

Research Day 2017

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

Aero-Propulsion, Mechatronics and Energy (AME) Building
Room 106 and lobby
2003 Levy Avenue, Tallahassee, FL 32310

8:30am – 2:00pm, Friday March 24, 2017

Table of Contents

	Page
Table of Contents & Schedule of Events.....	1
Keynote Presentation Abstract.....	2
Biography of Dr. Richard A. Register.....	3
List of Student Oral Presentations.....	4
Abstracts of Student Oral Presentations.....	5
List of Student Poster Presentations.....	9
Abstracts of Student Poster Presentations.....	10

Schedule of Events

8:30am	Student Oral Presentations
10:00am	Keynote Presentation
11:15am	Student Poster Session 1
12:00pm	Lunch
1:15pm	Student Poster Session 2
2:00pm	Adjournment

Keynote Presentation

Pervaporation Membranes from Addition Polynorbornenes for Effective Butanol Recovery

Dr. Richard A. Register

Department of Chemical and Biological Engineering
Princeton University, Princeton, NJ

While ethanol is the best-known fermentation product, there is growing interest (both research and commercial) in the production of higher alcohols, such *n*-butanol and isobutanol. Currently, such molecules are already utilized as chemical building blocks; in the longer term, they could potentially serve as biofuels more compatible than ethanol with our fuel distribution and utilization infrastructure, and with higher energy density. While there have been significant advances in the biosynthesis of such heavier alcohols, an unmet need is for their economical recovery from aqueous solutions (fermentation broth). Since the broth must be maintained dilute in these higher alcohols (which are toxic to the producing organisms), isolation of the alcohol by distillation is energetically prohibitive, and a lower-energy separation process is sought; membrane pervaporation (liquid feed, vapor permeate) is the leading candidate. Currently, the state-of-the-art membranes for such separations are based on crosslinked polydimethylsiloxane (PDMS), a soft rubbery polymer which must be applied as a relatively thick layer to maintain mechanical integrity.

Polymers derived by vinyl addition polymerization of substituted norbornenes—where the backbone of every repeat unit contains a bicyclic norbornene unit—have extremely high glass transition temperatures (T_g), and thus retain stiffness even in very thin, uncrosslinked films. Since transmembrane flux is inversely proportional to thickness, such high- T_g polymers are potentially attractive for separation membranes (high flux), if they can also exhibit high component selectivity—which is potentially tunable through the chemical identity of sidechains attached to the norbornene monomer. However, until recently, initiators which could enchain norbornenes via vinyl addition polymerization showed very poor tolerance of even relatively unreactive sidegroups. In collaboration with Promerus LLC, we have shown that certain Pd-trialkylphosphine complexes can initiate the living homopolymerization of a rather broad range of substituted norbornenes, bearing alkyl, aryl, perfluoroaryl, and even hexafluoroisopropanol (HFA) substituents. Moreover, these initiators can also yield random, gradient, and block copolymers of narrow molecular weight distribution and targeted block molecular weights. Optimized polymers containing the HFA substituent outperform PDMS in both selectivity and flux for recovery of *n*-butanol from dilute aqueous solution, providing a potential solution to this challenging separation problem.

Biography of Dr. Richard A. Register

Dr. Richard A. Register is Eugene Higgins Professor in the Department of Chemical and Biological Engineering at Princeton University. His research interests revolve around micro- and nanostructured polymers, such as block copolymers, polymer blends, semicrystalline polymers, and ionomers, ranging across their physics, synthesis, properties, and applications. He served as chair of his department from 2008-2016, and as Director of the Princeton Center for Complex Materials from 2005-2008. He received the Charles M.A. Stine Award from the American Institute of Chemical Engineers in 2002, and was honored with the Graduate Mentoring Award from Princeton University in 2008. He is a Fellow of the American Physical Society, of the American Chemical Society, and of the American Institute of Chemical Engineers.



List of Student Oral Presentations

1. “The Influence of Carrier Gas on Nanosecond-Pulsed Plasma Discharge Generated in A Water Film Plasma Reactor” by Huihui Wang
2. “Overall Isothermal Crystallization Kinetics of Precision Polyethylenes with Halogen in a Wide Temperature Range” by Xiaoshi Zhang
3. “Mechanism and Metabolic Control of Mesenchymal Stem Cell In vitro Aging” by Xuegang Yuan
4. “SANS-Supported Liquid-Liquid Phase Separation Drives the Inversion of Crystallization Rate from Heterogeneous Melts of Broadly Distributed Random Ethylene Copolymers” by Xuejian Chen

Student Oral Presentation #1

The Influence of Carrier Gas on Nanosecond-Pulsed Plasma Discharge Generated in a Water Film Plasma Reactor

Huihui Wang, Robert J. Wandell, Bruce R. Locke

Department of Chemical and Biomedical Engineering, Florida State University, Tallahassee, Florida,
United States

Abstract

Plasma discharge with liquid water has potential applications in water treatment and chemical synthesis. The main product of plasma discharge with water is hydroxyl radical, which is one of the strong oxidants and it can react with many organic pollutants in the water. However, the hydroxyl radicals are not stable, and the major stable product of plasma discharge with water is hydrogen peroxide which is mainly formed by the recombination of hydroxyl radicals. The production rate of hydrogen peroxide and water treatment efficiency are affected by reactor operating conditions such as reactor type and input power^{1,2}. However, previous studies have not fully investigated the influence of plasma properties on hydrogen peroxide production rate, water treatment efficiency, and the relationship between operating conditions and plasma properties. In the present study, we expand upon the previous work that utilized a nanosecond pulsed plasma discharge by considering the influence of carrier gas (argon and helium) on the plasma properties and the formation of hydrogen peroxide. The plasma properties, including electron density, plasma gas temperature, plasma volume, and the hydrogen peroxide production rate are measured in argon, helium, and argon/helium mixtures. We found that the helium plasma is more diffusive compared with the argon plasma. The helium plasma has a larger volume and lower electron density and gas temperature. These results may be due to the higher thermal conductivity of helium compared to argon. To further investigate the relationship between plasma properties and hydrogen peroxide production rate, a one-dimensional computer model was used to simulate the plasma discharge with different plasma properties. The simulation results show that the volume of plasma channel plays an important role in hydrogen peroxide production, since it determines the area of the boundary for mass and energy transfer. In addition, the volume is also important for determining the average gas temperature of the plasma channel. However, electron density was found to not significantly influence hydrogen peroxide production rate. Both the experimental and simulation results show that the more diffusive plasma has higher hydrogen peroxide production rate and water treatment efficiency.

References

1. R. J. Wandell and B. R. Locke, "Low-power pulsed plasma discharge in a water film reactor", IEEE Trans. Plasma Sci., 42.10 2014, pp. 2634-2635.
2. H. Kevin, C. H. Wang and B. R. Locke, "Analysis of Electrical Discharge Plasma in a Gas-Liquid Flow Reactor Using Optical Emission Spectroscopy and the Formation of Hydrogen Peroxide", Plasma Processes and Polymers, 13.9 2016, pp. 908-917.
3. R. J. Wandell et al. "Nanosecond pulsed plasma discharge over a flowing water film: Plasma characterization, hydrodynamic analysis, and hydrogen peroxide generation.", IEEE International Conference on Plasma Science, June 19-23, 2016, pp. 1-1.

Student Oral Presentation #2

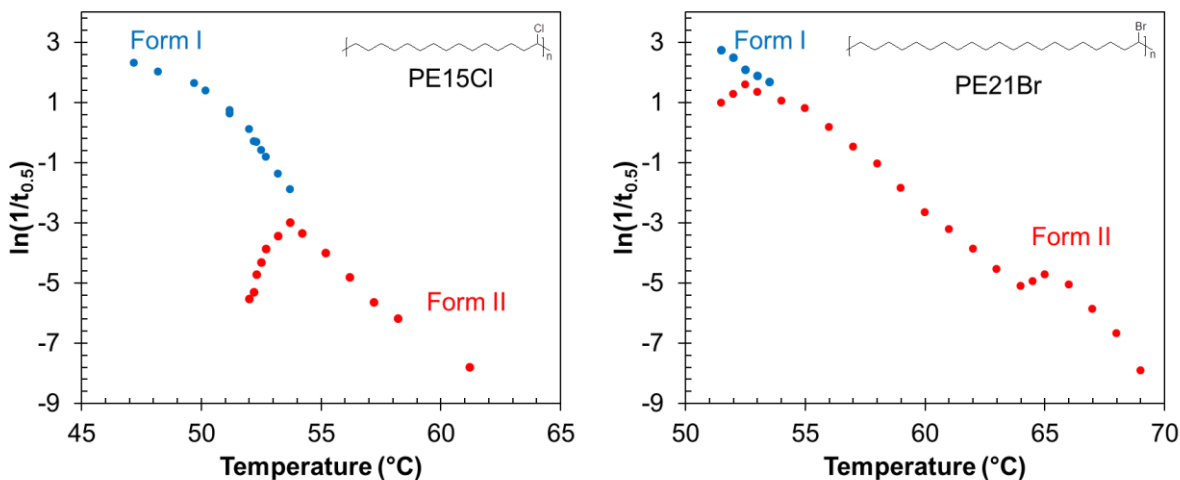
Overall Isothermal Crystallization Kinetics of Precision Polyethylenes with Halogen in a Wide Temperature Range

Xiaoshi Zhang, Rufina G. Alamo

FAMU/FSU College of Engineering, Chemical and Biomedical Engineering Department, 2525 Pottsdamer St., Tallahassee, FL 32310-6046, USA.

Abstract

Polyethylenes with halogen substitution at a fixed distance along the methylene backbone are unique models to study the effect of nanostructured chain-defects on folding and crystallization of polymers. Prior works showed that the halogen is accommodated in the crystal, yet crystallization and melting are proportional to the halogen's size and content. Furthermore, precision polyethylenes with chlorine and bromine precisely placed on each and every 9th, 15th, and 21st backbone carbons were found to develop polymorphs. At low temperatures, the chains pack in all-trans planar conformation (Form I). The crystals formed at higher temperatures pack in a non-planar herringbone-like structure (Form II). In this work, we study the independent overall crystallization kinetics of both forms. Parallel studies via differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) indicate an unusual temperature dependence of the overall crystallization rate for Form II. The overall crystallization rate of Form II displays an inversion with decreasing crystallization temperature in a range of temperatures where both forms coexist and a second inversion at higher crystallization temperatures near melting of Form I. The mechanism that leads to this unusual behavior will be discussed.



Mechanism and Metabolic Control of Mesenchymal Stem Cell *In vitro* Aging

Xuegang Yuan¹, Yijun Liu¹, Angchen Tsai¹, and Teng Ma¹

¹Chemical and Biomedical Engineering, The Florida State University, Tallahassee FL

Abstract

Human mesenchymal stem cells (hMSCs) have emerged as an important cell source for stem cell therapy because of their properties: self-renewal, multi-lineage differentiation, paracrine effect and immunomodulation. Clinical application requires allogenic and culture-expanded hMSCs with defined property and large scale production. However, *in vitro* culture-expansion of hMSCs leads to cell senescence and decrease of therapeutic potency, which is a major barrier for hMSCs based therapeutic application. Results from previous studies demonstrate that long-term culture of hMSCs results in phenotype change and metabolic shift from aerobic glycolysis towards oxidative phosphorylation (OXPHOS), leading cell to an *in vitro* aging state after rapid culture expansion¹.

In this work, we studied the metabolic reconfiguration of long-term cultured hMSCs at high passage to investigate the mechanism of metabolic shift and phenotype change. High passage hMSCs have increased mitochondria mass, reduced mitochondria membrane potential and autophagy compare to early passage hMSCs. Characterization of energy pathway and metabolic profile of high passage hMSCs showed the shift of metabolism to OXPHOS to support rapid proliferation rate, which contributes to the accumulation of cytotoxic metabolic byproducts. Engineering methods of maintaining or re-establishing culture-expanded hMSCs phenotype and cellular homeostasis could be applied to maintain or re-establish the therapeutic efficacy during culture expansion for clinical applications.

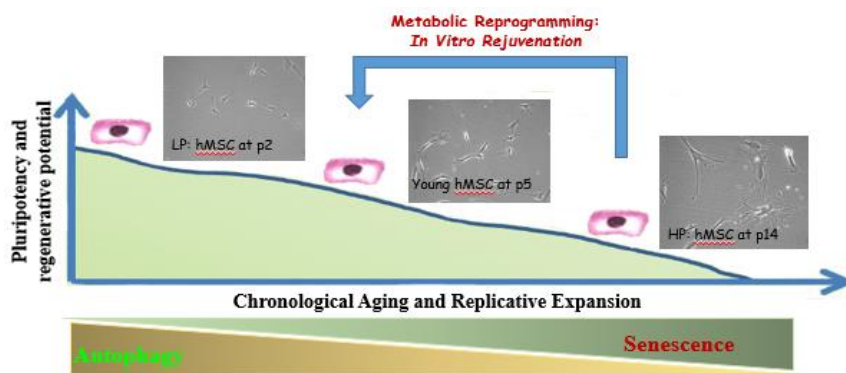


Figure 1. *in vitro* expansion of hMSCs leads to morphology change at high passage, with decreased cellular properties and increased senescence. Via metabolic reprogramming, high passage hMSCs can be “boosted” to maintain or re-establish their phenotypic properties.

Reference

1. Liu Y, Muñoz N, Tsai AC, Logan TM, Ma T. Metabolic Reconfiguration Supports Reacquisition of Primitive Phenotype in Human Mesenchymal Stem Cell Aggregates. *Stem Cells*, 2017. 35(2): p. 398-410.

SANS-Supported Liquid-Liquid Phase Separation Drives the Inversion of Crystallization Rate from Heterogeneous Melts of Broadly Distributed Random Ethylene Copolymers

Xuejian Chen¹, George D. Wignall², Lilin He², Carlos Lopez-Barron³, Rufina G. Alamo¹

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

²ORNL, Biology and Soft Matter Division, ³ExxonMobil Chemical Company

Abstract

Techniques aiming to control the rate of polymer crystallization have long been of industrial interest. It is known that crystallization rate of polymer strongly depends on the initial melt state. Prior work¹ using Differential Scanning Calorimetry (DSC) in broadly distributed (composition) random ethylene copolymers has reported an unprecedented inversion of crystallization kinetics from heterogeneous melt with lowering temperature. The mechanism behind this is further analyzed with detailed Small Angle Neutron Scattering (SANS) investigations of the melt structure of a broad ethylene 1-hexene copolymer (reproduced by a copolymer blend) in a wide range of temperatures that were reached either by heating the solid (from below) or cooling from homogeneous melt (from above).² In both cases, the observed SANS signal gradually changes from a pattern consistent with a one-phase melt (high temperature range) to a deviation toward higher intensity in the low Q region displaying signature of a minor disperse phase in a homogeneous matrix (low melt temperature range). The latter structure is consistent with demixing of the highly branched molecules and corroborates the postulated liquid-liquid phase separation (LLPS) as an explanation for the inversion of crystallization kinetics observed by DSC. In the melt approached from above, LLPS requires longer time to evolve to the same extent as in the melt approached from below. Nevertheless, SANS gives evidence of LLPS irrespective of the path taken to approach the melt.

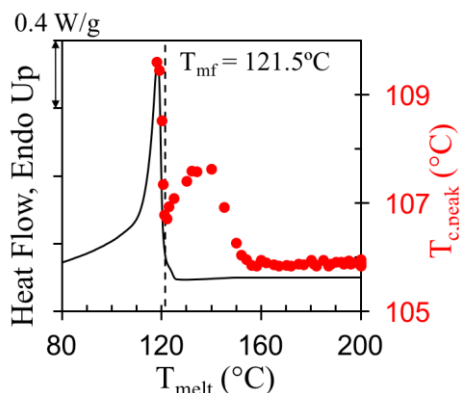


Figure 1. Inversion of crystallization rate ($T_{c,peak}$) with lowering melt temperature T_{melt} (closed symbol).

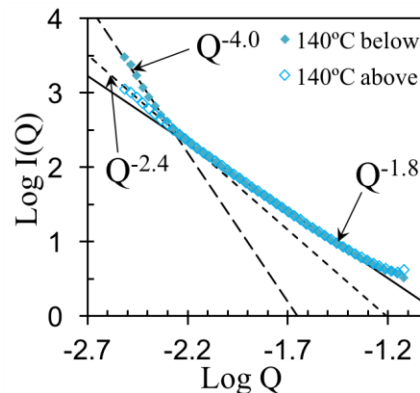


Figure 2. Deviation of scattering towards higher intensity in low Q indicates LLPS in the melt.

Reference

1. Mamun A, Chen X, Alamo RG. *Macromolecules*, 2014;47:7958.
2. Chen X, Wignall GD, He L, Lopez-Barron C, Alamo RG. Submitted.

List of Student Poster Presentations

Session 1

1. “Stable Pickering Emulsions Using Janus Particles via Microfluidics” by Bobby Haney
2. “Adipose Derived Stem Cell Reprograming as a Result of Size Dependent Aggregation” by Brent M. Bijonowski
3. “Recoverable Ruthenium-Based Olefin Metathesis Catalysts via Host-Guest Complexation” by Brian A. Ondrusek
4. “Bright White-Light-Emitting Mn-Doped One-Dimensional Lead Bromide Perovskites” by Chenkun Zhou
5. “Highly Efficient Recycle of Water Soluble NHC-Ru Catalyst via Host-Guest Interaction” by Cheoljae Kim
6. “DTI-based Network Analysis of APP/PS1 Mouse Brains with Age and Gender” by David Hike
7. “Gelation of Polymer-Grafted Silica Nanoparticles Studied with X-Ray Photon Correlation Spectroscopy (XPCS) and Rheology” by Divya Bahadur
8. “Development of Visible Light Induced Thiol-Ene Reaction on Natural Lignin and Its Applications to Synthesize New Sustainable Materials” by Hailing Liu
9. “New Type of Bulk-Quantum Materials Based on Zero-Dimensional Crystal Structures” by Haoran Lin
10. “Stimulus Responsive Bioinspired Adhesives for Finely Tunable Adhesion, Mechanical, and Optical Properties” by Irawan Pramudya
11. “Soret Effect on Symmetric Lithium Cells” by Jesufane Mentor

Session 2

12. “Effect of Extracellular Matrix Enzymes on A β Induced Alzheimer’s Models of Human Induced Pluripotent Stem Cells” by Julie Bejoy
13. “Heterotypic Cell-cell Interactions of Human Induced Pluripotent Stem Cells and Human Mesenchymal Stem Cells for Neural Differentiation” by Liqing Song
14. “Photo-responsive Bio-inspired Adhesives: Facile Control of Adhesion Strength via Photocleavable Crosslinker” by Minkyu Kim
15. “Dynamic Quantitative Imaging of Sodium During Onset of a Rat Migraine Model And Its Propagation at 21.1 T” by Nastaren Abad
16. “Structure and Dynamics of Lithium Polymer Electrolytes” by Onyekachi Oparaji
17. “Controlled Crosslinking of PEG Bottle-Brush Polymers for Medical Adhesive Applications via Oxime Ligation and Metal-Free Click Chemistry” by Rimantas Slegieris
18. “Sustainable Production of Nitrogen Fertilizer and Hydrogen Peroxide with Non-thermal Plasma” by Robert J. Wandell
19. “Binder Free Anodes for Lithium Ion Batteries (LIBs) via Electroless Deposition method” by Venroy Watson
20. “Oleyl Poly (Ethylene Glycol) Ether Grafted Microdevices for Cell-Borne Drug Delivery” by Yu Miao
21. “A Solution-Processed Organometal Halide Perovskite Hole Transport Layer for Highly Efficient Organic Light-Emitting Diodes” by Yu Tian

Student Poster Presentation #1 (Session 1)

Stable Pickering Emulsions Using Janus Particles via Microfluidics

Bobby Haney, Liheng Cai, Dong Chen, David A. Weitz, Subramanian Ramakrishnan

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Abstract

Stable Pickering emulsions are important to systems where controlled confinement of an oil or water phase are critical to its applications. The stability of the Pickering emulsions depend on the wetting properties of the particle. For this reason amphiphilic “Janus” particles have proven to be major assets in forming stable Pickering emulsions. The key to forming either o/w or w/o emulsions depends on the ratio of lengths of the hydrophobic to hydrophilic parts.

Polyethylene Glycol diacrylate (PEGDA), ethoxilated trimethylopropane triacrylate (ETPTA – monomer to be polymerized), 2-hydroxy-2-methyl-propiofenone (HMP – photo initiator), and water were mixed together to form the hydrophilic portion of the inner-phase. 99 wt% trimethylopropane triacrylate (TMPTA) and 1 wt% 2-hydroxy-2-methyl-propiofenone were added together to form the hydrophobic portion of the inner-phase. HMP would serve as the photo-initiator for polymerization under UV light. 95 wt% silicone oil (viscosity of 20 centi stokes) and 5 wt% Dow Corning Resin 749, as the surfactant served as the continuous phase. Janus particles were formed using flow of these solutions in a glass capillary microfluidic device. Flowrates were varied to control particle sizes (125- 400 microns) and hydrophilic to hydrophobic domain volume ratios (0.14 – 7). At a fixed surfactant concentration, variations of the ratio of inner water to oil flow rates lead to the formation of amphiphilic embedded particles of different sizes and hydrophobic portions. Using UV light, these droplets were cross-linked via photo-polymerization to form fairly monodispersed particles. The size of the emulsions were controlled by changing the size of the Janus particles.

Student Poster Presentation #2 (Session 1)

Adipose Derived Stem Cell Reprogramming as a Result of Size Dependent Aggregation

Brent M. Bijonowski M.Sc.,¹ Yijun Liu Ph.D.,² Ang-Chen Tsai Ph.D.,¹ Teng Ma Ph.D.¹

¹Florida State and Florida Agricultural and Mechanical University College of Engineering, Tallahassee, FL 32310. ²City of Hope National Medical Center, Duarte, CA 91010

Abstract

With increasing interest in embryonic development an tissue engineering the problem of aggregate oxygen and carbon consumption and diffusion is of great interest.^[1,2] Adipose derived stem cells[ASCs] undergo a metabolic reprogramming upon aggregation. Aggregates of ASC show a lower oxygen consumption rate than their monolayer counterparts.^[3] We hypothesize that this is a result of stress in response to the aggregation event. Aggregates were formed in a ultra-low attachment 96 well plate with approximate cell numbers of 5, 10, 30, and 50 thousand cells per aggregate which have diameters ranging from approximately 400 to 700µm. The aggregates were incubated for four days to allow cells to homogenize throughout the aggregate. The oxygen was measured via an orgo-metalic Ruthenium complex that was added to the culture media. Images were taken of the aggregates and were processed in a custom MatLab program. From this information we determined that there isn't a hypoxic zone in any of the aggregates and the oxygen consumption rate. The 50,000 cell aggregates had almost twice the consumption rate that was found in the 5000 cell aggregates. Analysis of the glucose and lactate showed that 5000 cell aggregates had larger glucose consumption than 50,000 cell. This suggests that the 5000 cell aggregates are undergoing anaerobic glycolysis instead of oxidative respiration. ASCs commonly undergo vascular niche differentiation in the body, and are highly mechanical sensitive. We investigated the Akt pathway as a means of this reprogramming. Upon inhibition of phosphorolation of the Akt protein with Wortammin (40nM) the oxygen consumption rate returned to nearly monolayer levels.

Reference

- [1] Murphy, Kaitlin C., Ben P. Hung, Stephen Browne-Bourne, Dejie Zhou, Jessica Yeung, Damian C. Genetos, and J. Kent Leach. "Measurement of Oxygen Tension within Mesenchymal Stem Cell Spheroids." *Journal of The Royal Society Interface* 14.127 (2017):
- [2] Van Winkle A, P, Gates I, D, Kallos M, S, Mass Transfer Limitations in Embryoid Bodies during Human Embryonic Stem Cell Differentiation. *Cells Tissues Organs* 2012; 196:34-47
- [3] Pattappa, Girish, Hannah K. Heywood, De Bruijn Joost D., and David A. Lee. "The Metabolism of Human Mesenchymal Stem Cells during Proliferation and Differentiation." *Journal of Cellular Physiology*. Wiley Subscription Services, Inc., A Wiley Company, 22 July 2011.

Recoverable Ruthenium-Based Olefin Metathesis Catalysts via Host-Guest Complexation

Brian A. Ondrusek and Hoyong Chung¹

¹Florida State University Department of Chemical and Biochemical Sciences

Abstract

The recovery and recycling of transition-metal based catalysts is important from the perspectives of practical industrial use as well as green chemistry in general. Ruthenium-based olefin metathesis catalysts, specifically, have become ubiquitous in research and industry alike and methods to improve their function are vigorously sought after. Several methods have been developed to this end, such as adhesion to a stationary phase such as silica or polymers,¹ the development of charged catalyst species for biphasic reactions,² as well as the preparation of catalyst structures bound to thermomorphic polymers for recovery by precipitation.³ Our research proposes a different route by utilizing a photosensitive host-guest interaction to recover the desired catalyst from a completed reaction. Tailoring an azobenzene moiety to the well-known Hoveyda-Grubbs second-generation structure allows for the recovery of the catalyst by interaction with a silica-supported β -cyclodextrin host, the supramolecular interaction for which is well understood. Our work has allowed us to synthesize the desired catalyst (Figure 1) and test it in a sample of characteristic reactions, showing activity comparable to that of the original H-G catalyst. Synthesis of the cyclodextrin moiety proceeds according to known procedures and results in a system which can be controlled very easily by the *cis/trans* photoisomerization of azobenzene, allowing us to attach/detach the catalyst at will and recycle it in subsequent reactions. Future work in this area will allow us to explore catalyst structures that are tailored for different kinds of metathesis reactions, and well as expand into reactions catalyzed by different transition metals such as palladium and platinum. These kinds of recyclable catalysts have the potential to reinvent the way that we think about using catalysts for chemical transformations on both the academic and industrial scale.

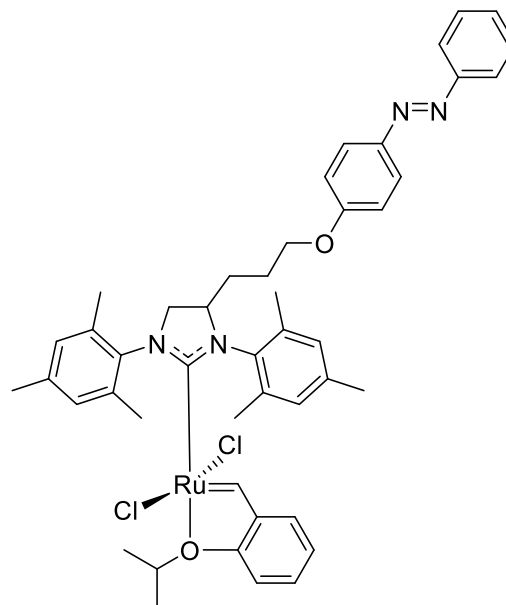


Fig 1. Structure of the described catalyst with tethered azobenzene functionality

Reference

1. a) Allen DP, Van Wingerden MM, Grubbs RH. 2009. Well-Defined Silica-Supported Olefin Metathesis Catalysts. *Org Lett.* 11: 1261. b) Mayr M, Wang D, Kröll R, Schuler N, Prühs S, Fürstner A, Buchmeiser MR. 2005. Monolithic Disk-Supported Metathesis Catalysts for Use in Combinatorial Chemistry. *Adv Synth Cat.* 347: 484.
2. Klučiar M, Grela K, Mauduit M. 2013. Ruthenium-Based Complexes Containing a Benzimidazolium Tag Covalently Connected to *N*-Heterocyclic Carbene Ligands: Environmentally Friendly Catalysts for Olefin Metathesis Transformations. *Dalton Trans.* 42: 7354.
3. Hobbs C, Yang Y-C, Ling J, Nicola S, Su H-L, Bazzi HS, Bergbreiter DE. 2011. Thermomorphic Polyethylene-Supported Olefin Metathesis Catalysts. *Org Lett.* 13: 3904.

4. Student Poster Presentation #4 (Session 1)

Bright White-Light-Emitting Mn-Doped One-Dimensional Lead Bromide Perovskites

Chenkun Zhou¹, Yu Tian², Oussama Khabou³, Michael Worku², Haoran Lin¹, Yan Zhou³, Biwu Ma^{1,2,3}

¹Department of Chemical and Biomedical Engineering, ²Materials Science Program, ³Department of Chemistry and Biochemistry

Abstract

Novel white light emitting diodes (WLEDs) based on luminescent nanocrystal materials attract considerable recent interest due to their promising applications in solid-state lighting. Two approaches are the most common to fabricate WLEDs. One is to coating a yellow phosphor or the mixture of green and red phosphors on a blue-LED chip. The other is to simply mixing different nanocrystals of the three primary colors (blue, green, and red) to generate white emission on an UV-LED. However, WLEDs based on these approaches are observed to suffer from poor stability over time due to the re-absorption of light and undesired energy transfer. Alternatively, the use of single-emitting component has great advantages in WLEDs over multi-component materials, such as higher stability, low-cost fabrication, and greater reproducibility.

Recently, our group reported a new one-dimensional (1D) organic lead bromide perovskite with broadband emissions and extremely large full width at half maximum (FWHM), which results from strong quantum confinement with the formation of self-trapped excited states¹. However, the strong quantum confinement in 1D structures leads to blue shift of the light emission, resulting in deficiency of red emission and low color rendering index (CRI). To improve the quality of white emission with higher CRI, integrating red emitting species in these 1D lead bromide perovskites without quenching the blue emission is desired.

Herein, we report the synthesis and characterization of a new class of white emitting phosphors based on Mn²⁺ doped one-dimensional organic lead bromide perovskites to overcome these drawbacks. These new phosphors can be prepared by facile one-step synthesis at room temperature in high yield. The bright white emission from these materials is the combination of blue emission from the indirect self-trapped excited states of the 1D perovskites and red emission from the doped Mn²⁺ ion. Due to the indirect nature of the self-trapped excited states, there is no energy transfer from them to the Mn²⁺ ions, resulting in independent dual emission. As compared to the pristine 1D perovskites with bluish white emission, these Mn²⁺ doped 1D perovskites exhibit much higher CRI and photoluminescence quantum efficiency.

Reference

Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; van de Burgt, L. J.; Kountouriotis, K.; Xin, Y.; Holt, E.; Schanze, K.; Clark, R.; Siegrist, T.; Ma, B., One-dimensional organic lead halide perovskites with efficient bluish white-light emission. *Nature Communications* **2017**, 8, 14051.

Highly Efficient Recycle of Water Soluble NHC-Ru Catalyst via Host-Guest Interaction

Cheoljae Kim and Hoyong Chung

Department of Chemical and Biomedical Engineering, Florida State University

Abstract

Host-guest interaction is one of the defining concepts of supramolecular chemistry which describes an idea of molecular recognition and interactions through non-covalent bonding between two or more molecules or ions. Based on the specific recognition of host molecules towards guest molecules, host-guest chemistry has been widely studied for drug carriers, dye encapsulation, nanoreactors, recovery of catalysts, and etc. Cyclodextrin (CD) is one of a well-known host molecule, and its hydrophobic cavity provides a strong binding interaction with azo benzenes and adamantyl group via van der Waals force in water solution. Using this property, we have newly developed a highly recoverable Hoveyda-Grubbs 2nd generation catalyst bearing extended ethylene glycols and adamantyl group on NHC ligand. In particular, extended ethylene glycol group provides a highly water soluble property for a homogenous catalytic reaction in water as well as a recovery of catalysts from organic solution by extraction with water. The adamantyl group combines with β -CD in aqueous solution, and this host-guest complex leads an efficient heterogeneous recovery of entire ruthenium catalyst after homogeneous reaction. The new recoverable NHC ligand will be extended to other transition metal catalysis (Pd, Cu), organocatalysis (ring-opening polymerization of lactides), flat surface modification, and medicinal application (anti-cancer agent, anti-infection agent).

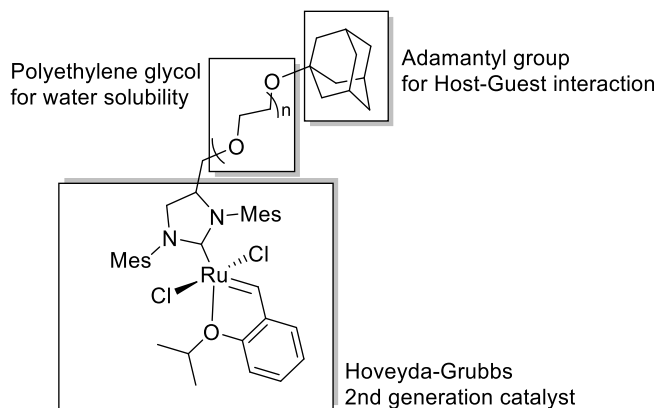


Figure 1. Our Hoveyda-Grubbs 2nd generation catalyst

DTI-based Network Analysis of APP/PS1 Mouse Brains with Age and Gender

David Hike¹, Scott Boebinger, Tara Palin and Samuel C. Grant

¹Chemical & Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University

Abstract

In this study, diffusion tensor imaging (DTI) is applied to the 5xFAD APP/PS1 double transgenic mouse model of familial Alzheimer's degeneration at multiple early time points with network theory analysis employed to examine structural connectivity alterations as a function of age and gender compared to wild type controls. DTI data was acquired with a multi-slice 2D spin echo using 18 diffusion encoding directions. Two to three brains were imaged simultaneously with an in-plane resolution of 100x100 μm and a slice thickness of 500 μm . To detect β -amyloid plaques, 3D images were acquired at 11.75 and 21.1 T using a true 3D gradient-recalled echo sequence to provide an isotropic 25- μm resolution in approximately 14.5 h. DTI data were analyzed using DSI Studio¹ to generate diffusion streamlines. Locally and globally, structural connectivity was analyzed utilizing 13 regions of interest (ROIs) positioned in cortical regions and a single manually segmented node representative of the hippocampus (**Fig 1**). Tracts were run to each individual node in order to derive quantifiable matrices that correspond to neural graphs (**Fig 2**). The decrease in FA has been found to continually decrease as a function of age. Current findings show a significant decrease in the FA in the temporal regions of the cortex in transgenic models (**Fig 3**). Extracellular plaques detected at 21.1 T without contrast agents are localized in regions with FA decreases (**Fig 4**). Least significant difference and one-way ANOVA were used to determine statistical significance.

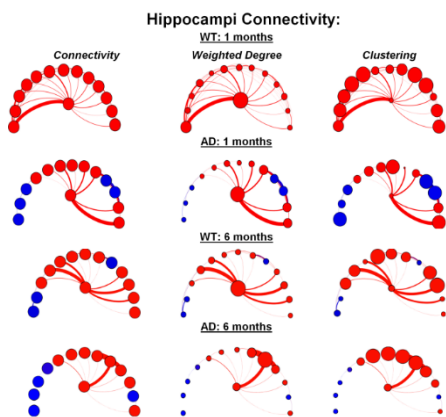


Figure 1: Visual representation of AD/WT tracts connectivity parameters and tracts at 1 and 6 months old. The structural connectivity in the hippocampi is investigated by quantifying distracted tracts that connect to cortical nodes. Blue nodes indicate an absence of connectivity between them and the hippocampus. Note that the connectivity tends to be impacted by both age and pathology. Nonetheless, AD 6 months samples exhibit less connectivity when compared to their matching controls.

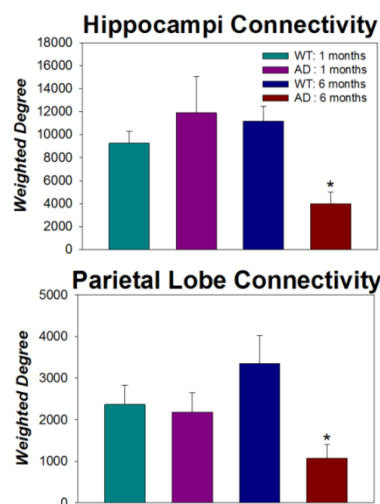


Figure 2: Weighted Degree in the 6-mon AD Hippocampi shows significant decrease when compared to 1 month WT and AD as well as 6 month WT. The parietal area of cortex shows a similar drop for 6-mon AD compared to younger samples as well as the age matching WT.

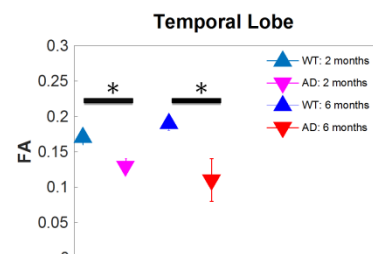


Figure 3: Decrease in FA of the temporal region of AD samples when compared to age matched controls.

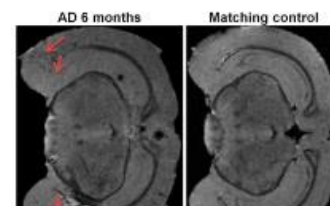


Figure 4: Plaques are visible in 5xFAD at 21.1 T with from T_2^* -weighted MRI at 25- μm resolution compared to age- matched control.

Student Poster Presentation #7 (Session 1)

Gelation of Polymer-Grafted Silica Nanoparticles Studied with X-Ray Photon Correlation Spectroscopy (XPCS) and Rheology

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Abstract

We report a combined XPCS study of particle dynamics and rheological study of moderately concentrated suspensions of **silica colloids and their binary mixtures** that form a gel on cooling. The suspensions are comprised of silica colloids (32nm, 86nm and 185 nm) coated with octadecyl-hydrocarbon chains and suspended in decalin at colloidal volume fractions (ϕ) ranging from 0.2 to 0.4. Different **scaling relationships are explored to predict the elastic modulus and the limit of linearity**. Gel temperatures of the different size particles and the elastic moduli, though different, collapse onto a single curve when scaled as $G'D^3/kT$ and **plotted versus $(1/T - 1/T_{gel})$** , where G' is the elastic modulus and T_{gel} is the gel temperature. This scaling is in line with predictions of mode coupling theory which emphasizes the importance of local structure (localization length) over longer-range correlations in determining the dynamical and mechanical properties of such gels. The **dynamics of nanoparticles during the gelation** process is measured using X-ray Photon Correlation Spectroscopy (XPCS) at Argonne National Labs. Using a newly developed ultrafast frame rate (11.8 kHz) pixel-array-detector, we have, for the first time, captured the complete transition of the dynamics of the suspension from tens of seconds in the gel state to hundreds of μs in the liquid state. The **transition is triggered when the gel is slowly heated**. Our nanoscale measurements of the colloid **dynamics as a function of temperature and particle size can be compared to macroscopic viscoelastic properties probed by rheology under the same conditions and suggest that smaller colloids form stronger networks when they gel**. This is in line with the measurements of the gel boundary with smaller particles gelling at higher temperatures. Efforts to extend the scaling relationships of elastic modulus to smaller particle sizes and their mixtures and limitations of the theories in predicting the mechanical properties will also be discussed.

Student Poster Presentation #8 (Session 1)

Development of Visible light induced thiol-ene reaction on natural lignin and its applications to synthesize new sustainable materials

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Abstract

Photo-redox catalyzed reaction gains high intention as sustainable and green chemistry synthetic methods due to low energy consumption and the excellent reaction performance under visible-light.¹ Recently, we have successfully applied the photo-redox catalyzed thiol-ene reaction to natural lignin modifications. Among various tested photochemical catalysts, 5 mol% Ru(bpy)₃Cl₂ revealed the highest reactivity under 3W blue LED. The successful thiol-ene reaction resulted fast modification (within 1 hour) of lignin with thiol containing organic compounds including polymer, poly(ethylene glycol). The developed photoredox catalyzed thiol-ene modification of lignin was very conveniently controlled by simply turning the light source on and off. Excellent conversion, 95%, of lignin thiol-ene modification was achieved even by natural sunlight after four hours of irradiation. Above all, this photochemical thiol-ene reaction for natural lignin modification is crucial from the standpoint of practical application. Due to the cost-effectiveness and environmentally benign nature of both sustainable basic materials and the modification method, various subsequent research and applications are inspired.

The high efficiency of visible light induced thiol-ene reaction allows fast and easy lignin modification through graft copolymerization with other polymers. The lignin-*graft*-chitin is a new polymer that is synthesized from all natural polymers. Chitin is a natural polymer from the cell walls of fungi, the exoskeletons of arthropods, and the beaks and internal shells of cephalopods. The chemical structure of chitin is a modified polysaccharide that contains nitrogen synthesized from units of 2-(acetylamino)-2-deoxy-D-glucose. The new lignin-*graft*-chitin has good biodegradability, sustainability and renewability. The second important application of the developed photo-redox thiol-ene reaction of lignin is preparation of double networked lignin-polymer for ultra-strong lignin-based hydrogel. The fast and easy thiol-ene reaction is an ideal method to synthesize lignin-PEG crosslinking polymer. In the matrix of lignin-PEG crosslinked copolymer, another crosslinked poly (acrylic amide) is synthesized to form a dual crosslinked polymer network. The double crosslinked polymers behave two net cloth across in each other's meshes, becoming a strong and elastic material. This material is expected to be a synthetic elastomer from natural lignin.

Reference

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New Type of Bulk-Quantum Materials Based on Zero-Dimensional Crystal Structures

Haoran Lin, Prof. Biwu Ma
Chemical and Biomedical Engineering, FSU

Abstract

A traditional ionic crystal constitutes charged atoms or molecules that are aligned periodically in the crystal's lattice. Usually, a three-dimensional (3-D) ionic crystal exhibits strong coulombic interactions between ions in all directions which means that the constituents are intensely coupled and form band structures in its energy diagram.

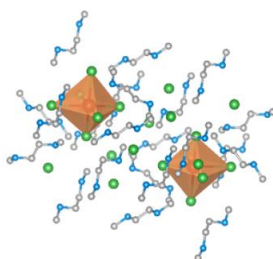


Figure 1. Single-crystal structure of $(\text{DMEDABr})_4\text{SnBr}_6$ 0-D material.

A recently study in our group reveals that, a zero-dimensional ionic crystal can be achieved by combining a metal-halide ion and a large organic ligand ion (Figure 1). In this structure, the SnBr_6^{4-} ions are surrounded by the bulky ligands which ensures a large distance between the metal-halide anions. Since the metal-halide cores are isolated from each other, no band structure is formed and the single crystal exhibits strong quantum-confinement effect as the inherent property of the metal-halide constituent. Also, due to elimination of the non-emissive recombination channels, the 0-D crystal can achieve a photoluminescence quantum efficiency near 100%. This discovery suggests strong potential application in LEDs, lighting, solar concentrators etc. and opens a research area that is barely explored before.

According to our previous results, my research focuses on developing new organic-inorganic hybrid compounds that based on this kind of 0-D structure and exploring their photo-physical properties. By varying the species and sizes of the organic or inorganic counterparts, we could effectively obtain 0-D ionic crystals with different crystal structures and quantum-confinement effects. Moreover, we are confident to develop a series of materials that give different but efficient emission behaviors for multiple applications.

Student Poster Presentation #10 (Session 1)

Stimulus Responsive Bioinspired Adhesives for Finely Tunable Adhesion, Mechanical, and Optical Properties

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Abstract

Bioinspired adhesive is often used to describe an adhesive that is synthesized from biological monomers and/or synthetic material to form a strong bond to biological tissue. In this work, three different types of bioinspired adhesives are synthesized by thermally initiated radical polymerization. First, an enhanced mechanical and optical properties were obtained from newly synthesized terpolymer adhesive, poly(2-methoxyethyl acrylate-*co*-*N*-methacryloyl 3,4-dihydroxyl-L-phenylalanine-*co*-heptaisobutyl substituted polyhedral oligomeric silsesquioxane propyl methacrylate) (poly(MEA-*co*-MDOPA-*co*-MPOSS)). Second, a photo-crosslinkable terpolymer adhesive, poly(*N*-methacryloyl-3,4-dihydroxyl-L-phenylalanine-*co*-9-(acryloyloxy)butyl anthracene-9-carboxylate-*co*-acrylic acid), was synthesized for precise control of adhesion strength via crosslinking formation of anthracene groups under UV irradiation. Finally, a new water soluble and lectin recognizable adhesive, poly(glucosamine methacrylate-*co*-*N*-methacryloyl-3,4-dihydroxyl-L-phenylalanine-*co*-3-azidopropyl methacrylate) was synthesized. Herein, the azide group is used to form controllable crosslinking, which enables to tune adhesion property, through metal free click chemistry. Adhesion strength of the terpolymer was characterized by uniaxial indentation and lap shear adhesion test. When small amount of MPOSS (0.5 mol %) was incorporated, the terpolymer displayed strong adhesion property by indentation adhesion test, $23.2 \pm 6.2 \text{ J/m}^2$ with 0.05 N preloading and 300 s holding time. The MPOSS increased optical transmittance in the visible light range, 450-750 nm. The POSS containing adhesive was tested with human embryonic kidney cells (HEK293) showing excellent bio-compatibility. In the second adhesive, the presence of anthracene monomer enhanced adhesion property in lap shear adhesion test (850% enhancement – J/m^2) after the terpolymer was UV-irradiated at 352 nm. The third adhesive, glucose-based terpolymer (glycopolymer) adhesive contains glycomonomer that resembles natural saccharides and its carbohydrate moieties makes it attractive due to high water solubility as well as potential applications in biological recognition systems.

Student Poster Presentation #11 (Session 1)

Soret Effect on Symmetric Lithium Cells

Dr. Daniel T. Hallinan, jr., Jesufane Mentor

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Abstract

Conversion of temperature gradients to electricity could be used to yield waste heat and improve energy efficiency across many areas. To this end, we are studying the Soret effect in a polymer electrolyte using an electrochemical cell. Symmetric lithium cells are subjected to temperature gradients. Thermal diffusion caused by the temperature gradient results in a concentration gradient, which in the absence of a current leads to an electrochemical potential. The potential at steady state is used to calculate the concentration gradient. This allows the calculation of the Soret coefficient which gives insight into the direction and magnitude of the mass flux of lithium salt in the polymer electrolyte due to thermal diffusion. We found that the Soret coefficient is positive, which means that the salt present in the electrolyte is diffusing from the heated part of the cell to the cooler part of the cell. With increasing temperature gradient, there is a positive increase of potential difference. At an average temperature of 30 ° C, we found that the Soret coefficient to be positive. However, in a separate study they found at a temperature of 22° C, the Soret coefficient is only positive when the polyethylene oxide is dissolved in water¹.

Reference

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Student Poster Presentation #12 (Session 2)

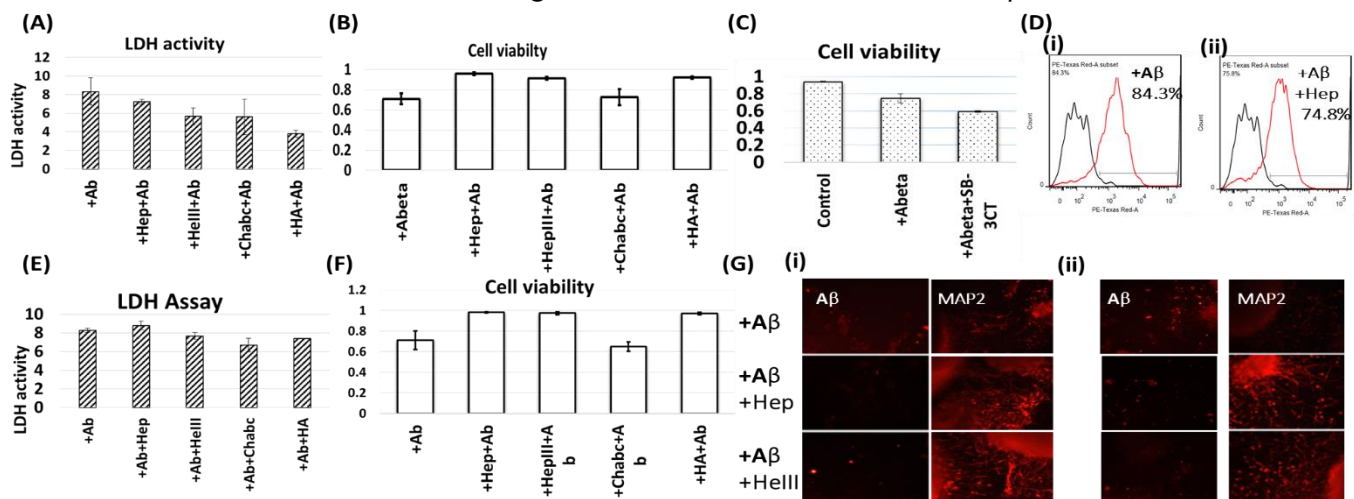
Effect of Extracellular Matrix Enzymes on A β Induced Alzheimer's Models of Human Induced Pluripotent Stem Cells

Julie Bejoy, Yan Li

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Abstract

Extracellular matrix (ECM) components of the brain are found to play important roles both in the neural development stage and in the neurodegeneration like Alzheimer's disease (AD). The hallmark of AD includes the accumulation of amyloid β peptides (A β 42) which form the plaques called senile plaques. The study of plaques and the surrounding microenvironment of AD brain revealed co-localized expressions of different ECM molecules such as proteoglycans (heparin sulfate proteoglycans (HSPGs) and chondroitin sulfate proteoglycans (CSPGs)), metalloproteinases (MMPs), and hyaluronic acid (HA) etc. compared to the normal brain. Since the disease modeling using transgenic animal models of AD does not reflect the microenvironment in humans, this creates a necessity of developing complementary models from human cells including induced pluripotent stem (iPS) cells. In this study, we used two previously established neuron differentiation paradigms for obtaining a forebrain dominant culture from iPS cells. The first protocol (cortical) used dual Smad inhibition followed by sonic hedgehog (Shh) pathway inhibition and stimulation with fibroblast growth factor-2 to generate glutamatergic neurons. The second protocol used inhibitors of WNT, Shh, and SMAD signaling to generate telencephalic neural precursors followed by activation of Wnt plus brain-derived growth factor to produce hippocampal dentate gyrus granule neurons (hippo). AD-associated neural pathology was obtained by exogenous A β 42 oligomers treatment. The cultures were then treated with heparin (A β affinity with HSPG), heparanase (digest HSPGs), chondroitinase (digest CSPGs), hyaluronic acid, and the MMP inhibitor (SB-3CT). The results from the study indicated that inhibition of HSPG binding to A β using either heparanase or heparin can attenuate the impact of A β related neural cell death. Whereas the inhibition of CSPG and MMP2/9 induced more neural cell death. The image analysis revealed that both heparin and heparinase treatment reduced A β expression and also supported the survival of developed neurons by showing increased expression of later stage neurons (MAP2+). The results should enhance our understanding of the contribution of ECMs to the A β -induced neural cell death.



Figures: Lactate dehydrogenase (LDH) results for the cortical protocol (A) and hippo protocol (E). Quantitative analysis of live/dead cell viability of the cortical protocol (B) and hippo protocol (F) and for MMP inhibitor (C). Flow analysis of reduced A β expression after Heparin treatment. Immunocytochemistry images for both A β and MAP2 expression after heparin and heparinase treatment for the cortical protocol (G(i)) and hippo protocol (G(ii)).

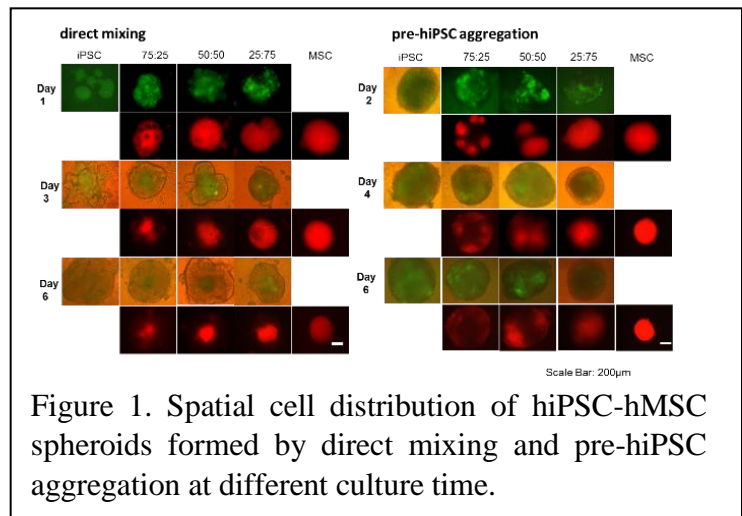
Heterotypic Cell-cell Interactions of Human Induced Pluripotent Stem Cells and Human Mesenchymal Stem Cells for Neural Differentiation

Liqing Song¹, Ang-Chen Tsai¹, Xuegang Yuan¹, Julie Bejoy¹,
Sébastien Sart², Teng Ma¹, Yan Li¹

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Abstract

Organ buds, the condensed 3-D tissues emerged at the early stage of organogenesis, are a promising transplantation entity to regenerate functional and vascularized organs. However, complex heterotypic interactions of different cell types, such as human mesenchymal stem cells (hMSCs) and human induced pluripotent stem cell (hiPSC) derived neural progenitors, and their secretory activities during neurogenesis have not been well understood. The objective of this study is to investigate the impact of the composition and structure of 3-D hybrid spheroids of hiPSCs and hMSCs on neural differentiation and the secretion of extracellular matrices and trophic factors in vitro. The hybrid spheroids were formed at different hiPSC:hMSC ratios (100:0, 75:25, 50:50, 25:75, 0:100) using direct mixing and pre-hiPSC aggregation method, which generated dynamic spheroid structure. The cellular organization, proliferation, neural marker expression, the secretion of extracellular matrix proteins and the cytokines were characterized. The incorporation of MSCs upregulated the neural marker expression, matrix remodeling proteins and the secretion of transforming growth factor (TGF)- β 1 and prostaglandin E2. This study indicates that the composition and structure of hiPSC-MSC spheroids differentially influence neural differentiation and trophic factor and matrix secretion due to the modulation of heterotypic cell-cell interactions.



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Student Poster Presentation #14 (Session 2)

Photo-responsive Bio-inspired Adhesives: Facile Control of Adhesion Strength via Photocleavable Crosslinker

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Abstract

A new bioinspired adhesive that includes zwitterionic polymer, poly(sulfobetaine methacrylate) (pSBMA), catechol group, and photocleavable nitrobenzyloxycarbonyl containing crosslinker was synthesized by convenient thermally-initiated free radical polymerization. The main component pSBMA is highly hydrophilic and biocompatible polymer which has high potential as the biocompatible materials. The mussel's adhesive protein inspired catechol group is recently studied bioinspired functionality that enhances adhesion property on universal surfaces even in the presence of water. The third component, nitrobenzyloxycarbonyl containing diacryl crosslinker cleaves upon UV irradiation. UV/vis spectra analysis revealed that chemical bonding cleavage rapidly occurs within 30 min and then slowly continued until 3hr, resulting in continuous decrease of crosslinking density. The loss of crosslinking results weakened adhesion property according to lap shear strength measurement. The decrease tendency in adhesion strength was similar with loss tendency of crosslinking in the polymer. By conducting ¹H NMR experiment, we could confirm pure crosslinker shows fast chemical bonding cleavage within 30 min and then slowly proceeds until 3hr in the same way as was discovered in adhesion property tests. The photo-cleavage of nitrobenzyloxycarbonyl group occurs through a sequential 3 steps of reaction with rate constants k_1 , k_2 , and k_3 , yielding carboxylic acid and aldehyde. The carboxylic acid and aldehyde follows third-exponential rate law with three rate constants. The third-exponential rate law can be simplified to a single exponential because a rate determining step k_3 is order of magnitude smaller than other rate constants. By using the obtained kinetic equation, the reduction of adhesion strength (kPa) could be conveniently predicted at designated UV irradiation time.

Controllable adhesive



Reference

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Dynamic Quantitative Imaging of Sodium During Onset of a Rat Migraine Model and Its Propagation at 21.1 T

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Abstract

Purpose Ionic instability and dysfunctional regulation is implicit in migraineurs. The brain allocates over 50% of its energy reserves on a cellular basis to the regulation of sodium homeostasis; therefore, the alteration of sodium concentrations and fluxes related to these distributions are critical¹. Accordingly, *it is hypothesized* that migraineurs have a distinct a prevailing mechanism that induces excess sodium to be pumped into the extracellular space, resulting in neuronal excitability that is sustained with the onset and progression of migraine. More specifically, the purpose of this study was to evaluate dynamic *in vivo* (²³Na) fluxes in the brain, using a migraine analogue in rodent. Ultra-high field of 21.1 T was utilized to allow for higher spatial and temporal resolution to quantify bulk sodium distributions during and following the onset of central sensitization, to study a longitudinal time course of >3hrs. This time course allowed for investigation of bulk sodium changes during the onset and propagation of central sensitization, while rigorously accounting for any cyclical or circadian variations in biological sodium.

Methods Animal Model: A total of 12 male Sprague-Dawley rats were used in this study. While in the MRI scanner and sedated with isoflurane, they were administered in situ with an IP injection of either 10 mg/kg of NTG (n=6) to induce central sensitization (CS), or saline (n=6) as controls. MRI protocol: Slice selective sodium images were acquired using a multi-slice FID-based Chemical Shift Imaging (CSI) sequence yielding an in-plane acquisition resolution of 1.1 x 1.1 mm and through-plane resolution of 3-mm. Using a repetition time (TR) of 180 ms, and with 6 averages, the complete dataset was acquired in 9 minutes. A total of twenty-seven repeated scans were acquired starting from pre-injection, followed by 3-h post injection scanning. Data Analysis: CSI data sets were analyzed using AMIRA (FEI Corp, Hillsboro OR). Images were manually segmented with ROIs placed in the eyes, olfactory bulb, third ventricle, neocortex, fourth ventricle, cerebellum, brainstem and cisterna magna along with a muscular region in the rat jaw to serve as an internal control for the ²³Na signal.

Results and Discussion Increase of ²³Na MRI signal was evident for NTG treated animals in the brainstem, 4th ventricle and the cisterna magna almost immediately after injection, gaining significance about 30-45 min post-injection. The cerebellum and 3rd ventricle also showed increasing trends of increased ²³Na post -injection, gaining delayed significance >1.5hrs. These dynamic changes (rapid increases in sodium concentration compared to the controls) indicate that the mechanism of Central sensitization is dependent on, specific to, and localized in certain anatomical regions. These time dependent fluctuations could provide prominent insight into dysregulations of migraine and subsequent therapeutic measures.

Reference

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Student Poster Presentation #16 (Session 2)

Structure and Dynamics of Lithium Polymer Electrolytes

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Abstract

Polymer electrolytes are promising materials for high energy density rechargeable batteries. They form ion – polymer complexes with alkali metal salts of low lattice energy through ionic association. The formation of these charged, associated species affect the ionic conductivity through the change in ionic mobility of the associated charge carriers.¹ We present a fundamental study of ion association effects and the ion-polymer interactions in high molecular weight poly(styrene–ethylene oxide) block copolymer (SEO) and complexes with lithium bis(trifluoromethane sulfonyl) imide salt (LiTFSI) as polymer electrolyte using FTIR-ATR spectroscopy. Dissolution of the lithium salt in the PEO phase is expected to affect the C-O-C vibrations of the PEO backbone. The infrared bands observed in the polymer – salt complexes as a function of salt concentration and temperature show different solvation and degree of ion association behavior. An understanding of the relationship between ionic conductivity and degree of solvation of lithium salts as a function of ion concentration will be explained from FTIR-ATR results. Since conductivity is a function of ion concentration and ion mobility, and ion mobility is coupled to polymer segmental mobility, we investigate the effect of salt concentration on the polymer segment mobility. We report the influence of lithium salt concentration on the structural relaxation time (XPCS) and stress relaxation time (rheology) of high molecular weight poly(styrene – ethylene oxide) block copolymer membranes.

Reference

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Controlled Crosslinking of PEG Bottle-Brush Polymers for Medical Adhesive Applications via Oxime Ligation and Metal-Free Click Chemistry

Rimantas Slegieris and Hoyong Chung¹

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Abstract

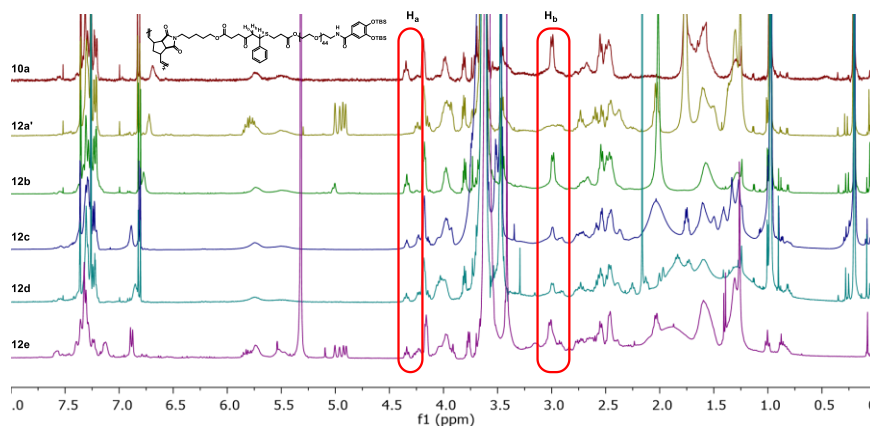
A synthetic route towards multifunctional bottle-brush polymers, containing internal ketone and catechol group have been developed. First, well-defined macromonomer was synthesized to incorporate norbornene, ketone, poly(ethylene glycol) (PEG) and catechol group. A subsequent ring opening metathesis polymerization yielded precisely controlled bottle-brush polymers. The internal ketone of obtained polymers, despite being sterically hindered, was successfully functionalized with different oxyamines in various degrees of functionalization (from 18 % to 100 %). The utility of this functionalization was further demonstrated by incorporating the azide-containing oxyamine into the polymeric structure, and subsequently crosslinking the polymer via (1R,8S,9s)-Bicyclo[6.1.0]non-4-yn-9-ylmethyl (BCN) bisfunctionalized PEG ($M_n = 6000$ g/mol) diamine crosslinker. The reaction between azide-containing bottle-brush polymer and the BCN-terminal crosslinker displayed rapid phase change due to covalent bond forming crosslinking (metal-free click chemistry) after incubation at physiologically compatible temperature (37 °C) and solvent (1 : 1 EtOH : H₂O).

Table1: Functionalization of 10a-d, e with **oxyamines**.

Reaction scheme: 10 or 11 $\xrightarrow[70^\circ\text{C}, 2\text{h}]{\text{MeOH}, \text{R}^1\text{-ONH}_2, \text{CH}_2\text{COOH}}$ 12a-e

Entry	S. M.	R ¹	R ²	D.F. ^b
12a ^a	10a		TBS	46 %
12a ^c	10a		TBS	100 %
12b	10b		TBS	18 %
12c	10c		TBS	61 %
12d	10d		TBS	65 %
12e ^b	11		H	43 %

^a – reaction time = 1h; ^b – rough estimate of degree of functionalization, estimated from NMR; ^c – reaction time 16h.



Sustainable Production of Nitrogen Fertilizer and Hydrogen Peroxide with Non-thermal Plasma

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Abstract

Annually, approximately 810 M barrels of oil (equivalent) are used globally as feed-stock to produce 147 M metric tons of synthetic nitrogen-based fertilizer which is vital for producing the food supply to sustain the world's population. The production of this fertilizer is not only energy intensive, but also leads to significant environmental pollution and affects the economic viability of farming in many parts of the world. In this work, a patented flowing film plasma reactor is utilized to generate nitrogen fertilizer in an environmentally friendly way using only air, water, and electricity. The environmentally friendly fungicide and bactericide, hydrogen peroxide, is also simultaneously produced. This process can provide these compounds continuously and on-demand as "green" nitrogen fertilizer and as a "green" fungicide/bactericide, enabling farmers to produce fertilizer on-site as needed and reduce the need to use harmful pesticides. Our system can produce locally the required concentrations of nitrate and hydrogen peroxide, thereby removing the need for shipping and storing large quantities of highly concentrated, hazardous, and potentially dangerous chemicals. The basic physics and chemistry of nitrate generation with plasma discharge is well known from naturally occurring lightning in thunderstorms. This work aims to develop a deeper understanding of how this reactive chemistry can be replicated and harnessed. Aspects of both the power supply and reactor geometry are investigated to increase both the energy yield and production rate of the process.

References

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Binder free Anodes for Lithium Ion Batteries (LIBs) via Electroless Deposition method

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Abstract

Graphite (372 mAh/g) powder is currently used as Li-battery anode material but urgent need exists to replace it with materials with higher capacity, energy and power density. Investigation of Sn (991mAh/g) as an alternative to graphite has been explored through many approaches which has not been able to address the large volume expansion (fabrication related) and performance limitations associated with Sn during cycling^{1,2}. In this work, by using electroless deposition method, a new approach of fabricating high performing Cu-Sn alloy for lithium battery anode with high capacity, power density and long cycle life will be presented.

In our approach, Cu was electrolessly deposited on carbon cloth followed by immersion of the Cu-plated cloth in a Sn bath for partial displacement of Cu and subsequent formation of Cu-Sn alloy. The Cu-Sn alloy deposited on carbon cloth over various times was used in Coin cell with Li metal as counter electrode. The open circuit voltage of freshly fabricated cell varied from 2.02V (for pristine carbon cloth) to 3V (for Cu-Sn plated carbon cloth). First cycle specific discharge capacity from open circuit voltage to 0.007V for our new electrodes varied between 561mAh/g to 656mAh/g based on the mass of Cu-Sn deposited on the cloth. The results of the cell's performance evaluation as a function of Sn Cu displacement time will be presented.

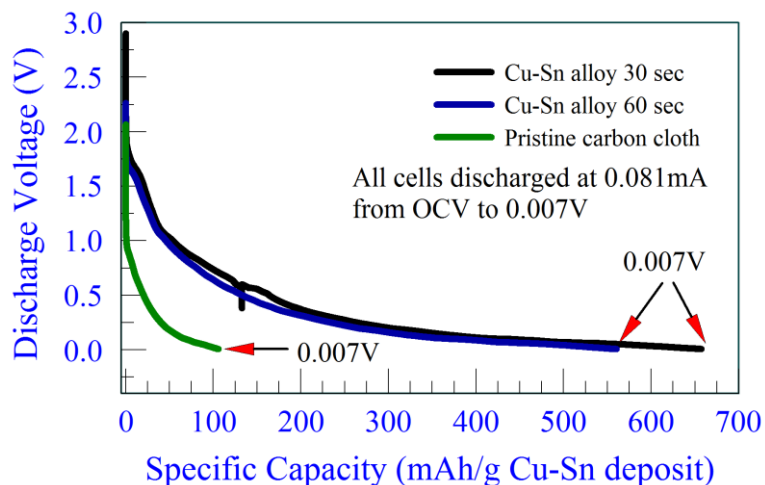


Fig. 1: First cycle specific discharge capacity from open circuit voltage to 0.007V based on the mass of Cu-Sn alloy deposited on one side of the cloth.

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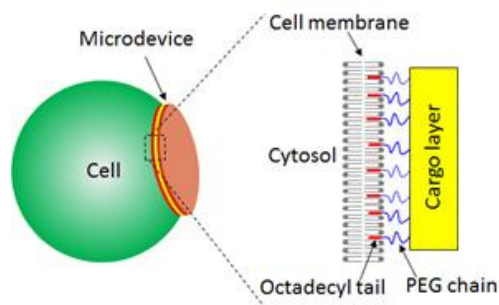
Oleyl Poly (Ethylene Glycol) Ether Grafted Microdevices for Cell-borne Drug Delivery

Yu Miao¹, Hailing Liu¹, Yi Ren², Hoyong Chung¹, Jingjiao Guan¹

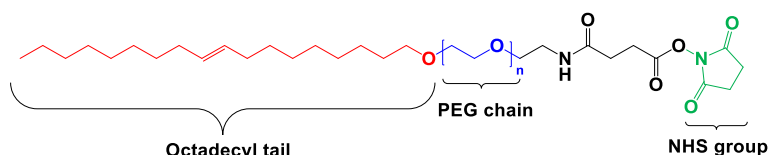
¹Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University, 2525 Pottsdamer Street, Tallahassee, Florida, 32310, USA. ²College of Medicine, Florida State University, 1115 West Call Street, Tallahassee, Florida, 32306, USA

Abstract

Integrating a cell with artificial micro/nanodevices into a single entity can make a hybrid system that possesses both the functionalities of the cell and the micro/nanodevices, which can serve as a novel drug delivery system. Researchers have utilized different kinds of interactions to make cell/micro or nanodevices complexes such as avidin-biotin, maleimide-thiol, CD44-hyaluronic acid and electrostatic force. However, due to the requirement of specific interactions, these methods are not suitable for all therapeutic cells. Additionally, some of them may be harmful to the bound cells. In order to solve these problems, we covalently grafted oleyl-o-poly(ethylene glycol)-succinyl-N-hydroxy-succinimidyl esters to one side of the microdevice. This molecule has a long carbon chain which can insert into cell's membrane and anchoring the microdevice to the cells. Because this interaction is more general, it can be used for many kinds of cells without the prerequisite of having specific functional groups presented on the cell's membrane. Non-covalently bonding mechanism also makes it less harmful to cells.



Structure of oleyl-o-poly(ethylene glycol)-succinyl-N-hydroxy-succinimidyl esters:



Reference

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A Solution-Processed Organometal Halide Perovskite Hole Transport Layer for Highly Efficient Organic Light-Emitting Diodes

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Abstract

Thin film optoelectronic devices have experienced tremendous development over the last decades. The charge transport layers, i.e., hole transport layer (HTL) and electron transport layer, play critical roles in determining the device performance. We have demonstrated a new type of hole transport layer based on organometal halide perovskite CH₃NH₃PbCl₃ for efficient OLEDs. The solvent passivation approach allowed for the formation of smooth neat perovskite thin films with great surface coverage. Solution processed multilayer green phosphorescent OLEDs based on this new perovskite HTL showed superior performance over the device using conventional PEDOT:PSS HTL, with lower turn on and operating voltages, as well as higher luminescence, EQE, power efficiency and luminous efficiency. The improved device performance is primarily attributed to the wide band gap of CH₃NH₃PbCl₃, suitable energy levels, and efficient hole injection and transport from ITO to CH₃NH₃PbCl₃ and light emitting layer. Our work demonstrates a new pathway toward highly efficient solution processed multilayer OLEDs, and further establishes organic-inorganic halide perovskites as a new class of semiconductors with highly desirable characteristics for thin film optoelectronic devices.

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