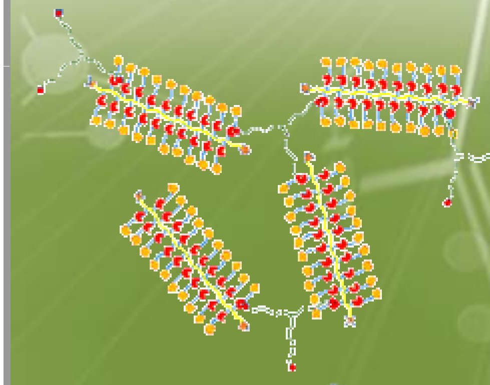
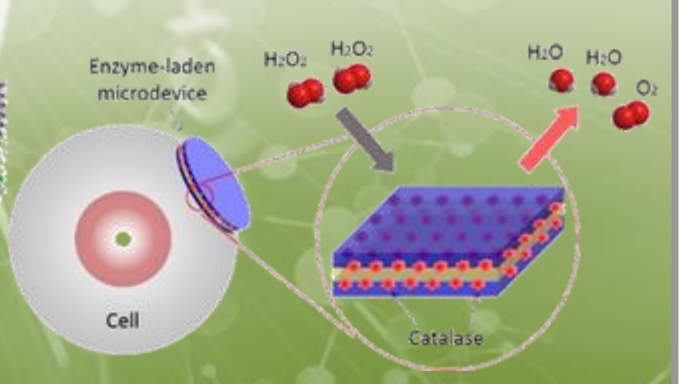
2016 Departmental Research Day

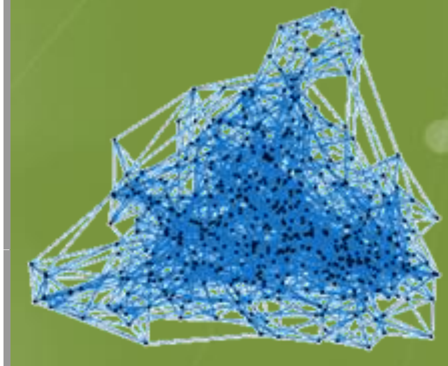
Department
of
Chemical & Biomedical Engineering
FAMU-FSU College of Engineering

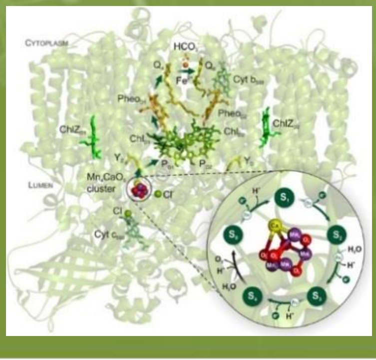
National High Magnetic Field Laboratory
2525 Pottsdamer Street, Tallahassee, FL

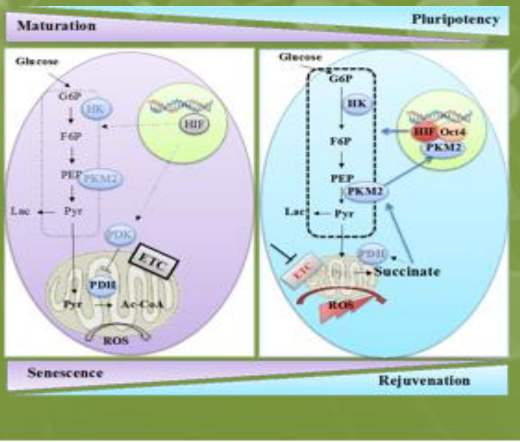
8:00 am – 2:00 pm, Friday April 15, 2016











Schedule of Events

08:00	**Poster and Presentation Setup – B101, NHMFL**
08:30	**Keynote – Dr. David A. Tirrell, Caltech – B101, NHMFL**
09:30	**Break**
09:40	**Graduate Student Oral Presentations**
11:20	**Graduate Student Poster Session I – Odd numbers**
12:00	**Lunch and Poster Session**
13:00	**Graduate Student Poster Session II – Even numbers**
14:00	**Adjournment & Cleanup**

Table of Contents

Page

Welcome!

On behalf of the Department of Chemical & Biomedical Engineering at the FAMU-FSU College of Engineering, I wish to extend to you our sincerest welcome to the Annual Departmental Research Day. This showcase provides our graduate students, undergraduates and postdoctoral fellows with the opportunity to display and discuss their research over the last year in an informal setting with fellow students and faculty. We are proud of the work performed by our students and postdoctoral researchers, and this event gives them the opportunity to defend their research and inform the local community about their progress and the advancements generated within the department. These kinds of exchanges are critical to the education and maturation of our trainees (our greatest resource) but also educate the faculty and local scientific community about the other resources and techniques available at and under development in Chemical & Biomedical Engineering.

This year, we are proud to have a keynote address provided by Dr. David A. Tirrell, the Ross McCollum-William H. Corcoran Professor of Chemistry and Chemical Engineering at the California Institute of Technology as well as the director of the Beckman Institute. Dr. Tirrell's contributions to macromolecular chemistry have been recognized by his election to the National Academy of Sciences, the National Academy of Engineering, the Institute of Medicine, and the American Academy of Arts and Sciences. He has been awarded the Arthur C. Cope Scholar, Carl Marvel, Harrison Howe, S. C. Lind and Madison Marshall Awards of the American Chemical Society, as well as the ACS Award in Polymer Chemistry. He holds the Chancellor's Medal of the University of Massachusetts, the G. N. Lewis Medal of the University of California Berkeley, and the degree of Doctor honoris causa from the Technical University of Eindhoven.

We look forward to a fascinating discussion with Dr. Tirrell and fruitful day of conversations and networking among students, fellows and faculty.

With Regards,

Samuel C. Grant

Keynote Address

Dr. David A. Tirrell, Ph.D.

Ross McCollum-William H. Corcoran Professor
Chemistry and Chemical Engineering
California Institute of Technology

Education
Ph.D., Polymer Science, University of Massachusetts
B.S., Chemistry, Massachusetts Institute of Technology

Reinterpreting the Genetic Code: How to Do It & Why You Might Want to

Abstract:

The genetic code, elucidated in the 1960s through the work of Nirenberg, Ochoa, Khorana and their coworkers, provides a set of molecular instructions for translating nucleic acids into proteins. Through the efforts of our laboratory and others over the last fifteen years, the code has been “reinterpreted” in various ways to enable the participation of an expanded set of amino acids in cellular protein synthesis. These developments have provided a basis for powerful new approaches to protein design and proteome-wide analysis of cellular processes.

Short Biography:

David A. Tirrell is the Ross McCollum-William H. Corcoran Professor of Chemistry and Chemical Engineering at the California Institute of Technology. After earning the B.S. in Chemistry at MIT in 1974, Tirrell enrolled in the Department of Polymer Science and Engineering at the University of Massachusetts, where he was awarded the Ph.D. in 1978 for work done under the supervision of Dr. Otto Vogl.

After a brief stay with Dr. Takeo Saegusa at Kyoto University, Tirrell accepted an assistant professorship in the Department of Chemistry at Carnegie-Mellon University in the fall of 1978. Tirrell returned to Amherst in 1984 and served as Director of the Materials Research Laboratory at the University of Massachusetts before moving to Caltech in 1998. He served as chairman of the Division of Chemistry and Chemical Engineering at Caltech from 1999 until 2009, and assumed the directorship of the Beckman Institute in 2012.

Tirrell’s research interests lie in macromolecular chemistry and in the use of non-canonical amino acids to engineer and probe protein behavior. His contributions to these fields have been recognized by his election to the American Academy of Arts and Sciences and to all three branches (Sciences, Engineering and Medicine) of the U.S. National Academies, one of only 20 fellows so honored.

List of Graduate Student Oral Presentations

Presentation Time	
9:40-10:05	**Hamed Janani,** *Development of Crystalline Structure in Blends of iPP and Isotactic Propylene- 1-Alkene Random Copolymers*
10:05-10:30	**Yijun Liu,** *Metabolic Re programming during Non-adherent Culture Selects Primitive Human Mesenchymal Stem Cells*
10:30-10:55	**Onyekachi Oparaji,** *Sorption and Diffusion of Water in Polystyrene-Poly(ethylene oxide) Block Copolymers*
10:55-11:20	**A.A.O. Ould Ismail,** *DTI-based Connectivity in Isolated Neural Ganglia: A Default Structural Graph in a Small World Framework*

List of Graduate Student Poster Presentations

Poster #

1. **Xuejian Chen**, *Effect Of Crystallinity On Melt Memory Of Random Ethylene 1-Alkene Copolymers*
2. **Xiaoshi Zhang**, *FTIR Spectroscopic Analysis Of The Crystallization Of Precision Halogen-Substituted Polyethylenes*
3. **Laura Santonja-Blasco**, *Polymorphism And Crystallization Kinetics Of Polyethylenes With Precise Chlorine Substitution*
4. **Hailing Liu**, *Development Of New Lignin-Based Polymers Via Photoredox Catalyzed Thiol-Ene Click Reaction*
5. **Rimantas Slegeris**, *Progress Towards Oxime Cross-Linkable, Dopamine Containing, Adhesive Polymeric Brushes via ROMP for Biomedical Applications*
6. **Nastaren Abad**, *Metabolic Assessments of Migraine using* ^{1}*H Spectroscopy at Ultra-High Field*
7. **David Hike**, *DTI-based Analysis Of APP/PS2 Mouse Brains As A Model Of Progressive Alzheimer's Disease*
8. **Ghoncheh Amouzandeh**, *Electrical Conductivity Mapping At 21.1T*
9. **Junfei Xia**, *Catalase-Laden Microdevices For Cell-Mediated Enzyme Delivery*
10. **Guang Yang**, *Gold Nanoparticle Monolayers With Tunable Optical And Electrical Properties*
11. **Sifei Zhou**, *Lithium-Graphite Block Copolymer Battery*
12. **Brandon McGill**, *An Electrochemical Approach To Measuring Oxidative Stability Of Solid Polymer Electrolytes For Lithium Batteries*
13. **Oyidia Elendu**, *Glycerol Oxidation On Supported Electroless CuNiMoP*
14. **Venroy Watson**, *Low Cost High Power Lithium Iron Phosphate* ($LiFePO_4$) *Battery*
15. **James Akrasi**, *Study Of Glycerol For Use As Renewable Biomass Fuel In Iron-Ion/Glycerol Redox Flow Battery*
16. **Yuanwei Yan**, *Derivation Of Cortical Spheroids From Human Induced Pluripotent Stem Cells In A Suspension Bioreactor*
17. **Liqing Song**, *Nanotopography Promotes Neuronal Differentiation of Human Induced Pluripotent Stem Cells*
18. **Julie Bejoy**, *WNY-YAP Interactions During Neural Tissue Patterning Of Human Induced Pluripotent Stem Cells*
19. **Robert J. Wandell**, *Nanosecond Pulsed Plasma Discharge Over A Flowing Water Film: Plasma Characterization, Hydrodynamic Analysis, And Hydrogen Peroxide Generation*
20. **Huihui Wang**, *Study Of The Nanosecond Pulsed Plasma Discharge Using Computer Simulation*
21. **Qiao Zhang**, *Analysis Of A Gas-Liquid Film Plasma Reactor For Degradation Of Methylene Blue*
22. **Yu Shu**, *Thermal Imprint Introduced Crystallization Of A Solution Processed Subphthalocyanine Thin Film*
23. **Chenkun Zhou**, *Phosphorescent Molecular Butterflies With Controlled Potential Energy Surfaces And Their Application As Luminescent Viscosity Sensor*
24. **Brent M. Bijonowski**, *Increased Angiogenic Potential From Transformed 3D Cultured Adipose Stem Cells*
25. **Ang-Chen Tsai**, *Producing Engineered Self-assembled Aggregates of Mesenchymal Stem Cells In WAVE bioreactor*^{TM} *for Cell Therapy*

26. **Xuegang Yuan**, *Aggregate-derived Human Mesenchymal Stem Cells Improve Cell Motility And Functional Recovery In A Rat MCAO Stroke Model*

27. **Oluwagbenga Iyiola**, *Layered Material To Capture Sunlight for Water-Splitting Catalysis*

28. **Srimanta Pakhira**, *First Principle DFT Study Of Activation Energy For* H_2 *Evolution In* MoS_2, WS_2 *And* $W_xMo_{1-X}S_2$

29. **Faheem Muhammed**, *The Development of Well-Disperse-Polymer Composites Exhibiting Tuned Mechanical and Electrical Properties*

30. **Golda C. Louis**, *Structure, Dynamics, Rheology And Thermal Properties Of Polymer Grafted Nanoparticles Diluted With Free Polymer Chains*

31. **Lianyang Dong**, *Crystal Growth Of Elpasolite* $K_2PbCu(NO_2)_6$ *In Gel*

Graduate Student Oral Presentation 1

Development of Crystalline Structure in Blends of iPP and Isotactic Propylene-1-Alkene Random Copolymers

Hamed Janani, Rufina G. Alamo [1]

[1]FAMU-FSU College of Engineering, Department of Chemical and Biomedical Engineering

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Abstract

The study of melt miscibility and structure-property relations of different types of polyolefins provide an important pathway to material design for different applications. In this work we study melt and crystalline properties of blends of iPP and isotactic propylene-1-hexene (PH) random copolymers with 11 and 21 mol% 1-hexene, (PH11, PH21). The study of melt miscibility using thermodynamic estimations coupled with experimental data from DSC, DMA, and AFM techniques indicate that blends of iPP/PH11 and PH11/PH21 are miscible in the melt while blends iPP/PH21 are immiscible. Depending on crystallization conditions, iPP and PH11 may crystallize in monoclinic (α) or mesophase, and PH21 crystallizes in the trigonal phase exclusively. The effect of isotactic sequence length distribution (ISLD) on polymorphism and crystallization kinetics was quantitatively studied in miscible PH11/PH21 blends. An enhanced rate of formation of trigonal phase with increasing PH11 was attributed to the increasing composition of 1-hexene in the melt during evolution of the monoclinic phase in the first stage of isothermal crystallization of the blends [1].

The addition of only 25 wt.% of an elastomer such as PH11 or PH21 to iPP decreases slightly the level of crystallinity, from ~70% in neat iPP to ~60% in the blend; however, blending leads to a dramatic effect on the tensile properties of iPP, i.e. makes the brittle iPP to be ductile at room temperature. In-situ WAXS-tensile experiments indicate that the significant ductility and strain hardening behavior observed in iPP/PH copolymers are accompanied by a significant polymorphic transformation of monoclinic to mesophase under deformation of miscible iPP/PH11 blends, and by additional trigonal orientation in blends of iPP/PH21.

References

1. Janani H, Alamo RG. Enhanced rate of formation of trigonal phase in blends of homogenous isotactic propylene-1-hexene copolymers. Polymer 2015;64:163-175.

Graduate Student Oral Presentation 2

Metabolic Reprograming during Non-adherent Culture Selects Primitive Human Mesenchymal Stem Cells

Yijun Liu[1], Ang-Chen Tsai[1], Teng Ma[1]

[1]Chemical and Biomedical, Florida State University

Abstract

Removal of human mesenchymal stem cells (hMSCs) from *in vivo* niche for *in vitro* bioprocessing in an artificial culture environment induces senescence that reduce hMSC potency and impede translation of hMSC to clinical application[1]. Recent studies on the non-adherent culture of anchorage-dependent cells suggest the strong correlation between self-assembled aggregates and cellular 'stemmess', and indeed aggregates of hMSCs exhibit enhanced pluripotent stem cells genes expression and primitive stem cells functions. Although it has been suggested that in vitro aggregation mimics mesenchymal condensation and recapitulates the cellular events of in vivo microenvironment, the molecular link between aggregation and hMSCs stemness is still undefined. In the present study, we test the hypotheses that hMSC aggregation on non-adherent substratum initiates mitochondrial remodeling and metabolism reconfiguration, resulting in a metabolic profile that resembles primitive stem cells. Our results show that aggregation of hMSCs influences mitochondrial dynamics and results in a reduction in mitochondrial function. Adaptive changes as a result of mitochondrial dysfunction includes increased glycolytic and anaplerotic flux, which fuel the self-digestion program named autophagy. Importantly, we identify that alteration of mitochondrial respiration chain is responsible for the enhanced expression of stem cell genes because treatment of respiration chain targeted small molecules partially recapitulates stemness enhancement event in planar culture. Our finding demonstrates that mitochondria play significant role in stem cell pluripotency by its retrograde signaling with stem cell gene expression program (Fig.1).

Reference

2. Ma T, Tsai A, Liu Y. 2015. Biomanufacturing of Human Mesenchymal Stem Cells in Cell Therapy: Influence of Microenvironment on Scalable Expansion in Bioreactors. Biochemical Engineering Journal. 108: 44.

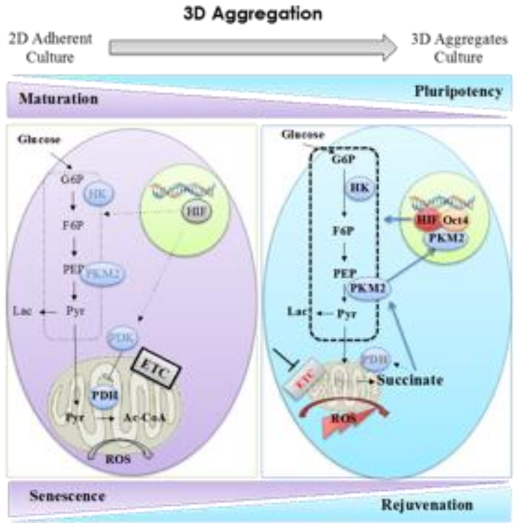


Fig.1 Mitochondrial retrograde signaling in hMSCs aggregates.

Graduate Student Oral Presentation 3

Sorption and Diffusion of Water in Polystyrene-Poly(ethylene oxide) Block Copolymers

Onyekachi Oparaji and Daniel Hallinan Jr.

Department of Chemical and Biomedical Engineering, FAMU-FSU, COE

Poly(styrene-*block*-ethylene oxide) (PS–*b*–PEO) is a model hierarchically nanostructured polymer for a water sorption and diffusion study. Amphiphilic block copolymers such as PS–*b*–PEO are of interest for a wide-range of applications, but accurate measurement of water transport is needed to determine the appropriate application(s) for this material. PEO crystallinity and block copolymer structure were measured as a function of water activity. They were found to change appreciably at high water activity. Gravimetric water sorption and transport were also measured over a range of water vapor activity (0.05 – 0.95). Due to the structural changes in the polymer, water sorption was found to increase exponentially at high water activity. Water diffusion was measured using Fourier transform infrared – attenuated total reflectance (FTIR-ATR) spectroscopy. The water content and diffusion in PS–*b*–PEO was compared to a poly(ethylene oxide) (PEO) homopolymer. The interplay of water content and PEO crystallinity resulted in interesting transport results. The crystalline content of the PEO and the presence of glassy PS lamellae will be used to explain the transport results

Graduate Student Oral Presentation 4

DTI-based Connectivity in Isolated Neural Ganglia: A Default Structural Graph in A Small World Framework

A.A.O. Ould Ismail [1,2], Ghoncheh Amouzandeh [1,3], Samuel C. Grant [1,2]

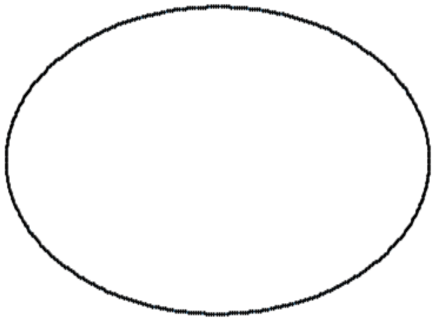
[1]The National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, USA

[2]Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL, USA

[3] Department of Physics, Florida State University, Tallahassee, FL, USA

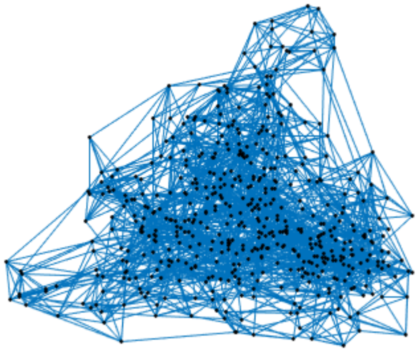
Diffusion Tensor Imaging (DTI) provides a unique contrast based on the restricted directionality of water movement in an anisotropic environment. As such, DTI-based tractography can be used to characterize and quantify the structural connectivity within neural tissue. Here, DTI-based connectivity within isolated abdominal ganglia (ABG) of *aplysia Californica* is analyzed using network theory. In addition to quantifying the regional physical proprieties of the fractional anisotropy (FA) and apparent diffusion coefficient (ADC), DTI tractography was used to probe inner-connections of local communities, yielding unweighted, undirected graphs that represent community structures. Local and global efficiency, characteristic path lengths, and clustering analysis are performed on both experimental and simulated data. The relevant intensity and velocity by which these specific nodes communicate is probed through weighted clustering coefficient measurements for the descriptive weighted matrices. Both small-worldness and novel small world metrics (ω) were used as tools to verify the small-world properties for the experimental results. The aim of this manuscript is to categorize and quantify the properties exhibited by structural networks in a model neural tissue to derive unique mean field information that quantitatively describe macroscopic connectivity. For ABG, findings demonstrate a default structural network (b) with preferential specific small-world properties when compared to simulated lattice (a) and random networks (c) that are equivalent in order and degree.

(a) Lattice Network



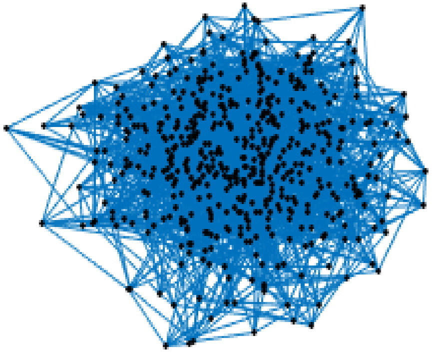
$\omega = -0.93$

(b) Simulation of ABG Data



$\omega = 0.45$

(c) Random Network



$\omega = 0.99$

References

1. Grant S, Buckley D, Gibbs S, Webb A & Blackband S (2001) MR microscopy of multicomponent diffusion in single neurons. *Magnetic Resonance in Medicine* 46(6): 1107-1112.
2. Telesford QK, Joyce KE, Hayasaka S, Burdette JH & Laurienti PJ (2011) The ubiquity of small-world networks. *Brain Connectivity* 1(5): 367-375.
3. Ould Ismail AAO, Amouzandeh G & Grant SC (2016) DTI-based Connectivity in Isolated Neural Ganglia.PNAS. Submitted.

Poster Presentation 1

EFFECT OF CRYSTALLINITY ON MELT MEMORY OF RANDOM ETHYLENE 1-ALKENE COPOLYMERS

Xuejian Chen[1], Al Mamun[1], Rufina G. Alamo[1]

[1]Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, 2525 Pottsdamer St,
Tallahassee, Florida 32310-6046

Abstract

A strong memory effect of crystallization has been observed in melts of random ethylene copolymers even above the equilibrium melting temperature. Melt memory is correlated with self-seeds that increase the crystallization rate of ethylene copolymers. The seeds are associated with molten ethylene sequences from the initial crystals that remain in close proximity and are unable to diffuse quickly to the randomized melt state. Fast diffusion is restricted by topological chain constraints (loops, knots, and other entanglements) that build in the intercrystalline region during crystallization. The effect of topological constraints on melt memory, or on number of remaining seeds in the melt, was analyzed studying copolymers with different levels of crystallinity. There is a threshold level of crystallinity below which copolymers do not display strong melt memory. A faster development of the initial crystallinity by dynamic cooling traps more efficiently knots and loops around the crystallites leading to a lower crystallinity threshold compared to slower isothermal crystallization. Higher thresholds of crystallinity level is required for observing melt memory in copolymers with lower molecular weight due to faster sequence diffusion in the melt. Besides, the threshold crystallinity level is found to display Arrhenius type temperature dependence with the activation energy being independent of molecular weight, further highlighting its correlation with diffusion. Finally, with increasing branch content, the threshold crystallinity level decreases as a result of creating more entanglements by selecting a larger number of sequences with shorter length to make the same amount of crystal.

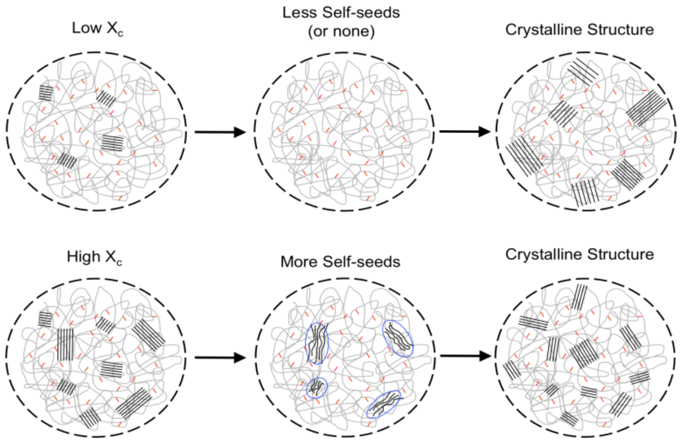


Fig 1. Evolution of melt and subsequent crystalline structure from different initial crystallinity.

Reference:

1. X. Chen, A. Mamun, R. G. Alamo, *Macromol. Chem. Phys.* **2015**, 216, 1220.

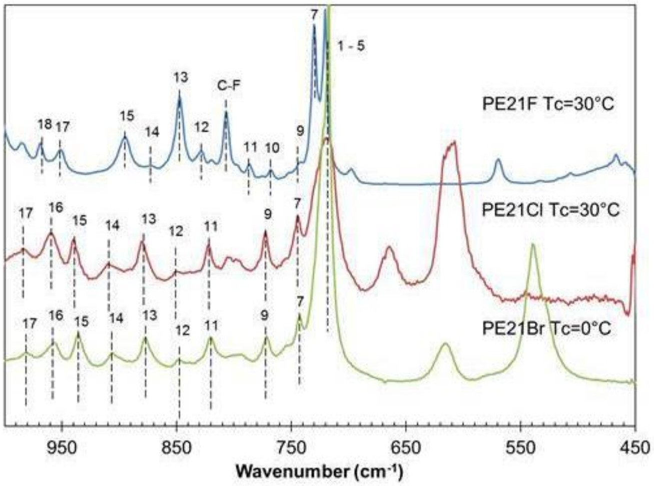
Poster Presentation 2

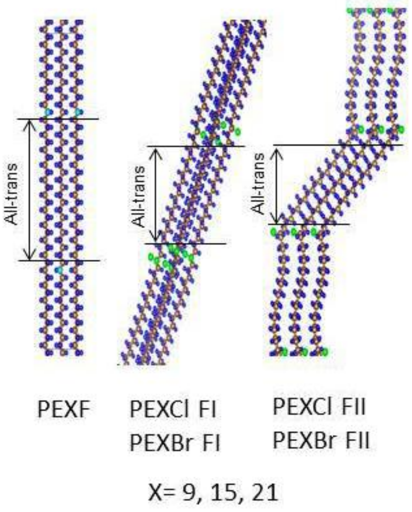
FTIR Spectroscopic Analysis of the Crystallization of Precision Halogen-substituted Polyethylenes

Xiaoshi Zhang[1], Laura Santonja[1], Kenneth Wagener[2], Emine Boz[2], Rufina Alamo[1]

[1] Chemical and Biomedical Engineering, Florida State University, Tallahassee, Florida, United States;
[2] Chemistry, University of Florida, Gainesville, Florida, United States

Abstract
Polyethylenes with halogen substitution at a precise distance along the methylene backbone are unique models to study the effect of nano-structured chain-defects on folding and crystallization of polymers. Prior work has shown that a crystal structure transition occurs in precision chlorine and bromine substituted polyethylenes within one degree of undercooling. In the present work we have carried out a complete analysis of the FTIR progression rocking and stretching modes of series of isothermally crystallized samples using the simple oscillator model. The effect of halogen size to the periodic oscillation changes the effective number of oscillators between F and Cl or Br substituted systems. Quantitative analysis of the C-halogen stretching region and this analysis support the polymorphic transition and documents a C-C all-trans conformation of the methylenes between halogens. Upon crystallization from the melt below the transition temperature the chains pack in an all-trans planar conformation (Form I) with layered crystalline chlorines that present some longitudinal disorder. The crystals formed at higher temperatures pack in a non-planar herringbone-like structure (Form II) with a TGGT….TG'G'T backbone conformation around the substitution, while conserving the all-trans packing of the methylene sequence, as shown in the graphical abstract.





Poster Presentation 3

Polymorphism and Crystallization Kinetics of Polyethylenes with Precise Chlorine Substitution

L. Santonja-Blasco[1], X. Zhang[1], K.B. Wagener[2], E. Boz[2], R. G. Alamo[1]

[1]Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee FL, USA, 32310
[2]Department of Chemistry, University of Florida, Gainesville FL, USA, 32611-7200

Abstract

Polyethylenes with halogen substitution at a precise distance along the methylene backbone are unique models to study the effect of nano-structured chain-defects on folding and crystallization of polymers. Prior work showed that the halogen is accommodated in the crystal; crystallization and melting are proportionally to the halogen's size [1, 2]. Furthermore, packing of the chlorine units in the crystallites of a polyethylene with chlorine substitution on every 15th backbone carbon was found to undergo a transition within one degree of undercooling [3]. At high undercoolings the chains pack in all-trans planar conformation (Form I) with layered crystalline chlorines with some longitudinal disorder as demonstrated by FTIR and WAXD. The crystals formed at higher temperatures pack in a non-planar herringbone-like structure with a TGGT….TG'G'T backbone conformation around the substitution, while conserving the trans packing of the methylene sequence (Form II). We have extended the structural analysis to precision samples with chlorine on the 9th, 19th and 21st carbons, and compared the polymorphic behavior to analogs with random substitution. The unique polymorphic transition is found in all members of the precision series. Polymorphism is absent when the chlorine is randomly distributed. The overall crystallization kinetics measured by DSC of Forms I and II showed that with decreasing crystallization temperature, the rate of Form I follows the usual negative temperature coefficient, while the overall rate of Form II shows a maximum at crystallization temperatures where both forms coexist. The polymorphic transition and equilibrium melting temperatures of both forms scale linearly with chlorine content.

References

3. Alamo RG, Jeon K, Smith RL, Boz E, Wagener KB, Bockstaller MR. 2008. Crystallization of polyethylenes containing chlorines: precise vs random placement *Macromolecules* 41:7141.
4. Boz E, Nemeth AJ, Wagener KB, Jeon K, Smith R, Nazirov F, Bockstaller MR, Alamo RG. 2008. Well-defined precision ethylene/vinyl fluoride polymers: synthesis and crystalline properties. *Macromolecules* 41:1647.
5. Kaner P, Ruiz-Orta C, Boz E, Wagener KB, Tasaki M, Tashiro K, Alamo RG. 2014. Kinetic control of chlorine packing in crystals of a precisely substituted polyethylene. toward advanced polyolefin materials. *Macromolecules* 47: 236.

Poster Presentation 4

Development of new lignin-based polymers via photoredox catalyzed thiol-ene click reaction

Hailing Liu, Hoyong Chung

Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University,
Tallahassee, Florida, USA

Abstract

Most commercial lignins are produced by treatment of sulfur containing chemical reagents. Therefore, it is reasonable to suppose that the produced lignin has thiol groups in the structure. However, there has been no systematic/scientific characterization of thiol group contents in a commercial lignin. In this report, we present strong evidence of the existence of thiol in lignin using a fluorometer as shown in Figure 1. The emission spectra in Figure 1 demonstrate typical emission spectra of thiol-conjugated N-1-pyrenylmaleimide. Pristine lignin without conjugation reveal no emission as shown in blue dotted line (Blue dotted line is overlaid on red dotted line with no intensity.). This spectrometry result clearly indicates that commercial lignin contains thiol group, and the thiol can be used for diverse chemical modification.[1]

Based upon the thiol group discovery, we performed covalent bond forming integration methods (thiol-ene click reaction) between lignin and a petroleum-based polymer, poly(acrylic acid) in the presence of photoredox catalysts, $Ru(bpy)_3Cl_2$.[2] The photo activated thiol-ene reaction needs a very small amount of the photoredox catalyst—as small as 0.25 mol%—and those reactions can occur in a wide range of solvents, even in water. Also, the photoredox catalysts can be activated by a visible sunlight wavelength range, blue light irradiation (λ_{max} = 460 nm) as shown in Figure 2.

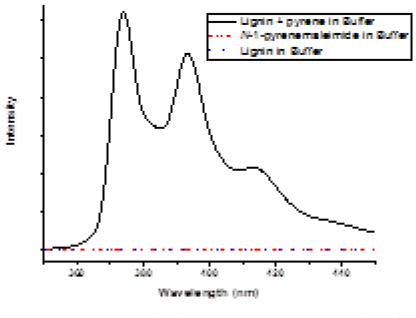


Figure 1. Emission spectra of lignin (solid line) before and (dashed/dotted line) after reaction with *N*-1-pyrenemaleimide.

Figure 2. A scene of photoredox catalyzed lignin modification under sunlight.

References

1. Wu, C.-W.; Yarbrough, L. R.; Wu, F. Y. H. *Biochemistry* **1976,** 15, (13), 2863-2868.
2. Xu, J.; Boyer, C. *Macromolecules* **2015,** 48, (3), 520-529.

Poster Presentation 5

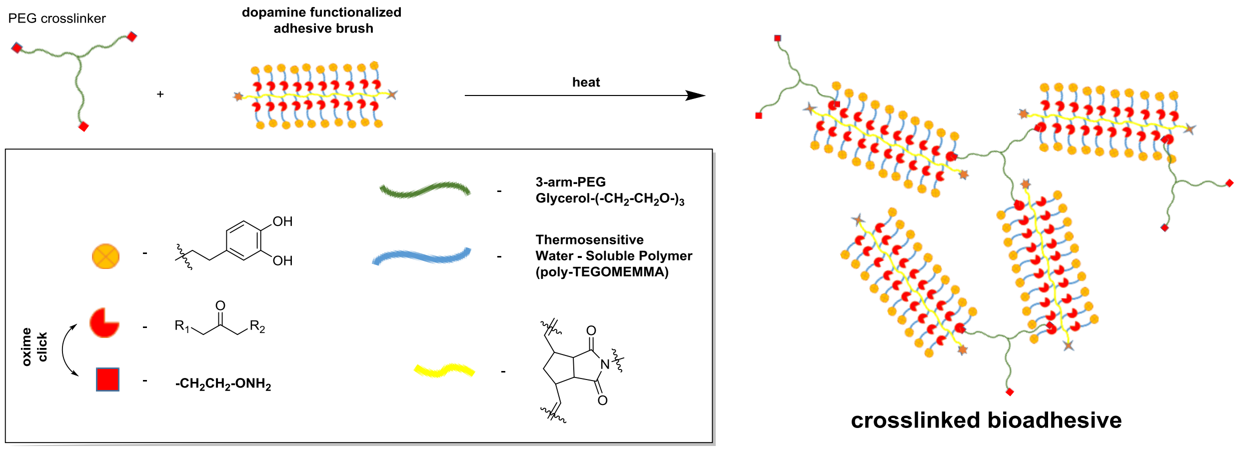
Progress Towards Oxime Cross-Linkable, Dopamine Containing, Adhesive Polymeric Brushes via ROMP for Biomedical Applications

Rimantas Slegeris, Hoyong Chung[1]

[1]Florida State University, Department of Chemical & Biochemical Engineering, 2525 Pottsdamer St, Tallahassee, FL 32310

Abstract

Bioadhesives are an important class of polymers which are widely used as medical patches, surgical sealants or drug delivery systems. Different application areas of adhesives require materials with various degrees of crosslinking and adhesion strength, therefore the tunability of these factors has to be considered when designing an adhesive. Ideally, a bioadhesive would be easy to deliver (i.e. liquid form) when not in use; and the adhesive should be immobile when it administered to the body. Such a viscosity change can be addressed by having 2 components – adhesive and crosslinker. Typically, those two components have to be stored separately and have to be mixed before use. To address this issue we designed a complex polymer that has a crosslinker and integrated thermoresponsive polymer to control the phase behavior.



The bioadhesive presented in this study is based on multi-functional two polymer components. The main component is a brush polymer with key functionalities: 1) a ketone to provide an anchor for crosslinking using oxime click chemistry; 2) dopamine at pendant terminals to provide enhanced wet adhesion; 3) a thermoresponsive polymer side chain to control the phase-transition. The second component is the 3-arm-PEG oxyamine to crosslink via ketone within the main brush. Synthetic routes, characterization of the polymer, crosslinking effect and the effects of catechol to the adhesion property will be presented in this study.

Poster Presentation 6

Metabolic Assessments of Migraine using ^{1}H Spectroscopy at Ultra-High Field

Nastaren Abad and Samuel C. Grant[1, 2]; Jens T. Rosenberg[2]; Michael G. Harrington[3]
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High-field MR spectroscopy provides the opportunity to interrogate metabolites dynamically and *in vivo* during progression of neurological disorders, such as migraine, that have rapid onset but potentially longer impacts. It thus follows that identification of specific metabolic changes, potentially influenced by excitatory and inhibitory neurotransmitters, may improve understanding of onset and progression of migraine and open up new avenues for therapy development. This study, therefore, evaluates biochemical and metabolic imbalances that may result in a collection of dysfunctional pathways that are distinct in migraineurs. To enhance sensitivity while reducing individual experiment acquisitions times, we utilized relaxation-enhanced MR spectroscopy (RE-MRS) to analyze quantitative changes in brain metabolites during migraine progression. All scans were performed using the 21.1-T, 900-MHz ultra-wide bore using a double tuned ^{23}Na-^{1}H birdcage coil at the National High Magnetic Field Laboratory, Tallahassee, FL. After baseline scans, 17 anesthetized Sprague-Dawley male rats were administered *in situ* an intra-peritoneal injection of either nitroglycerine (NTG, N=11) to induce migraine or saline (N=6) to serve as a control. A highly selective RE-MRS [1] sequence was utilized to target upfield metabolites from a (4-mm)^3 voxel, without water suppression. Total of 14 scans (10 min/scan) were acquired from pre-injection to 2.5-h post injection.

Statistical significance is reported in Taurine, total Creatine and Lactate. Elevated levels of Glycine are also reported. Alterations in total Creatine and Lactate levels with migraine are indicative of anaerobic metabolism while Taurine increases show osmoregulatory action and dysfunction.

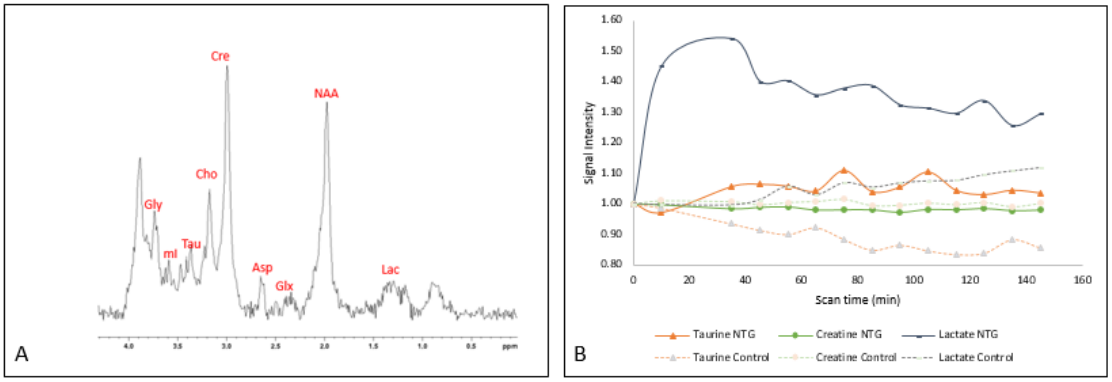

Figure 1. A) Representative 1D RE-MRS from *in vivo* rodent model (10-min acq). B) Signal intensities for induced migraine vs control levels of Taurine, total Creatine and Lactate, normalized to the pre-injection values.

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Poster Presentation 7

DTI-based Analysis of APP/PS2 Mouse Brains as a Model of Progressive Alzheimer's Disease

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Alzheimer's disease is the most common form of dementia. It is characterized by memory loss, changes in behavior, and difficulty thinking[1]. Currently, over 5 million people in the US have Alzheimer's disease, and there is no known cure[1]. In 2012, it was estimated that $200 billion was spent in direct costs for Alzheimer's disease while in 2011, unpaid care by family members and friends exceeded $210 billion[2].

Magnetic Resonance Imaging potentially plays an important role in the diagnosis of Alzheimer's disease (AD) with its high resolution and non-invasive nature. Here, we focus on angular resolution to map water diffusion using DTI. We used 18 diffusion directions and 4 unweighted directions. We used an 11.75-T, 500-MHz MRI scanner located at the FAMU-FSU College of Engineering and collected data using APP/PS1 mouse models with 2 variables (age and AD). Our in-plane resolution was 100 x 100 microns with a matrix size of 256 x 256. Repetition timae of 2 sec and an echo time of 30 ms utilizing acquisition parameters of Δ=21ms and δ=3ms with 15 averages provided us with a high signal-to-noise ratios and an approximate acquisition time of 47 hours per sample. The study used all female brains fixed with 4% paraformaldehyde.

The six main areas we focused on were the dentate gyrus, fornix columns, corpus callosum, putamen, frontal cortex, and temporal cortex. Our reports indicate a significant decrease in FA in the temporal cortex. As we could not detect plaques utilizing gradient echo scans, we relied on detecting significant stages at early ages using high resolution and high angular DTI approach. We have conducted a preliminary graph theoretical analysis in which we use a binary approach to study the structural connectivity in the models. Additionally, we detected significant increase in the characteristic path length between the young controls and young AD model mice.

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Poster Presentation 8

Electrical Conductivity Mapping at 21.1T

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Magnetic Resonance electrical properties tomography (MR-EPT) is a recently introduced method to map electrical properties of body tissues using a standard MRI machine [1], [2]. Mapping tissue electrical properties like conductivity and permittivity can be used as an additional diagnostic parameter, e.g. in tumor diagnosis and stroke therapy evaluation. According to *ex vivo* studies, breast tumors exhibit a significantly altered electrical conductivity [3], [4]. The electrical conductivity of the tissue is also needed to correctly estimate the distribution of local specific absorption rate (SAR) of the transmitted radio frequency (RF) wave in body tissues for RF safety purposes.

Earlier studies have shown the feasibility of phase-based MR-EPT that uses only the phase data of the MR image to infer the RF transmit field (B_1^+) map conductivity at low fields [5]. Although phase-based conductivity mapping will benefit from higher field strength, which is related to increased signal-to-noise ratio (SNR), the validity of the underlying assumptions will be affected by the higher dielectric properties of the object [6]. As a result, the required Laplacian of the phase data for conductivity reconstruction is not straight forward at ultra-high fields (> 3T).

This work shows the possibility of reconstructing conductivity distributions from phase images of the RF transmit field in ultra-high field (21.1T). To be able to use phase-based MR-EPT, a new reconstruction algorithm, based on fitting local parabolic functions to the local phase changes is developed. The average conductivity values for tubes with different salt concentrations are evaluated. This phantom study can be used as a step toward *in vivo* conductivity mapping at ultra-high fields.

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Poster Presentation 9

Catalase-Laden Microdevices for Cell-Mediated Enzyme Delivery

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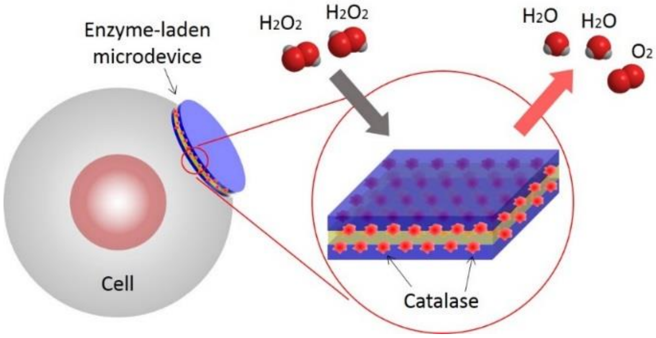
Abstract

Enzymes have been used as drugs to treat a wide variety of human diseases and traumas. However, therapeutic utility of free enzymes is generally impeded by short circulation time, lack of targeting ability, immunogenicity, and inability to cross certain biological barriers. Various strategies have been developed to overcome these limitations. Among them is cell-mediated drug delivery, which is featured by integrating drugs with live cells and taking advantage of the unique capabilities of the cells to achieve controlled drug delivery. We developed simple and inexpensive methods based on soft lithography and layer-by-layer (LbL) assembly for fabricating disk-shaped microparticles termed microdevices and generating the cell-microdevice complexes. [1, 2] We herein applied these methods to the fabrication of enzyme-laden microdevices and corresponding cell-microdevices complexes for the first time. We used catalase as a model enzyme in this study. It is a water soluble protein with an isoelectric point of 5.8. It is thus negatively charged at pH 7. Poly(diallyldimethyl ammonium chloride) (PDAC) was chosen here as a polycation to form a bilayer with catalase. Catalase in the microdevices was catalytically active and active catalase was slowly released from the microdevices. The catalase-laden microdevices were attached to the external surface of live suspension and adhesion cells respectively to form cell-microdevice complexes. This technique is applicable to other therapeutic enzymes and therapeutic cells, and thus promises to find clinical applications for treating various human diseases and traumas.



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Poster Presentation 10

Gold Nanoparticle Monolayers with Tunable Optical and Electrical Properties

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ABSTRACT

Centimeter-scale gold nanoparticle (Au NP) monolayer films have been fabricated using a water/organic solvent self-assembly strategy. A recently-developed approach, “drain to deposit”, is demonstrated most effective to transfer the Au NP films from the water/organic solvent interface to various solid substrates while maintaining their integrity. The interparticle spacing was tuned from 1.4 nm to 3.1 nm using different length alkylamine ligands. The ordering of the films increased with increasing ligand length. The surface plasmon resonance and the in-plane electrical conductivity of the Au NP films both exhibit an exponential dependence on the interparticle spacing. These findings show great potential in scaling up the manufacturing of high-performance optical and electronic devices based on two-dimensional metallic nanoparticle superlattices.

Poster Presentation 11

Lithium-Graphite Block Copolymer Battery

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Abstract

Lithium provides the highest cell voltage and specific energy of any lithium battery negative electrode. However, it is incompatible with flammable classic liquid electrolyte which causes some safety problems. This leads to intensive work on high performance rechargeable lithium polymer batteries. Most work has used a lithium metal anode and an oxide cathode with poly(ethylene oxide) (PEO) based polymer electrolyte. Despite much effort having been devoted in the last several years, many issues remain unsolved for lithium polymer batteries. Improvement in cycle life, operating temperature and energy density are required.

Graphite has good lifetime and rate capability in liquid electrolyte-based batteries and supercapacitors. It is commonly recognized that graphite and PEO-based polymer electrolyte have poor compatibility due to high interfacial resistance and exfoliation phenomenon. However, it was reported recently that high molecular weight PEO electrolyte provides lower interfacial resistance in graphite composite electrodes. Based on this, it will be interesting to use a high molecular weight block copolymer (polystyrene-b-PEO) to replace PEO as polymer electrolyte to see if the same trend applies. In addition, the block copolymer has better mechanical properties that might stabilize the graphite structure and decrease exfoliation, which benefits the cycling performance.

Poster Presentation 12

An Electrochemical Approach to Measuring Oxidative Stability of Solid Polymer Electrolytes for Lithium Batteries

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Abstract

Polymer electrolytes are an interesting class of electrolytes that hold promise for safer, flexible, high-energy batteries. Their unique properties stem from being a solid-state ion conductor. This benefit is a challenge for electrochemical investigations, since most electrochemical experiments have been designed for liquid electrolyte. In order to quantitatively evaluate polymer electrolyte stability, an electrochemical approach especially designed for solid electrolytes is presented. This approach uses a set of linear sweep voltammograms from different, large overpotentials to open circuit voltage, which the authors term variable reverse linear sweep voltammetry. By allowing the cell to relax between each polarization, the first data points of each voltammogram are not mass transfer limited. This yields current versus overpotential data that can be analyzed with a kinetic model, such as the Butler-Volmer model. Oxidative stability of poly(ethylene oxide) and polystyrene-*b*-poly(ethylene oxide) with lithium bis-trifluoromethanesulfonimide salt has been investigated on several electrode materials. The block copolymer electrolyte has been found to be quite stable to electrochemical oxidation, up to 5 V at 40 °C. The degradation reaction has been found to be slow with large thermal activation energy.

Poster Presentation 13

Glycerol Oxidation on Supported Electroless CuNiMoP

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Abstract

Glycerol is a bye-product of the transesterification of vegetable oils and fats, a process through which biodiesel is made. Government's encouragement of greener and renewable energy alternatives have led to an increase in the production of biofuel and thus, glycerol. This abundance, and consequently, low price is one reason that glycerol is among twelve chemicals that US[1] government is interested in as building blocks for families of compounds. Another reason is that it is a relatively simple molecule, and many different functional groups can be attached to its three carbon backbone; understanding these reactions can lead to a better understanding when/if more complex molecules are being investigated.

One way to use this glycerol derived from biodiesel production is as fuel in a direct glycerol fuel cell operated under alkaline conditions. This electrochemical avenue has considerable economic appeal, both as a source of power and a source of fine chemicals. The sequential oxidation reactions which take place in the fuel cell – in which there are many reaction intermediates - can yield various fine chemicals.

In this work, the oxidation of glycerol under alkaline conditions are investigated using electrochemical techniques. The methods of preparation of the CuNiMoP electro-catalysts on these different supports, and the effects of these on the kinetics of glycerol oxidation, will be shown.

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Poster Presentation 14

Low Cost High Power Lithium Iron Phosphate ($LiFePO_4$) Battery

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$LiFePO_4$ has gained popularity in recent times and increasingly being used as one of the cathode materials [1] in lithium ion batteries, due to its environmentally benign nature and most importantly because of its thermal stability [2] at higher discharge rates. The $LiFePO_4$ battery fabrication process currently suffers from high costs and complexity due to the use of wet slurry method that requires extra safety measures as a result of the use of potentially harmful chemicals. A cost effective and safer battery fabrication method is a necessity for its mass production for applications in transportation & portables.

We are presently working on developing a method of electrode fabrication and dry-room assembly for the battery, which is safer and reduces its production costs. The potential cost savings will be achieved through the elimination of material, lower capital equipment expenses, and energy and manufacturing costs. This elimination of energy expenditures and elimination of carcinogenic solvents from the battery production process will also reduce its environmental impact. During battery's charge and discharge characterization we have observed better performance by our electrode material when compared to commercially available electrode materials. The results obtained by our improved fabrication method will be compared with the classical traditional fabrication method.

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Poster Presentation 15

Study of glycerol for use as renewable biomass fuel in iron-ion/glycerol redox flow battery

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Abstract

The need to reduce the global emissions associated with use of fossil based fuels is a key driver in the development of clean and renewable alternatives. Hydrogen gas which is used in the conventional iron ion-hydrogen redox flow battery; and the main fuel of consideration for the hydrogen economy is not readily available and is reformed from other fossil sources. For this reason, it has become imperative to find renewable alternatives to its use.

The electrochemical oxidation of glycerol has been studied and known to be a source of several chemicals of premium industrial value and has also been utilized in the concept of direct glycerol fuel cells to produce electrical energy additionally. In the current study however, this concept is extended to cover both electrochemical oxidation and reduction of glycerol as a substitute for the hydrogen ion in redox flow battery with a Fe^{2+}/Fe^{3+} couple as cathode. A conceptual Iron-ion/Glycerol redox flow battery is proposed and its feasibility during discharge evaluated for the cases of partial, and complete oxidation of glycerol to mesoxalic acid, tartronic acid, glyceraldehyde and carbon dioxide, respectively. This is based on a predictive thermodynamic study, through the establishment of the minimum electric potential (E^0) required to drive the half-reactions under galvanic and electrochemical conditions. The reduction of glycerol to propane-1, 2-diol in acidic media during charging is also considered.

A mathematical schematic is developed to analytically estimate the Gibbs free energy change of the products and reaction intermediates of aqueous organic species and hence calculation of electric potentials of the associated half-reactions at room temperature using an extension of the Benson's group additivity method. The theoretical data obtained were compared to the data obtained through cyclic voltammetry technique in acidic media to validate the mathematical model used. The scope and feasibility of a working iron-ion/glycerol flow battery will be discussed across a range of operating temperature and different concentrations (activity) of aqueous glycerol solution.

Poster Presentation 16

Derivation of Cortical Spheroids from Human Induced Pluripotent Stem Cells in a Suspension Bioreactor

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Abstract:

Human induced pluripotent stem cells (hiPSCs) emerge as a promising source to construct human brain-like tissue in vitro for disease modeling and drug screening. While a suspension bioreactor can be used to generate large size of brain organoids from hPSCs through enhanced diffusion, the influence of a dynamic bioreactor culture environment on the brain tissue development from hiPSCs has not been well understood. The objective of this study is to assess the effect of a suspension bioreactor on the cortical spheroid (i.e., forebrain-like organoids) formation from hiPSCs. The bioreactor was seeded either with single undifferentiated hiPSK3 cells or pre-formed embryoid bodies that were induced toward neural lineages. Aggregate size distribution, neural marker expression (e.g., Nestin, PAX6, HOXB4, and beta-tubulin III), and cortical tissue patterning markers (e.g., TBR1, BRN2, SATB2, and vGlut1) were evaluated in comparison to static culture control. Bioreactor culture was found to promote the expression of TBR1, a deep cortical layer VI marker, and accelerated the expression of SATB2, a superficial cortical layer II-IV marker that appears later according to "inside-out" development pattern during cortical tissue generation. Prolonged culture after 71 days showed layer-specific cortical structure in the spheroids. Differential gene expression of matrix metalloproteinase (MMP)-2 and -3 was also observed for bioreactor culture and static culture. The altered expression of cortical markers by a suspension bioreactor indicates the importance of culture environment on the cortical tissue development from hiPSCs.

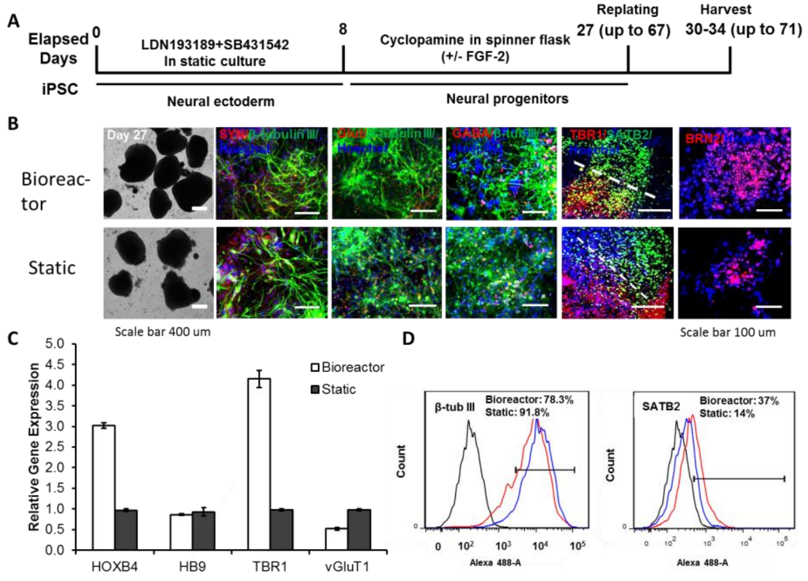

Figure 1. A: The derivation schematic paradigm of cortical spheroid in the bioreactor. B: Representative phase contract images of spheroid at day 27 (scale bar 400 µm) and fluorescent images of cortical markers (Glut, GABA, TBR1, SATB2, and BRN2) and synaptic activity-related markers (SYN) (scale bar: 100 µm). C: The gene expression of neural markers by RT-PCR (day 32). D: Quantitative analysis of neurons (β-tubulin III) and cortical superficial layer marker (SATB2) (day 30).

Poster Presentation 17

Nanotopography Promotes Neuronal Differentiation of Human Induced Pluripotent Stem Cells

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Abstract

Inefficient neural differentiation of human pluripotent stem cells (hPSCs), including human induced pluripotent stem cells (hiPSCs), motivates the investigations of the influence of biophysical microenvironment, in particular nanotopography, on hPSC fate decisions recently. However, the contributions of the shape and dimensions of nanotopography to neural lineage commitment of hPSCs have not been well understood. The objective of this study is to delineate the effects of the shape, feature size and height of nanotopography on neuronal differentiation of hiPSCs. Equally spaced, anisotropic nanogratings (500 and 1000 nm in linewidth) and hexagonally arranged isotropic nanopillars (500 nm in diameter, 450 nm in edge-to-edge distance), each having a height of 150 or 560 nm, were seeded with human iPSK3 cells and induced for neuronal differentiation. The gratings of 560 nm height reduced cell proliferation, promoted cytoplasmic localization of Yes-associated protein (YAP), and enhanced neuronal differentiation (up to 60% βIII-tubulin+ cells) compared with the flat control. Differential gene expression of TBR1, a cortical glutamatergic neuron marker, was observed for different substrates, while HOXB4, a marker for hindbrain/spinal cord, was less affected by different nanotopographies. The derived neuronal cells express MAP-2, Tau, Islet-1 (motor neuron progenitors), GABA and vGAT (GABAergic neurons), and glutamate (glutamatergic neurons), indicating the existence of multiple neuronal subtypes. The nanotopography also affected the gene expression of matrix metalloproteinases. This study provides the insights of how different nanotopography parameters (shape, feature size and height) modulate hPSC neural lineage commitment.

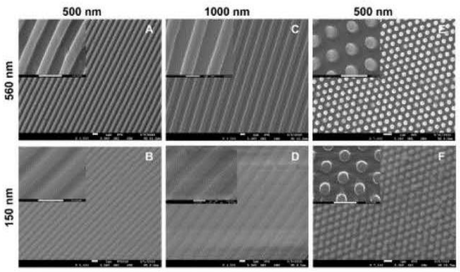

Fig.1. Scanning electron SEM micrographs of nanotopographgies.

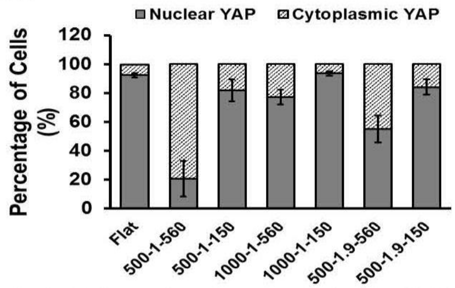

Fig 2. Effect of nanotopography on YAP nucleocytoplasmic localization.

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Poster Presentation 18

WNT-YAP INTERACTIONS DURING NEURAL TISSUE PATTERNING OF HUMAN INDUCED PLURIPOTENT STEM CELLS

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ABSTRACT

Human induced pluripotent stem cells (hiPSCs) have special ability to self-assemble into mini-organ like structures (e.g., organoids, mini-brains). In this process, Wnt signaling impacts regional patterning and positional identity of hiPSC-derived neural progenitors. One important function of Wnt signaling is to regulate Yes-associated protein (YAP) expression (nuclear or cytoplasmic), the pivotal regulator of cell proliferation and differentiation during organ growth and tissue generation. However, the crosstalk between Wnt and YAP expression during neural patterning of hiPSCs has not been well investigated. The objective of this study is to reveal the capability of Wnt signaling in the regulation of YAP expression to modulate 3-D neural spheroid formation from hiPSCs. Human iPSK3 cells were induced toward neural lineages through embryoid body formation. Wnt signaling was activated using CHIR99021, which was found to induce nuclear localization of YAP. CHIR99021 treatment upregulated the expression of HOXB4, the marker for hindbrain/spinal cord, while in the absence of Wnt activation, the cells maintained rostral forebrain neural identity (expression of TBR1) (by RT-PCR analysis and immunocytochemistry). Modulation of YAP expression with cytochalasin D (Cyto D) also influenced neural cell identity, indicating bi-directional interactions of Wnt signaling and YAP expression. The perturbation of neural patterning was also evaluated by incorporating the neural spheroids with microparticles. This study should advance our understanding on the biological processes regulated by Wnt signaling and YAP activity during neural tissue patterning. The results have the significance in neurological disease modeling, drug screening, and neural tissue regeneration.

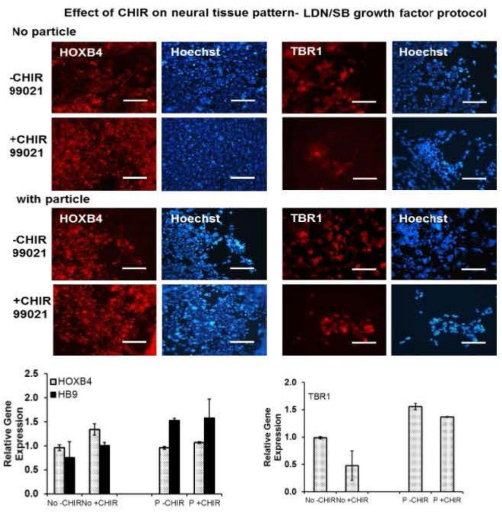

Figure 1. Effect of CHIR on neural patterning.

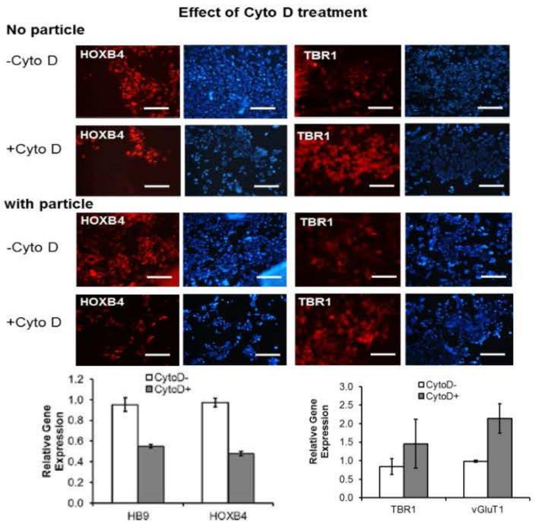

Figure 2. Effect of Cyto D on neural patterning.

Poster Presentation 19

Nanosecond Pulsed Plasma Discharge Over a Flowing Water Film: Plasma Characterization, Hydrodynamic Analysis, and Hydrogen Peroxide Generation

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Abstract

Low energy pulsed plasma discharges in a flowing carrier gas with liquid water have been shown capable of producing hydrogen peroxide at reasonably high energy yields. The leading hypothesis for the success of this production method is that the liquid water serves as both a source of water vapor from which hydroxyl radicals can be produced during the on cycle of the pulsed discharge, as well as a sink for hydrogen peroxide generated from these radicals during the off cycle of the pulse. Many reactor designs have been explored with various gas-liquid contact schemes in order to enhance the overall efficiency of this process. A continuously flowing, liquid film, reactor has been developed in our laboratory which we believe has a number of significant benefits over the previously explored configurations. In previous studies with this flowing film reactor, an automobile ignition coil was used to generate the pulsed plasma discharge. While this ignition coil provided high energy yields for hydrogen peroxide production, analysis of the system was difficult due to the large pulse widths required by the coil. Multiple arcing events were found to occur within these microsecond pulses which were extremely difficult to control or accurately measure and quantify. For this reason a nanosecond power supply is utilized in this study which is capable independently varying pulse width, input voltage, and pulse repetition. With this controllable power supply the plasma properties such as gas temperature and electron density can be measured for various input pulse characteristics to study the resulting effect on hydrogen peroxide generation on a per arc basis. High speed imaging of the hydrodynamic properties of the flowing liquid film is also performed in order to calculate gas and liquid residence times and provide physical insight on the gas-liquid interface across which the plasma propagates.

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Poster Presentation 20

Study of the Nanosecond Pulsed Plasma Discharge Using Computer Simulation

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Abstract

The plasma technology is a promising technology that can be used for water treatment [1]. This technology is much faster and more compact than the traditional bio-degradation method for water treatment. However, the energy efficiency of this technology is very low, which impedes its industrial application. Therefore, several studies have been conducted to study the mechanism of plasma discharge and to improve the energy efficiency of plasma technology.

The basic principle of using plasma technology to treat polluted water is degrading the organic pollutant by using the oxidative radicals generated in the plasma. Basically, a plasma discharge is initiated in the plasma reactor when the wasted water flows through the plasma reactor, and the chemical reactions happen when the species formed during the plasma discharge, such as hydroxyl radical and hydrogen peroxide, contact with the water.

Studying the mechanism of plasma discharge in the plasma reactor is helpful for improving the energy efficiency of plasma technology, and several studies have been successfully conducted to study the mechanism of plasma discharge of their experiment set-up by using computer simulation [2][3]. Thus, in this study, computer modeling was used to study the chemical reactions, energy transfer, and mass transfer inside the plasma reactor. A one-dimensional computer model that only considers the concentration and temperature gradient along the x-axis of the plasma channel was built based on the parameters measured from the experiment. The concentration and temperature variation with time and position were obtained through the model. According to the modeling results, the simulated temperature coincides well with the temperature measured in experiment. However, further modification is still needed to improve the accuracy of the computer model.

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Poster Presentation 21

Analysis of a Gas-Liquid Film Plasma Reactor for Degradation of Methylene Blue

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Abstract

Advanced oxidation process (AOP) for dye removal by non-thermal pulsed discharge plasma in water is of growing interest. It is based on the generation of highly oxidized species such as hydrogen peroxide, ozone, and especially hydroxyl radical. Degradation of methylene blue in a hybrid gas-liquid pulsed electrical discharge plasma reactor was analyzed with flowing carrier gas of argon mixed with oxygen. The effect of inlet oxygen concentration, liquid conductivity, dye type and liquid flowrate on dye decoloration and degradation and hydrogen peroxide production were determined. Effluent ozone concentration in the gas phase was determined by standard indigo method.

In liquid phase analysis, the results show that adding oxygen does not significantly change dye decoloration and TOC removal, yet it does affect the hydrogen peroxide production rate. The highest dye decoloration was achieved in pure argon. Our hypothesis was that OH radical from the plasma goes into the liquid to decolor dye and react with dye and dye breakdown products. While ozone is formed in the gas, mass transfer of ozone into the liquid is limited by perhaps the short contact time for the ozone with the liquid and also by the lower solubility of ozone in the liquid and perhaps the lower rate of ozone reactions with the dye, which hasn't been proved yet.

Higher initial liquid conductivity resulted in lower ozone concentration and hydrogen peroxide production rate. In this case, more input power was dissipated by bulk liquid instead of plasma channel. Ozone and hydrogen peroxide production was decreased as a reason of less discharge power.

Poster Presentation 22

Thermal Imprint Introduced Crystallization of A Solution Processed Subphthalocyanine Thin Film

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Abstract

The use of organic molecules for thin film electronic devices has been extensively explored over the last decades, with great success realized in organic light emitting diodes (OLEDs), organic photovoltaic cells (OPVs), organic field-effect transistors (OFETs), and so on.[1] Boron subphthlocyanines (SubPcs) are an emerging class of molecular semiconductors with unique optical/electronic properties.[2] Herein, we report a facile post-treatment approach to introducing molecular ordering (crystallization) for solution processed organic semiconductor thin films by thermal imprint (or thermal annealing under pressure). We show that large area phase change from amorphous to crystalline morphology for solution processed 2-allylphenoxy-(subphthalocyaninato)boron(III) (SubPc-A) thin films can be realized by thermal imprint with a patterned or flat mold.[3,4] Using optical microscope, X-ray diffraction, atomic force microscope (AFM), and scanning electron microscope (SEM), we have characterized the thin film morphological properties upon different post-treatments. The morphological change induced by thermal imprint results in enhanced electronic properties, in particular the hole carrier mobility that increases from ~ 1×10^{-7} $cm^2V^{-1}s^{-1}$ to ~ 2×10^{-3} $cm^2V^{-1}s^{-1}$. This change of morphological and electronic properties could not be achieved by either thermal annealing or room temperature imprint alone.

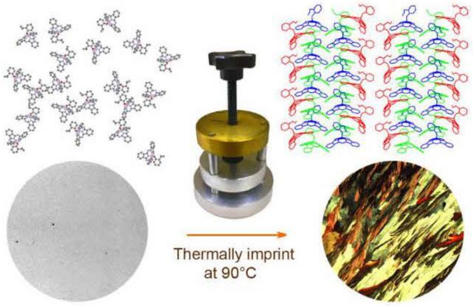

Fig 1. Process of changing from amorphous to crystal structure of SubPc-A

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Poster Presentation 23

Phosphorescent Molecular Butterflies with Controlled Potential Energy Surfaces and Their Application as Luminescent Viscosity Sensor

Chenkun Zhou[1], Lin Yuan[1], Zhao Yuan[1], Divya Bahadur[1], Subramanian Ramakrishnan[1], Albert Dearden[4], Chen Huang[4], Biwu Ma[123]*

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Abstract

Molecular excited states generated by the interactions between molecules and light/charge carriers are the foundation for solar energy conversion, photocatalysis, molecular machines, and electroluminescent devices. The form of energy output from an excited state relies on the potential energy surfaces (PESs) and the energy decay pathways. Precise control of the PESs would allow for effective utilization of the excited state energy for desired applications, and the emission color and quantum efficiency for luminescent molecules. Researchers have been succeeded in developing luminescent molecules by controlling the lowest excited state PES with one energy minimum. However, little has been done for precise manipulation of the PESs of luminescent molecular systems with multiple excited state energy minima.

Recently, we have demonstrated molecular engineering to achieve precise control of the PESs of a series of molecular butterflies, **BFPtPZ** and its derivatives.[1] The relative position of two excited state energy minima T_{1a} and T_{1b} can be well manipulated by synthetic control of the molecular steric bulkiness of the cyclometallating and pyrazolate bridging ligands.

Herein, I will present our continuous efforts in manipulating the PESs of this class of molecular butterflies, by introducing a new controlling factor, the electronic structure of the cyclometallating ligand. By synthetic control of the steric bulkiness of the pyrazolate bridging ligand and the electronic structure of the cyclometallating ligand, we have been able to manipulate T_{1a} and T_{1b} simultaneously. Dual emissions can be extended from blue/red to new energy territories. We have also demonstrated the use of these molecular butterflies as luminescent viscosity sensor.

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Poster Presentation 24

Increased Angiogenic Potential From Transformed 3D Cultured Adipose Stem Cells

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It has been suggested that mesenchymal stem cells can be used as a treatment for ischemic tissue since they can differentiate in the niche environment into vasculature. Building from this we set out to better understand this transformation from stem cell to endothelial (EC) and stromal cell found in the vessel development. To understand this phenomenon adipose derived stem cells (ASC) were cultured either in EGM (Lonza Inc.) or α-MEM for 9 days either in 2D or 3D (aggregate) culture. 2D culture took place on standard tissue culture plastic, while 3D culture took place on ultra-low attachment plates. After 9 days, cells and aggregates, were moved to Matrigel coated plates and were cultured for another 7 days. Radius of vessel outgrowth was measured each day by light microscopy images analyzed using ImageJ. Endothelial and stromal cell differentiation was measured by immunohistochemistry with CD31 and Hoechst staining. 3D cultured cells outperformed their 2D counterparts. This can be attributed to a greater priming in the aggregate culture for differentiation. The vessel length and CD31 staining was greater in the 3D EGM culture of ASC, suggesting a greater differentiation of ASC to EC due to factors found in the culture media such as VEGF. Stromal cells were observed surrounding CD31 positive cells in all conditions.

Poster Presentation 25

Producing Engineered Self-assembled Aggregates of Mesenchymal Stem Cells in WAVE Bioreactor™ for Cell Therapy

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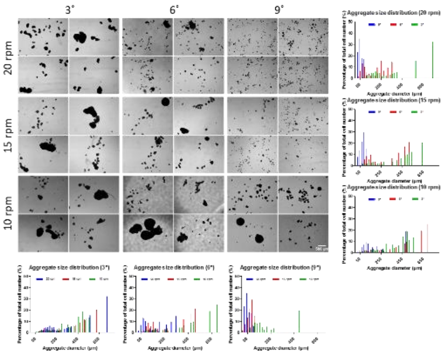
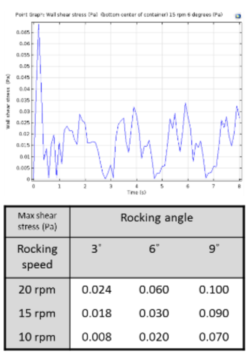
Abstract

Human mesenchymal stem cells (hMSCs) are primary candidates in cell therapy and regenerative medicine and have been tested in clinical trials for a wide range of diseases. Recent studies showed that hMSC have natural ability to self-assemble into 3D aggregates that enhance their therapeutic functions with higher multi-lineage potential expression, increased migration ability, up-regulated secretion of anti-inflammatory and angiogenic factors, and improved resistance to ischemic conditions after transplantation. Presently, various laboratory methods have been developed for hMSC aggregates production, including manual hanging drops, centrifugation with microfabricated surface, low attachment surface treatment, thermal lifting, and microfluidic technologies. However, these method have limited scalability and/or poor control in aggregate size. Our current study presented the accessibility to culture hMSCs as size-controlled aggregates scalably in WAVE bioreactor™ by adjusting the rocking angle and speed. Our experimental results combined with simulation modeling suggested that the aggregate size is reverse to the rocking angle and speed which are proportional to the calculated shear stress. According to the Smoluchowski coagulation equation, suspended hMSCs formed aggregates because of the balance of valid cell-cell collision and aggregate disaggregation, and hydrodynamics, in particular the shear stress, plays an important role. We also shifted the aggregate size distribution in varying the collision frequency by altering seeding density and in modifying the cell-cell binding kinetics by adding small molecules, such as EDTA and Collagenase. Therapeutic functional tests also supported that hMSCs derived from engineered aggregates in WAVE bioreactor™ have higher therapeutic gene and protein expression compared with those from monolayer culture.

A.

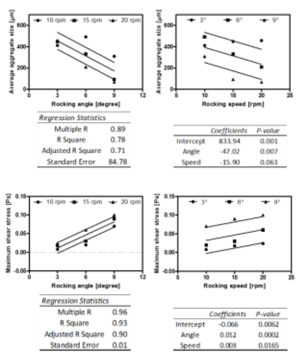


B.



Max shear stress (Pa)	Rocking angle		
Rocking speed	3°	6°	9°
20 rpm	0.024	0.060	0.100
15 rpm	0.018	0.030	0.090
10 rpm	0.008	0.020	0.070

C.



Regression Statistics	
Multiple R	0.89
R Square	0.78
Adjusted R Square	0.71
Standard Error	84.78

	Coefficients	P-value
Intercept	833.94	0.001
Angle	-47.02	0.007
Speed	-15.90	0.061

Regression Statistics	
Multiple R	0.96
R Square	0.93
Adjusted R Square	0.90
Standard Error	0.01

	Coefficients	P-value
Intercept	-0.066	0.0062
Angle	0.012	0.0002
Speed	0.003	0.0165

Fig. A. Experimental result. Fig. B. Simulation modeling. Fig. C. Two-variable regression

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Poster Presentation 26

Aggregate-derived Human Mesenchymal Stem Cells Improves Cell Motility and Functional Recovery in a Rat MCAO Stroke Model

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Abstract

In the US, stroke is the primary cause of severe disability and the third leading cause of death. To date, the only FDA-approved drug for stroke is tissue plasminogen activator (tPA), a thrombolytic agent that has limited benefits to patients. Human mesenchymal stem cells (hMSCs) have emerged as an important cell source in stroke treatment and clinical trials have yielded promising results.

Originally isolated from bone marrow as the progenitor cells responsible for the repair and regeneration of mesenchymal tissues, hMSC-based cell therapy is promising for stroke due to their trophic effects that promote endogenous tissue repair by forming a molecular milieu. However, hMSCs have low cell survival and secretory function post-transplantation in stroke lesion, which significantly reduced their therapeutic potency. Studies have demonstrated that in vitro hMSC preconditioning by exposure to sub-lethal hypoxia and 3D aggregation can significantly improve hMSC migration and therapeutic efficacy in stroke animal.[1]

For hMSCs transplantation, cellular damages induced by the microenvironment at the stroke lesion site, such as ischemia, high level of reactive oxygen species (ROS) and inflammation challenge the survival and function of transplanted hMSCs. 3D aggregation of hMSCs increases cell adhesion, retention, migration, and persistence post-transplantation. Better maintenance of their pluripotency and lineage-specific differentiation by aggregation may also allow the transplanted hMSCs to engraft in the host damaged tissue, improving the therapeutic outcome of transplantation.[2] PI3K/Akt pathway is activated via 3D aggregation of hMSCs and improves the resistance of ischemia and ROS, leads to better recovery of stroke lesion and neurological function in rodent MCAO model.

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Poster Presentation 27

Layered Material to Capture Sunlight for Water-Splitting Catalysis

Kevin Lutch[1], Oluwagbenga Iyiola[1], Srimanta Pakhira[1] and Jose L. Mendoza-Cortes[1,2*]

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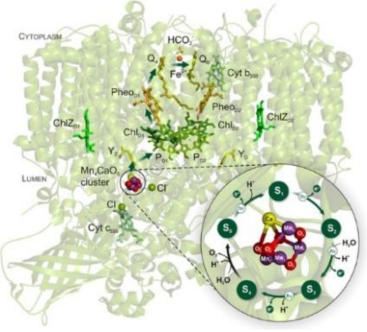
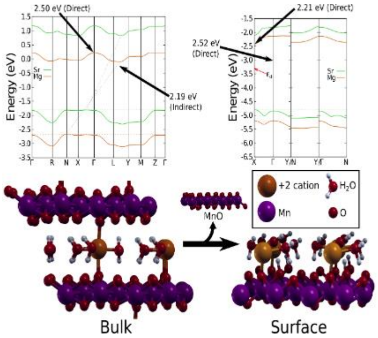
Abstract: Water remains potentially the most abundant energy reserve on the earth as it contains a huge amount of H_2 which can be used directly as a fuel or utilized by reducing CO_2 into liquid fuels such as methanol [1]. However, the oxidation of water to yield its constituents require additional energy. Over the years, nature has successfully engineered plants to split water using the stored energy from the sun in a process known as photosynthesis. At the heart of this process is the oxygen evolution center (OEC) composed of Mn_4O_5Ca in a cubane-like structure [2]. Taking inspiration from these green plants, we are developing new materials that can reduce the additional energy (overpotential) required to oxidize water. A major step is to develop materials with the right band gap which can capture sunlight and at the same time act as a catalyst for the water splitting reaction. We show that the intercalation of cations (Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, B^{3+}, Al^{3+}, Ga^{3+}, Sc^{3+} and Y^{3+}) in a layered manganese oxide commonly known as birnessite can effectively tune the indirect band gap from 2.63 to $\approx 2.2eV$ and the direct band gap from 3.09 to $\approx 2.50eV$. Interestingly, the single layer manganese oxide surfaces differ drastically from their bulk counterparts as there is a band transition from indirect in the bulk to direct in band gap in the surface [3]. The result from DFT calculations for Sr, Ca, B and Al structures are particularly appealing due to the alignment of the structures band. Thus these materials provide the much desired properties to resemble green plants in the photosynthesis process. Preliminary results and analysis from our DFT calculations show that this material can split water at reduced overpotential. We are currently studying the catalytic properties of these materials.





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Poster Presentation 28

First Principle DFT Study of Activation Energy for H_2 Evolution in MoS_2, WS_2 and $W_xMo_{1-x}S_2$

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Abstract

The design and development of inexpensive highly efficient catalysts for hydrogen production, underpins several emerging clean-energy technologies and chemical engineering. Recently molybdenum disulfide (MoS_2) [1] and tungsten disulfide (WS_2) [2] clusters and bulk materials have been attracted a great attention as an emerging material for electrochemical hydrogen evolution reaction (HER) catalyst. Here we have computationally designed a new type of cluster, $W_xMo_{1-x}S_2$ substituting either Mo atoms by W atoms in MoS_2 cluster or W atoms by Mo atoms in WS_2 cluster using *ab initio* DFT method (here M06L), and we have found the catalytic activity of the cluster has been increased due to the substitution/doping. In the computation, we have used 6-31+G** basis sets for H, S, and O atoms, as well as LANL2DZ basis sets with effective core potentials (ECP) for Mo and W atoms. Our computational study reveals that the $W_{0.4}M_{0.6}S_2$ cluster has the lowest activation energy barrier for H_2 evolution, about 4.40 kcal mol^{-1} in gas phase, and 10.31 kcal mol^{-1} in solvent phase (water) with four explicit water molecules as shown in Figure 1 and Figure 2. Hydronium protonation of the hydride on the Mo site is about 21.67 kcal/mol in MoS_2, and it is about 20.17 kcal mol^{-1} on the W site in WS_2. We predict the Volmer-Tafel mechanism in which hydrogen atoms bound to tungsten and sulfur sites recombine to form H_2 has a barrier of 10.31 kcal mol^{-1} in the $W_{0.4}M_{0.6}S_2$ cluster. The $W_{0.4}M_{0.6}S_2$ cluster shows the highest catalytic activity among the three clusters.

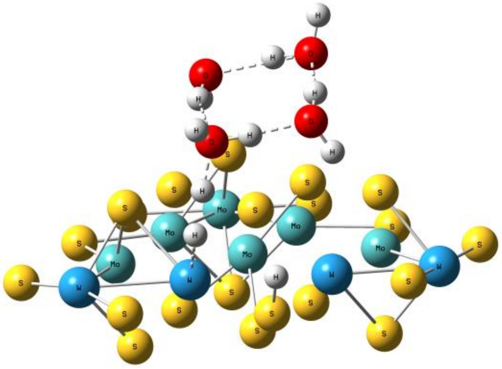

Figure 1.

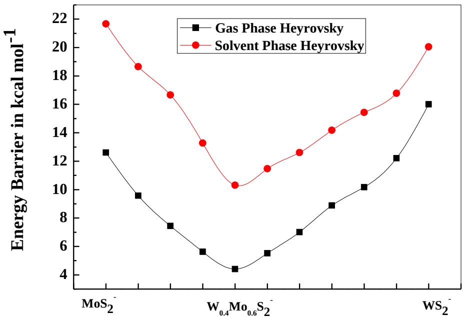

Figure 2.

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Poster Presentation 29

The Development of Well-Disperse-Polymer Composites Exhibiting Tuned Mechanical and Electrical Properties

Faheem Muhammed[1]. Parth Vakil[2], Julian Montoya[1], Golda C. Louis[1], Subramanian Ramakrishnan[1], Tarik Dickens[3]

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[3]FAMU/FSU College of Engineering – Industrial Engineering

The development of ligand-stabilized nanoparticles is critical to advancements in additive manufacturing, high density magnetic memory, electromagnetic interference shielding, and medicinal purposes. This study focused on incorporating mono-dispersed magnetite (Fe_3O_4) nanoparticles in various polymers (polystyrene, polyimide, and lower molecular weight varieties) with the goal of increasing the physical, magnetic, and dielectric properties of the matrix. Magnetite was chosen primarily for its ease of synthesis, extensive literature presence, negligible hysteresis, and low magnetic moment. In conjunction with fatty-acid-surface-modification, the magnetite exhibited stability in both solution and the dried powder form. This property made it possible for even distributions in polymer media when thin films and composite filaments were manufactured. The magnetic properties of this composite system allowed for soft magnetic behavior that is influenced solely by an external field. This phenomenon generated electrical property variations in the material due to differences in the applied magnetic field. These variations gave insight into the dielectric behavior (conductance, resistance, and polarizability) of the material. Characterization methodologies included the use of thermo-gravimetric analysis, scanning electron microscopy, dielectric spectrometry, and dynamic mechanical analysis. Through these characterizations, composites can be tuned for desired mechanical and electrical properties.

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Poster Presentation 30

Structure, Dynamics, Rheology and Thermal Properties of Polymer Grafted Nanoparticles Diluted with Free Polymer Chains

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Studies on the mechanical reinforcement of polymer composites with polymer grafted nanoparticles achieves much scientific attention. Addition of polymer grafted nanoparticles can improve the dispersion and mechanical properties of composites by tailoring the parameters like graft density (σ), graft chain length (N_g), graft (M_g) and matrix (M_m) molecular weight. Unlike the previous reported studies, the present research work is dedicated to explore the influence of dilution after the addition of free polymer chains on the structure, dynamics and thermal properties of polymer grafted nanoparticles. In the present scenario, polystyrene (PS) grafted silica nanoparticles were synthesized through surface initiated atom transfer radical polymerization (SI-ATRP). For the studies, we varied the graft densities (0.33 chains/nm^2 and 0.06 chains/nm^2), graft molecular weight (28 kDa and 55 kDa) of graft PS chains and free PS (10 kDa and 100 kDa) for a volume fraction, $\phi = 0.05$. The graft particle-free polymer blend was characterized by rheology, structure and morphology through grazing incidence small angle x-ray scattering (GISAXS) and transmission electron microscopy (TEM), dynamics through x-ray photon correlation spectroscopy (XPCS) and thermal properties through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Poster Presentation 31

Crystal Growth of Elpasolite $K_2PbCu(NO_2)_6$ in Gel

Lianyang Dong

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Florida State University, Tallahassee, Florida, USA

The non-conducting hexanitro copper compound $K_2PbCu(NO_2)_6$ has attracted special interest because it exhibits successive phase transitions at 281 K and 273 K due to the cooperative Jahn-Teller effect[1-5]. In $K_2PbCu(NO_2)_6$, The spins from *Cu* are weakly interacting due to the long contact distance (7.55Å) between *Cu* atoms, so low temperature ordering effects are expected.

Single crystals of $K_2PbCu(NO_2)_6$ can be grown by slow cooling a saturated aqueous solution containing proper amounts of potassium nitrite, lead acetate and copper nitrate[1,4]. However, the rapid nucleation rate and convective transport makes it difficult to obtain large high quality single crystals. To reduce the convective transport and high nucleation rate, we grew elpasolite $K_2PbCu(NO_2)_6$ single crystals in gel.

A number of variables were investigated in the growth of $K_2PbM(NO_2)_6$ crystals in gels: the pH before gel formation, the concentration of reactants, the choice of where to disperse the reactants, and the type of tube to use during the experiments . All growth experiments were carried out at room temperature. The U-tube setup with a neutral gel tended to produce large single crystals up to 2 mm cubes for $K_2PbCu(NO_2)_6$ (figure. 1.).

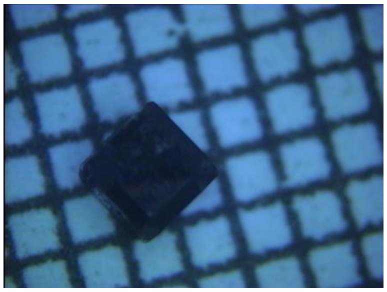

Figure. 1. $K_2PbCu(NO_2)_6$ single crystal

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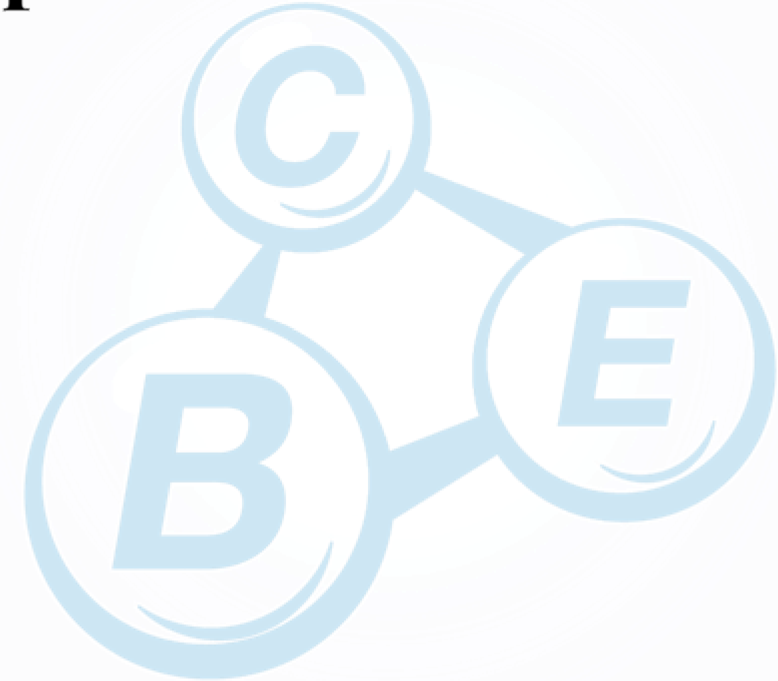

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