrial natriuretic factor (ANF), Nkx2.5, Gata4 and human beta-Myosin Heavy Chain (β-MHC) Functional assay were also performed by pharmacological stimuli (IBMX). The dose-dependent increased beating rate of cells indicated a cAMP-dependent mechanism that mediated the contracting of cells.

Overall, the hESCs-derived cells meet the requirement of cardiomyocytes, including expression of genes, makers and functional assay. Now we are trying to isolate differentiated cardiomyocytes for animal experiment to check its function in vivo and applying this protocol for large scale production in bioreactor.

Key Words: embryonic stem cell, differentiation, cardiomyocytes
Human embryonic stem cells (hESCs) can be an inexhaustible source of islet cells for transplantation in diabetes treatment. In this study, we describe the development of a robust method for directing hESCs fate towards pancreatic islets (PIs). A stage-wise differentiation protocol was developed and applied to direct hESCs into definitive endoderm (DE), pancreatic endocrine precursor (PEP) and PIs. To that end, we exposed hESCs to factors and environmental cues similar to those present during embryo pancreatic development. Differentiated hESCs undergo morphological and biochemical changes. The resulting PEP cells are positive for markers important for insulin transcription including HNF6, PDX1, NKX-2.2, -6.1, and NGN3. Marker expression was assessed by quantitative PCR, immunocytochemistry and flow cytometry. For the identification of insulin-secreting PIs among differentiated cells, we developed an adenoviral construct (AdRIPRED) encoding red fluorescence protein gene flanked by the insulin gene promoter. Further, we explored the application of our differentiation protocol in conjunction with large-scale expansion of hESCs. Pluripotent hESCs were grown on microcarriers in a stirred suspension bioreactor. These cells were able to attach and grow on the beads with 36-fold increase in cell number while ~85% of the cells remain pluripotent as shown by OCT4 and SSEA4 expression. Human ESCs on the beads were successfully directed into DE cells co-expressing SOX17 and FOXA2. Our system shows the possibility of large-scale expansion and differentiation of hESCs into endoderm progeny and may contribute to bioprocesses for the generation of islet cells from stem cells in therapeutically useful quantities.

Key Words: embryonic stem cells, pancreatic islet, differentiation, bioreactor, microcarrier, definitive endoderm
Directed Differentiation of Mouse Embryonic Stem Cells to Cardiomyocytes in an Encapsulated Environment

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Heart diseases are top ranked as causes of morbidity and mortality in the US and most developed countries. Myocardial infarction is associated with significant cardiomyocyte death and permanently impaired cardiac function. Widespread utility of heart transplantation is hindered due to severe shortage of donor organs. Hence, the search for alternative sources of heart cells including embryonic stem cells (ESCs) has intensified in recent years.

In this study we explored the differentiation of mouse ESCs (mESCs) towards cardiomyocytes in the absence of serum and with factors involved in embryonic heart development. Current methods for ESC-to-cardiomyocyte differentiation rely on the use of serum which makes challenging the control of ESC specification. The resulting cell populations are heterogeneous and contain only minute fractions of cells displaying cardiomyocyte markers.

We have identified conditions using defined serum-free medium and TGF-β ligands for directing the differentiation of mESCs to cardiomyocyte-like cells. When cultured in dishes, mESCs formed beating foci and the fraction reached 90% within 2 weeks and remained constant thereafter. The cells displayed cardiac α-actinin, α-myosin heavy chain, cardiac troponins and Nkx2.5 as assessed by reverse transcription-PCR (RT-PCR) and the immunostaining.

Given the need for generating heart cells in adequate quantities for clinical uses, scale-up methods in a stirred-suspension bioreactor is investigated. Culture in alginate beads demonstrates advantages over other scale-up methods with exposed cells which permit lower control on proliferation and differentiation due to tendency of cells to agglomerate.

Key Words: Embryonic stem cell, cardiomyocyte, bioreactor, directed differentiation, defined serum free medium, myocardial infarction, alginate encapsulation
29. On the Use of Entropy-Scaling to Describe Dynamic Properties of a Dumbbell Model under Confinement

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Understanding transport coefficients such as the diffusivity, viscosity, and thermal conductivity of a fluid under confinement is valuable for both scientific research and engineering design. Empirical scaling relationships have emerged as a promising approach for predicting such quantities. In fact, recent studies [Phys. Rev. Lett 96, 177804 (2006), J. Chem. Phys. 125, 0761402 (2006), J. Phys. Chem. B 110, 18147 (2006)] have demonstrated that entropy-scaling relations provide a robust means to describe the dynamics of bulk and confined atomistic fluids. In this work we examine the extent to which these ideas can be used to characterize molecular fluids under confinement. Through the use of molecular dynamics and transition-matrix Monte Carlo simulations we study how confinement between atomic structured walls modifies the relationships between transport (translational and rotational diffusivity, characteristic relaxation times) and thermodynamic (excess entropy) properties of a dumbbell model.

Key words: excess entropy scaling, molecular dynamics, transition-matrix Monte Carlo, diatomic fluids, confinement

30. Effect of Roughness on Wetting

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In order to describe various physical phenomena, knowledge of wetting behavior of a fluid on a surface is important. Surface roughness plays an important role in wetting, extreme behaviors ranging from complete wetting to superhydrophobicity can be attained by tuning in surface roughness. Molecular simulations can provide useful insight on the topic. In this presentation we show how grand canonical and expanded ensemble transition matrix Monte Carlo simulation techniques are used to determine the surface excess free energy of a system. Properties like surface tension, spreading coefficient, and contact angle are calculated from this free energy information. These techniques are used to examine the wetting behavior of water on surfaces with roughness ranging from molecular to nanoscopic length scales. Our results for the contact angle are compared with those predicted by the macroscopically-based Wenzel and Cassie-Baxter equations. High performance computing techniques are required to run these simulations, hence use of GPU’s to speed up our calculations is a subject of interest in the near future.

Key Words: roughness, wetting, Monte Carlo
31. A Molecular-Based Computational Approach to Develop Equations of State for Polar Fluids

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The virial equation of state (VEOS) can describe accurately the PVT behavior of nonpolar fluids. However, in polar fluids, hydrogen bonding can cause a breakdown of the virial series approach because the virial series does not explicitly consider strong molecular association via hydrogen bonding. Also, higher-order VEOSs are required to describe the thermodynamic behavior of the strongly associating fluids at a given density. Calculation of these higher-order virial coefficients requires considerable CPU running time. Therefore, it would be helpful to use an alternative thermodynamic method which maintains molecular-level detail, but incorporates fluid association. Here, we consider Wertheim’s 2-density series expansion, with a single association-site model comprised of a Lennard-Jones interaction and a short-ranged square-well site-site interaction. Both the VEOS and Wertheim-theory cluster diagrams are evaluated using the Mayer-sampling Monte Carlo algorithm. We find that Wertheim-theory series require fewer terms to describe the true PVT behavior than the conventional VEOS. We also apply Wertheim’s association theory to examine a double association-site interaction.

Key Words: association, VEOS, Wertheim, hydrogen bonding, Mayer-sampling Monte Carlo

32. Atomistic Modeling of Tin Grain Boundary Diffusion

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As analysis tools in computational materials science develop, transport properties at the atomistic level play an increasingly important role in the study of a material's behavior at larger scales. Quantitative transport data explaining diffusion, cracking, or crystal growth, often difficult to study experimentally, can be had with relative ease using a molecular simulation package and a few workstation grade computers. The field of electronics packaging can benefit from this kind of analysis, specifically in the study of electromigration in thin films and SnAgCu (SAC) alloy solder joints. Grain boundaries in these structures provide fast diffusion paths for tin solute atoms, alloyed elements, and vacancies. In addition, atoms and vacancies are given a strong diffusive force from the electrical current’s inherent electron wind. Modeling the diffusive process in the microstructure of tin will aid in the prediction of failure rates of these types of thin films and solder joints—key parameters for the realization of nano-electronics. We use molecular dynamics simulations to compute the diffusivity of tin atoms in our systems. Various angles of symmetric tilt grain boundaries are simulated and diffusional widths of the boundaries are computed. Values for activation energies and diffusion coefficients are also presented and compared to experiment.

Key Words: grain boundary diffusion, electromigration, lead-free solder, molecular dynamics
Improving the Efficiency of Virial-Coefficient Calculations: Hybrid Approaches Employing Integral-Equation Theories and Mayer-Sampling Monte Carlo

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Mayer-sampling Monte Carlo (MSMC) has enabled calculation of Lennard-Jones (LJ) virial coefficients of up to eighth order [1]. However, virial coefficients of even higher order would be required to compute accurate critical densities from the virial equation of state, and computing these coefficients by MSMC alone is not feasible. For spherically symmetric potentials like LJ, some of the cluster integrals comprising the virial coefficients can be decomposed into products of low-dimensional integrals through Fourier transforms [2]. In particular, the Percus-Yevick [3] and hypernetted-chain [4] integral-equation theories define approximate virial coefficients comprised only of these simple integrals. Here, we present two hybrid methods that apply MSMC more judiciously by taking advantage of these theories.

In the first method, we decompose the virial coefficients directly, computing the approximate virial coefficient by FFT and the correction by MSMC. We demonstrate that this hybrid approach is faster than MSMC alone for computing LJ fourth and fifth virial coefficients. However, because of the recursive nature of the integral equations, the approximations are more severe at higher order, reducing the benefit of the hybrid approach. We present a second hybrid approach, in which the corresponding coefficient of the direct correlation function, rather than the virial coefficient, is decomposed into approximation and correction. The corrected coefficient of the direct correlation function is then applied within the recursive formalism, reducing the severity of the approximation at the next order. Thus, this second hybrid method should prove more useful for calculating the high-order coefficients currently beyond consideration with MSMC alone.

Key Words: virial coefficient, Mayer-sampling, integral-equation theory

34. **Consideration of the Entropy in the Free-Energy Calculation for the Stable Crystalline Polymorphs**

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In order to predict the stable crystalline polymorph, we can compare the free energy of each polymorph and select the one with the lowest free energy. Most of the current prediction techniques only take into account the energetic contribution to the free energy and have ignored the entropic contribution. This is mainly because determining the entropic contribution is another degree of complication. In order to improve the accuracy of these approximation methods, we have included the neglected entropic term into our free-energy calculation by using methods that build on the lattice-dynamics approach. This idea is motivated by many previous studies, which have reported that in many cases, the difference between the energies of the most stable polymorphs is relatively small and the stability is believed in some cases to be influenced by entropy.

Calculation of true free energy is performed by computing the difference with respect to a known reference. In this work, we use a harmonic reference system with spring constants given to match the configurational correlations measured in the target system. We consider various perturbation techniques that compute the free energy difference between the target and reference systems while avoiding lengthy thermodynamic integration procedures. The basic methods we look at are free-energy perturbation approaches involving a single intermediate stage, which include overlap sampling and umbrella sampling. Such methods require only one or two simulations (of the target and/or reference system) to yield a result, and for small enough systems we show that these methods can be effective. In larger or more difficult systems we consider a process of switching on various harmonic modes in groups, and evaluate the free-energy change for each before summing to determine the total difference. We consider whether and how this process may be abbreviated in a way that does not require transformation of all harmonic modes. Different prototype systems are studied and discussed in the context of these methods.

*Key Words:* molecular crystal, polymorph stability, entropy, free energy calculation, normal modes and perturbation techniques
Nanoscale Materials Science and Engineering

35. Amphiphilic Block Copolymers in Aqueous-Polar Organic Solvent Mixtures: Phase Behavior and Structure

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Amphipilic block copolymers of the poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) family are well known for self-assembling in the presence of water (selective solvent for PEO) into cubic, hexagonal and lamellar lyotropic liquid crystals. We are interested on how the aqueous phase behavior and structure of these polymeric amphiphiles can be modulated by the addition of polar organic solvents (e.g., glycerol, ethanol, propylene carbonate, triacetin). Mixtures of water with two organic solvents constitute a specific focus of this work. Our studies combine macroscopic observations (e.g., phase diagrams) with microscopic measurements (from small-angle X-ray scattering), and aim to relate the type of structure formed and its characteristic dimensions to the relative swelling of the polymer blocks and to the location of the solvent in the amphiphile assembly. Solvent-induced structural changes of block copolymers have interesting repercussions on the formulations and nanomaterials synthesis in such media.

Key words: block copolymers, amphiphile, lyotropic liquid crystals

36. Dissolution of Cellulose

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Cellulose is a unique stereoregular, chiral, biocompatible and reactive polymer which at the same time constitutes an abundant and renewable natural resource. However, the efficient conversion of cellulose towards speciality polymers and its hydrolysis to biofuels is severely hindered by the crystallinity inherent in native cellulose. A few solvent systems have been found effective for molecular dissolution of cellulose, but they operate under rather strict conditions of composition and temperature. We are studying the dissolution of solid cellulose in aqueous NaOH solutions with the aims (i) to elucidate the transport phenomena governing the dissolution process and (ii) to evaluate the solution structure of dissolved cellulose as affected by its interactions with the solvent at various solution compositions and temperatures.

Keywords: cellulose, crystallinity, molecular dissolution, aqueous NaOH solutions
37. Block Copolymer Self-Assembly for Nanoparticle Organization

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Block copolymers provide a self-organizing system with great versatility as to the types of nanostructures formed and the conditions under which they are stable. Hybrid nanocomposite materials can be generated by the spatial organization of nanoparticles in these self-assembled matrices. In our research we address fundamental questions pertaining to the nanoparticle-polymer interactions (as affected by the nanoparticle surface chemistry, size, and shape) and effect of nanoparticle type and loading to the self-assembled structure, as well as practical issues related to the loading procedure of the polymer matrix with nanoparticles, equilibration time, and long-range structural alignment of the nanocomposite. We are very interested in the role that solvents can play in facilitating nanoparticle loading and organization in self-assembled block copolymers.

Key Words: block copolymer nanocomposite, self assembly, nanoparticle, template, small angle scattering

38. Self-Assembly in Ionic Liquids

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In the context of developing self-assembly as a useful approach to the synthesis and manufacturing of complex systems and materials, our group has a long-standing interest on the utilization of selective solvents for the modulation of the organization of amphiphilic molecules such as block copolymers and surfactants. Room-temperature ionic liquids (ILs) have emerged recently as solvents with unique properties, including high thermal stability and low vapor pressure. We are studying the self-assembly of nonionic block copolymers in ionic liquids, as affected by their chemical composition and intermolecular interactions, and as reflected in the formation/stability and structure of ordered (lyotropic liquid crystalline) phases. Fundamental knowledge of self-assembly and nanoscale organization in ILs will impact their potential applications in synthesis, separations, batteries, and specialty products.

Key Words: amphiphilic block copolymers, protic ionic liquids, mesophases, nanostructures, self-assembly
39. **Blood Proteins in Aqueous Solutions**

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The conformation of proteins in solution and on surfaces, as well as changes in the protein conformation caused by other molecules present in solution or external stimuli (e.g., temperature), are central to the biological activity and function of the respective proteins. Our research addresses conformation, association and interactions in aqueous solution of the blood protein fibrinogen which is involved in haemostasis and thrombosis. We are particularly interested in interactions of fibrinogen with poly(ethylene glycol) (PEG) and PEG-containing block copolymers that are known to prevent non-specific protein adsorption on surfaces. These we probe via a combination of Fluorescence and scattering techniques. The changes in the conformation of fibrinogen in aqueous solutions of synthetic water soluble polymers (PEG6000, PEO100000, Pluronic127) was studied using, DLS (Dynamic light scattering), SAXS (Small angle X-ray scattering), Fluorescence as the main experimental tools. The objective of the project was to find out the type of changes and the conditions under which these conformational changes were induced on fibrinogen. Knowledge of these interactions is very essential for pharmaceutical formulations, biocompatibility of implant materials, blood storage and transfusion, and protein separations.

*Key Words:* fibrinogen, haemostatis, thrombosis, poly(ethylene glycol), poly(ethylene oxide), Pluronic 127

40. **Novel Macromonomers for the Construction of Complex Polymeric Nanostructures**

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Diblock macromonomers with norbornene (NB) monomer functionalities carried by block junctions were synthesized and used for the construction of complex polymeric nanostructures. Poly(ethylene oxide)-b-poly(lactide)-based macromonomer was obtained by the preparation of poly(ethylene oxide) with both NB and hydroxyl groups, followed by ring-opening polymerization (ROP) of lactide via the hydroxyl site. On the other hand, polystyrene-b-poly(lactide)-based macromonomer was prepared by simultaneous reversible addition-fragmentation transfer (RAFT) polymerization of styrene and ROP of lactide via a NB-functionalized RAFT-ROP dual agent/initiator. Janus double-brush copolymers with two kinds of grafts were synthesized by ring-opening metathesis polymerization (ROMP) of these macromonomers. Other types of complex polymeric nanostructures, such as interface-crosslinked core-shell micelles and inner surface-crosslinked polymeric nanocages, may also be further achieved via these novel macromonomers.

*Key Words:* polymeric nanostructures, macromonomer, ring-opening polymerization, reversible addition-fragmentation transfer polymerization, ring-opening metathesis polymerization
41. **pH-Sensitive Brush Polymer-Drug Conjugates**

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Brush polymer-drug conjugates (BPDCs) were designed and synthesized. By choosing paclitaxol (PTXL), a powerful anti-cancer drug, as the drug moiety, PTXL-based norbornene (NB) monomer with pH-sensitive cycloacetal linkage was prepared via multi-step organic synthesis. Using the 1st and 3rd generation of Grubbs’ catalysts as the initiators, ring-opening metathesis copolymerization (ROMCP) of the NB-PTXL monomer and NB-functionalized poly(ethylene oxide) (PEG) macromonomer gave BPDCs. As either random or block copolymers, these BPDCs had well-controlled degree of polymerization and narrow molecular weight distributions. Relative to PTXL, the BPDCs can carry >1000 times of the drug moieties into aqueous systems. The nanostructures of BPDCs were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), and dynamic light scattering (DLS). Acid-sensitive drug release behavior of the BPDCs was investigated under different pH conditions via either UV-Vis spectroscopy or TLC measurements.

**Key Words:** brush polymer, nanomedicine, polymer-drug conjugate, paclitaxol

42. **Kinetic Study and Deactivation Mechanism of Gold-Ferrochrome Catalyst under Low Temperature Water-Gas Shift Conditions**

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Gold-ferrochrome catalysts deactivate rapidly under low temperature water-gas shift reaction conditions. A power-law model accounting for deactivation was developed using a bracketing technique to describe the kinetics of water-gas shift reaction over these catalysts in the temperature range of 160-180 °C. A positive order with respect to the reactants, carbon monoxide and water and a slight inhibition due to the presence of carbon dioxide has been reported. Characterization of the fresh and deactivated samples was done to find the main cause of catalyst deactivation. High resolution transmission electron microscopy (HRTEM) images and X-ray diffraction (XRD) data indicate a slight degree of sintering of gold particles as one of the causes of deactivation. No evidence of physical or chemical change of the ferrochrome support was seen in terms of morphological structure and phase of iron using BET surface area measurement, scanning electron microscopy (SEM) and near edge X-Ray absorption fine structure techniques (NEXAFS). Carbon deposition on the catalyst was found to be the most likely cause of catalyst deactivation as suggested by the mass increase during water-gas shift conditions using a highly sensitive tapered element oscillating microbalance (TEOM). Evidence of fouling by carbon deposition was also obtained by comparing the catalyst behavior in an environment with and without carbon containing gases. TEOM, NEXAFS and Raman spectroscopy data indicate that the degree of deactivation of the catalyst is related to the amount of carbon deposited on the catalyst samples during long term isothermal operation under low temperature water-gas shift conditions.

**Key Words:** water-gas shift, power-law kinetics, deactivation, gold-ferrochrome, carbon, characterization
43. **Dye-Sensitized Titanium Dioxide Materials for Photo-Degradation Reactions**

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Water contamination is a serious health and environmental issue all over the world. Many processes are being developed to oxidize the organic/inorganic contaminants in aqueous media to inorganic compounds such as carbon-dioxide, water, acids etc. Among these methods the ones which use hydroxyl radicals for oxidation purpose are collectively known as advanced oxidation processes (AOPs). Heterogeneous photocatalysis is an important process among AOPs as this process can be applied for degrading pollutants in both aqueous and gaseous medium. This technique involves oxidation of contaminants on the surface of a semi-conductor when irradiated with ultra-violet/sunlight. Titanium dioxide (TiO$_2$) semi-conductor has been studied for many years in photo-oxidation of organic compounds. Its poor absorption of visible light makes it difficult to use as a viable catalyst. Dye sensitization is a widely used technique to expand photo-response of TiO$_2$ in the visible spectrum. The objectives of this work are to develop novel visible active photocatalysts for photo oxidation/degradation of organic pollutants in aqueous media and to study the effect of dye-dye interaction, dye-surface interaction, and the structures of both dye and surface on photoactivity of dye sensitized semiconductor photocatalysts. This will be accomplished by synthesizing novel porphyrin dyes, functionalizing them on mesoporous TiO$_2$ surface and characterizing these materials.

*Key Words:* organic contaminants, photocatalyst, TiO$_2$, dye, ultra-violet light, photo-oxidation

44. **Dye-Incorporated Hydrogels for Use in Photocatalytic Applications**

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Hydrogels are a relatively new class of materials that are prevalent in many different disciplines of science and engineering. These unique polymers experience changes in material properties when confronted with changes in the immediate environment, such as pH and temperature. One of the most notable features of a hydrogel is its ability to expand, or swell, to several times its original volume when contacted by water. Swelling transforms the glassy nonporous solid to a rubbery porous gel. Upon drying, the original glassy material can be recovered without any noticeable degradation of properties. The ability to swell and de-swell without any significant change in material properties allows hydrogels to be carriers for other more reactive species. Porphyrins are essentially dyes which display photocatalytic properties when exposed to ultraviolet light. By incorporating reactive porphyrins into a hydrogel matrix, it is possible to focus their photocatalytic abilities on specific targets instead of degrading everything they come into contact with. The dye-incorporated hydrogel is also easy to recover and reuse, and has proven to be sustainable over many cycles of swelling and deswelling. The objective of this work is to create novel dye-incorporated hydrogels with various precursors to see how the dye interacts with the hydrogel matrix. This will be done by synthesizing hydrogels of varying compositions, incorporating them with several dyes, and characterizing the composite products.

*Key Words:* hydrogel, porphyrin, photocatalyst, dye, ultraviolet light
Investigation of Si Quantum Dots as Donors or Acceptors in the FRET Process

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Quantum dots (QDs) have interesting optoelectronic properties that make them excellent donors or acceptors for fluorescent resonance energy transfer (FRET) processes. Taking advantage of these FRET related properties allows for the creation of new types of biosensors that can be helpful for medical diagnostics and therapies. The promise of conventional quantum dots (e.g CdSe) in biological applications is limited by the toxicity of their heavy metal constituent elements. Silicon QDs have the potential to overcome the toxicity barrier; however its energy transfer properties are relatively unknown. Our development of highly stable aqueous suspensions of Si QDs using phospholipid micelles enables us to investigate the potential of silicon QDs as donors or acceptors in the FRET processes. Preliminary results indicate that silicon is a viable donor to Rhodamine 6G and is a viable acceptor from anthracene-based dyes. This suggests that FRET based biosensors may be developed from silicon quantum dots and used for biomedical applications.

Key Words: Silicon QDs, FRET, biosensor

Combustion-Driven Synthesis of Non-Oxide Nanoparticles in a High Temperature Reducing Jet

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In vapor-phase synthesis of nanoparticles, conditions are created where the vapor phase mixture is thermodynamically unstable relative to formation of the solid material to be prepared in nanoparticulate form. If the degree of supersaturation is sufficient, and the reaction and condensation kinetics permit, particles will nucleate homogeneously. Once nucleation occurs, remaining supersaturation can be relieved by condensation or reaction of the vapor-phase molecules on the resulting particles, and particle growth occurs, rather than further nucleation. Flame based aerosol reactors typically have lower operating costs than reactors based on plasma heating, laser heating, etc., due to lower energy cost. We have developed a nanoparticle synthesis process based on Praxair’s thermal nozzle technology using a hydrogen flame. By operating with hydrogen as a fuel and a fuel-rich stoichiometry, a high-temperature reducing environment is produced for particle formation allowing the preparation of non-oxide materials that cannot usually be prepared in flame reactors. The thermal nozzle provides heating and mixing rates as high as those in a flame or other competing technologies, but the chemistry can be separated from the flame to allow different reactions to occur. As the first test materials, copper nitrate (a low-cost and water soluble copper salt) is used as a precursor to produce copper nanoparticles. Copper nanoparticles have a variety of potential applications in the areas such as thermal conductivity enhancement in heat transfer fluids, antimicrobial formulations and coatings, catalysis, printable electronics and conducting films, thermally and electrically conductive composites, and antifouling agents. There are a few reports of copper nanoparticles preparation in the literature, which enumerate these and other potential applications. However, there is not yet a scalable, low-cost method of production copper nanopowders. Here, we present our reactor design and the first results on copper nanoparticle production in it. Early tests demonstrate the ability to produce copper nanoparticles less than 10 nm in diameter in substantial quantities.

Key Words: Combustion, nano, nanoparticle, spray pyrolysis, thermal nozzle
47. **Spray Pyrolysis Synthesis of Mn doped ZnS**

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Zinc sulfide (ZnS), a II-VI semiconductor, has been extensively investigated for its photoluminescence and other properties and has applications in solar cells, biologic sensors, phosphors, and photocatalysts. Mn-doped ZnS can have higher quantum efficiency than ZnS, for photoluminescence and photocatalysis. Precipitation, sol-gel, chemical vapor deposition and molecular beam epitaxy have been used in the preparation of these particles. In our research plan we use spray pyrolysis. The Mn and Zn single-source precursors are premixed and nebulized together. We studied the effect of amount of Mn precursor, temperature, and residence time on the size of the particles and photoluminescent properties of the particles. This was analyzed using XRD, HRTEM and photoluminescence spectroscopy. These studies can be extended to study and explore many other kinds of semiconductors. Finally, the reproducible, controllable and scalable continuous process of spray pyrolysis can be scaled up to produce high quality materials at high throughput.

*Key Words*: photoluminescence, spray pyrolysis, single-source precursor

48. **Synthesis of ZnS Nanoparticle with Different Geometry and Properties from the Same Precursors**

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Nanoparticles of zinc sulfide, a II-VI semiconductor with large band gap in the near UV region, have potential applications in solar cells, displays, photocatalysts and related fields. We have prepared ZnS nanoparticles through spray pyrolysis using zinc acetate and thiourea as precursors. For the same precursors, we used different reaction systems to produce nanoparticles with varying size, geometry and properties. In one system, the precursors were premixed and heated together in a single reaction line at different ratios. The size of particles produced in this system ranged from tens to hundreds nanometers and they were porous. Decreasing the ratio of thiourea to zinc acetate increased the porosity of the particles and helped us to identify the interactions of the two precursors. In the other system, two atomizers and separate reaction lines have been used. ZnO nanoparticles were synthesized from zinc acetate in one line, and then met with chemicals from the other line, either thiourea or thiourea together with zinc acetate. Mixtures of ZnS and ZnO nanoparticles were produced. Both large spheres (tens of nm in diameter) and small irregular particles (5 to 10 nm in diameter) were produced in these experiments. The particles produced in this system show photoluminescence peaks at around 430 nm, which suggests that ZnO-ZnS core-shell nanoparticles have been produced.

*Key Words*: spray pyrolysis, ZnS, ZnO, nanoparticles, porous, core-shell
49. Stable Water-Dispersible Silicon Nanocrystals

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Semiconductor nanocrystals (quantum dots) are attractive replacements for fluorescent dyes because of their size tunable luminescence, photostability, and brightness; however, they require surface modification before they can be used for most applications. Silicon QD’s are of particular interest because of they are biocompatible and free of heavy metals. Because biological systems are mostly aqueous, the most important step in modifying quantum dots for bio-applications is making them water dispersible/bio-functional while retaining their desirable optoelectronic properties. Developing stable water-dispersible silicon quantum dots has been a persistent challenge, due to loss of desirable optical properties when functionalized with small hydrophilic groups or oxygen containing groups. Our group has produced water dispersible silicon quantum dots that maintain most of their desirable properties, using a unique three step synthesis and encapsulation method. We are currently exploring use of various PEGylated reagents (silanes, acrylates, polymers, amphiphiles) to improve Si QD’s flexibility for biological applications. This will provide a library of silicon quantum dot probes of variable overall size, number of QD’s per probe, and surface chemistry, thereby establishing them as biological probes that maintain the vast promise of quantum dots while overcoming toxicity concerns associated with QDs based on CdSe and heavy-metal containing semiconductors.

Key Words: water dispersible, silicon quantum dots, biosensor, PEG

50. Investigation of Non-Faradaic Reactions in Silver Vanadium Oxyphosphate and Silver Vanadium Oxide Lithium Cells

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Lithium ion batteries have huge potential for power applications. These batteries are being used in portable electronic, biomedical and aerospace applications. A single lithium ion battery is able to generate a potential of 3.5-3.6 V and has a high specific energy of 200 Wh/kg. For solid state cathode materials, scientists have used different materials in the past. Some of them are silver chromate (Ag2CrO4), iodine (I2), copper (II) oxide and lithium iron phosphate (LiFePO4). Out of these, silver vanadium oxyphosphate (SVOP) (Ag2VO3PO4) and silver vanadium oxide (SVO) (Ag2V4O11) are of great interest to our research. We are looking into non-Faradaic reactions in Li-SVO/SVOP system which can lower the life of a battery. These parasitic reactions set local voltage gradients in the battery and may consume some of its power. In our present work we are looking into the formation of a solid electrolyte interphase (SEI) which gets formed at the surface of metallic lithium anode due to various chemical reactions inside the battery during the discharge process. This layer, though only a few nanometers thick, can pose significant resistance which eventually lowers the operating potential of the battery. The SVOP material was synthesized via reflux and hydrothermal routes and characterized using BET, XRD, DSC, SEM and Optical microscopy. The material was analyzed for its electrochemical performance using a coin cell battery. The future work involves understanding the failure mechanism of silver vanadium oxide (SVO) and silver vanadium oxide phosphate (SVOP) material in detail.

Key Words: non-Faradaic, SVOP, SVO, reflux, hydrothermal, coin cell
Preparation and Characterization of Amorphous Sodium Vanadium Oxide Gels (Na$_x$V$_2$O$_5$·nH$_2$O) as Cathode Materials for Rechargeable Batteries

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One of the most interesting properties of amorphous vanadium pentoxide gels is their layered structure which can host Li$^+$ for reversible intercalation. Based on this property, amorphous vanadium pentoxide gels have been adopted as cathode materials for Lithium-ion batteries. In order to fabricate amorphous gels, we used a novel sol-gel synthesis method where Sodium metavandate (NaVO$_3$) solution was protonated by Dowex ion-exchange resin to control Sodium content. After aging the solution for five days, the gel formed by self-polymerization. Different Na levels ($x = 0.13 - 0.32$) of amorphous sodium vanadium pentoxide gels (Na$_x$V$_2$O$_5$·nH$_2$O) were synthesized and verified by Inductively Coupled Plasma (ICP). As evidenced by Thermogravimetric Analysis (TGA), different hydration levels ($n= 1.14 - 1.74$) of gels at room temperature were observed. Structural investigations conducted by X-Ray Diffraction (XRD), showed that the interlayer spacing of the gel is correlated to the Na and hydration level. Evolution of the gel morphology with different Na levels was characterized by Scanning Electron Microscopy (SEM). We also processed the gel into cathode composites by incorporating the gel with highly conductive carbon nanotubes. The cathode composites were assembled into coin cells using lithium metal anodes and LiPF$_6$ in ethylene carbonate/dimethyl carbonate as the electrolyte. By discharging the coin cells at rate of C/20, more than 250 mAh/g discharge capacity was achieved. Charge-discharge tests showed the capacity fade rate is less than 8% at C/5 discharge, and less than 10% at C/2 discharge. We successfully prepared rechargeable batteries from amorphous vanadium pentoxide gels and demonstrated their high capacity and rechargeability.

Key Words: vanadium pentoxide gel, lithium-ion batteries, sol-gel synthesis, rechargeability

Figure 1. SEM image of nanostructured Vanadium oxide gel for lithium-ion batteries
52. Development of the Ag/Polymer/Carbon Composite Electrode and the Investigation of Oxygen Reduction Reaction in a Non-Aqueous Solution

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The lithium/oxygen battery features high energy density, stable discharge voltage, low cost (on metal use basis), and has almost no ecological problems. In addition, the lithium/air battery is attractive because lithium has the highest theoretical voltage and electrochemical equivalence among the metal anodes considered for practical battery systems. It has been reported that the oxygen reduction reaction taking place at the cathode discharge of the lithium/oxygen battery plays a key role in the battery performance. This research focuses on developing a silver/polymer/carbon composite electrode on which the oxygen can be reduced to produce current during discharge of the lithium/oxygen battery. Techniques for the deposition of polypyrrole (PPy) and silver (Ag) on to a carbon (C) matrix have been developed. The oxygen reduction reaction in a non-aqueous acetonitrile solution in the presence of oxygen at different concentrations has been investigated. Several types of composite electrodes were utilized to reduce the oxygen. It was observed that the silver coating greatly enhanced the oxygen reduction reaction.

Key Words: lithium/oxygen battery, oxygen cathode, composite electrode, oxygen reduction

![Figure 1. Cyclic voltammetry of oxygen reduction by different electrode types under pure oxygen.](image-url)
53. Synthesis Control of Silver Vanadium Phosphorous Oxide and Its Effects on Electrochemical Performance

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Recently, silver vanadium phosphorous oxide, Ag₂VO₂PO₄, has been identified as a cathode material of the lithium battery system for implantable cardioverter defibrillators (ICD). While the material had been typically prepared by hydrothermal reaction method, different synthesis method using reflux reaction was used for material preparation. Some samples were treated by additional heating after the synthesis. As employing different synthesis conditions can cause changes in physical properties such as morphology, particle size, and surface area, following characterizations were performed: X-ray diffraction (XRD), scattering electron microscopy (SEM), thermal analysis (TGA/DSC), particle size measurement, and surface area measurement. From the characterization results, the sample prepared by reflux reaction method displayed dramatic changes in physical properties. In order to examine the effects of these changes on electrochemical performance of the battery system, test cells were fabricated and discharged under constant-current or alternating pulses. Test results showed improvements in cell performance achieved from the sample having controlled physical properties.

Key Words: silver vanadium phosphorous oxide, morphology, particle size, surface area, lithium battery, electrochemical performance

Figure 1. Morphology of SVOP samples prepared by hydrothermal (left) and reflux (right) method
There has been a tremendously increasing demand for the improvement of battery technology in the past decade due to the advancement in electronic technology. To supply energy, newer batteries with greater charge capacity and energy density need to be developed. One of the cathode materials that has been widely studied for application in micro-batteries is vanadium pentoxide gels. This material has been known to exhibit good electronic, ionic and electrochemical properties. My current research focuses on improving the characteristics of this cathode material by incorporating Carbon nanotubes into the Vanadium oxide slurry mixture used to prepare a cathode to increase its conductivity. Three methods have been developed and investigated. The first method involves dispersing Carbon nanotubes in a solvent (N-Methyl Pyrrolidone) along with Vanadium oxide and other carbon additives (Ketjen Black and Graphite). This slurry is then used to uniformly coat aluminum foil which is used to make the cathode. The second method involves depositing the cathode slurry onto preformed Carbon nanotube discs with vacuum assist. Third method involves dipping the carbon nanotubes during the formation of the vanadium oxide gel during the sol-gel process. These methods then involve post treatment processes namely; pressing at 4000psi and then drying at 110°C overnight. Cells were assembled using this cathode, using Lithium metal as anode and its charge and discharge capacities were studied. The cells produced by this method have shown improved capacities of 250mAh/g respectively over coating method having capacity of 210mAh/g (Figure 1).

Key Words: vanadium oxide gel, cathode preparation, carbon nanotubes, coating

![Figure 1. Discharge curve showing the capacities of the three methods used to prepare cathode](image-url)
55. **Crystallization of Calcium Carbonate and Calcium Oxalate Mediated by Polymers and Surfactants**

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Controlled crystallization of calcium carbonate and calcium oxalate in terms of crystal morphology, polymorphic selectivity, and the aggregation state of the polymorphic phases is of great interest due to their biological relevance. Calcium carbonate is often deposited as biomineral by various organisms and constitutes a common ingredient of many skeletal structures. Calcium oxalate on the other hand, is the main constituent of kidney and gall bladder stones. Preferential adsorption of additives on the growing crystal surfaces induces morphological and polymorphic phase changes. In our research, we evaluate the roles of various organic additives on controlling crystal morphology and polymorphic selectivity, and we investigate the influence of different parameters (e.g., pH, ionic strength of the aqueous media, concentration ratio of additive and mineral) that modulate the interfacial interactions between additives and crystal surfaces. Scanning Electron Microscopy, Optical Microscopy, Infrared Spectroscopy, and X-ray Diffraction are used for morphological and polymorphic phase identification. Finally, we also address the fundamental issues that relate to the thermodynamics and kinetics of the process and try to elucidate the crystal growth mechanisms in the presence of various additives.

*Key Words:* crystallization, calcium carbonate, calcium oxalate, additives, crystal nucleation, crystal growth, polymorph

56. **Polymer-Clay Multilayer Assemblies**

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Multilayered thin films have been the focus of intense research because of their vast array of applications such as advanced food packaging materials, superhydrophobic surfaces, resistant coatings, electrical diodes, semi-permeable membranes, drug delivery vehicles, etc. In our research, we capitalize on the Layer-by-Layer (LbL) assembly, a bottom-up nanofabrication technique to generate multilayered films of polymers and clays. The resulting materials can show an exceptionally broad range of structural characteristics and thus unique functional properties, different from those of the individual building blocks of which they are composed. We focus on the fundamentals governing the LbL assembly process in order to get a better understanding of the mechanisms that control the internal ordering and organization in these films. We have confirmed the presence of layering in these nanostructures by scanning electron microscopy (SEM), investigated and calculated the regular spacing in these layers by X-ray diffraction (XRD), and studied the layer growth using UV-vis absorbance spectroscopy. We evaluate the structural characteristics and properties of these multilayers, and we are especially interested in investigating their sensitivity to external stimuli such as pH, temperature, humidity, and ionic strength.

*Key Words:* Layer-by-Layer (LbL) assembly, bottom-up fabrication, polymer, clay
57. Cyclodextrin Modulated Surfactant Self-Assembly in Aqueous Solutions

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Micelles (self-assembled structures of amphiphilic surfactant molecules) in aqueous solutions have been extensively studied because of their ability to encapsulate hydrophobic species in their core. Controlling the release of the encapsulated species is essential for the potential application of these micelles as drug delivery carriers. We have utilized the ability of cyclodextrins (CDs) to form inclusion complexes with hydrophobic species in aqueous solution to investigate the interactions between CDs and self-assembled micelles. In the present study, the effect of CDs on sodium dodecyl sulphate (SDS) micelles in aqueous solution has been studied using small angle neutron scattering (SANS) technique. SANS data analysis provides information on the effect of CDs on structural parameters such as aggregation number, charge, shape, and size of the micelles, and elucidates the mechanism by which CDs act.

Key Words: small angle neutron scattering (SANS), self-assembly, surfactant, micellization, cyclodextrin (CD), sodium dodecyl sulphate (SDS)
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