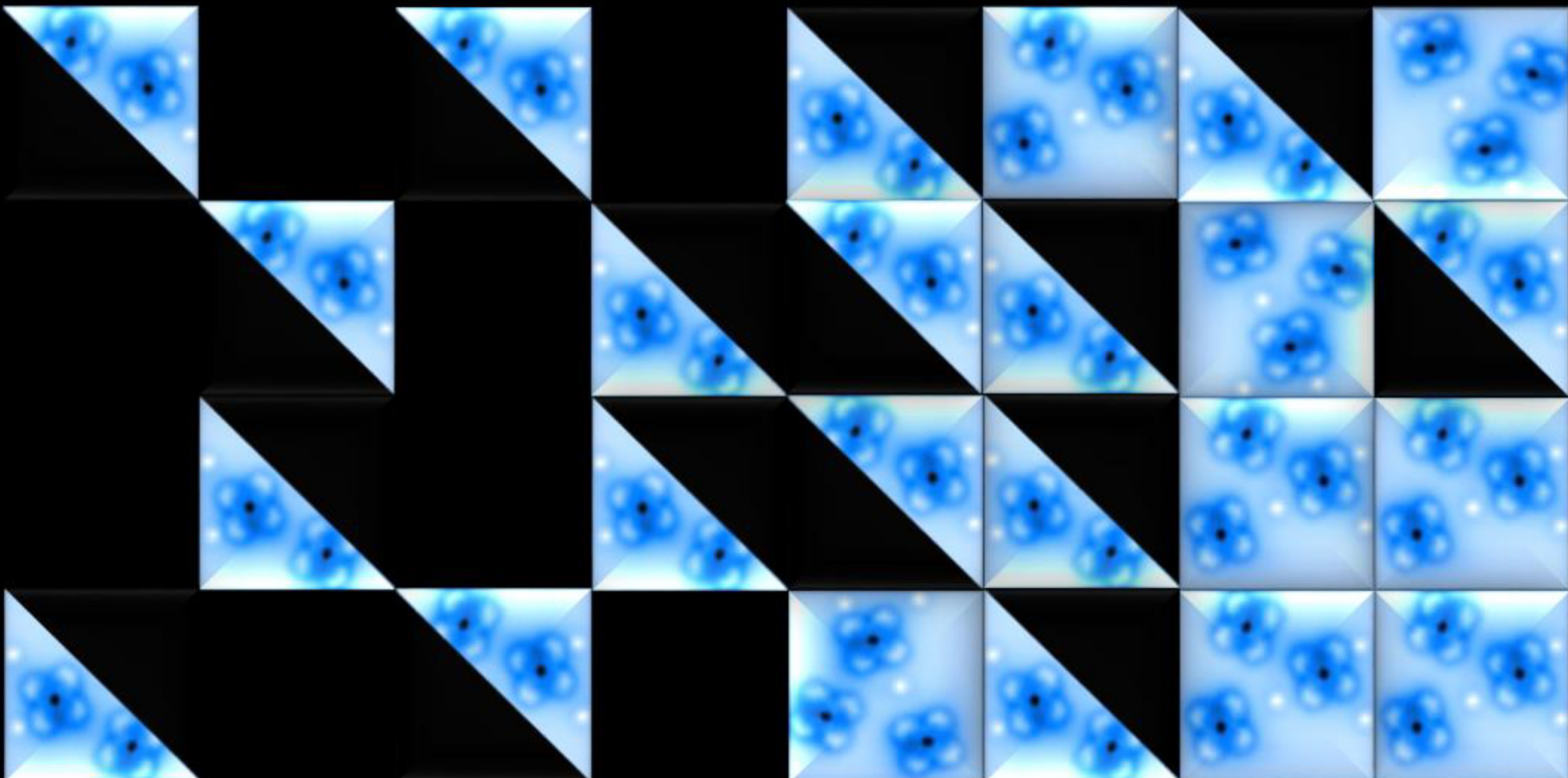


RESEARCH REPORT

Imaging and Analysis Center
PRISM



2019



A MESSAGE FROM THE DIRECTORS

Dear Friends of the PRISM Imaging and Analysis Center,

The PRISM Imaging and Analysis Center (IAC) offers high-end, state-of-the-art instrumentation and expertise for characterization of hard, soft, and biological materials to stimulate research and education at Princeton University and beyond. The IAC houses and operates a full range of instruments employing visible photons, electrons, ions, X-rays, and scanning probe microscopy for the physical examination and analysis of complex materials. With 25 years of continuous support from Princeton University, as well as the National Science Foundation, the Air Force Office of Scientific Research, the Office of Naval Research, the State of New Jersey, Industrial Companies, etc., the IAC has become the largest central facility at Princeton and a world-leader in advanced materials characterization.

A central mission of the IAC is the education, research, and training of students at Princeton University. The IAC supports more than ten regular courses annually. The award-winning course, MSE505-Characterization of Materials is conducted at the IAC for both graduate and undergraduate students. The IAC also offers a full range of training courses, which involve direct experimental demonstrations and hands-on instruction ranging from basic sample preparation, to the operation of high-end electron microscopes. The IAC's short courses have drawn over 3,500 student enrollments. Additionally, over 700 industrial scientists from more than 120 companies and 40 institutions have utilized instruments in the IAC. Our efforts have helped build bridges between Princeton and Industry that have fostered many innovations and new product developments.

Recent IAC internal users include over 300 students and researchers from more than 90 research groups. The IAC supports ~230 current research contracts worth a total of ~\$440M. In the IAC, undergraduate students are provided with the opportunity to operate various electron microscopes during class and later utilize these instruments in research for their senior thesis. The research experience provided by the IAC has helped students win many national awards including the Fannie and John Hertz Foundation Fellowship, Rhode Scholarship, the Barry M. Goldwater National Scholarship, Fulbright Scholarship, National Science Foundation Fellowship, etc.

In this report, we highlight many recent research projects conducted by our internal users, which were enabled by the IAC's facilities and expertise. These topics cover a wide range of scientific disciplines, reflecting the great diversity in research conducted at Princeton. We hope this report will encourage learning from our students and stimulate research and education in the years to come.

Thank you for your continued support and please enjoy learning about the IAC and the exciting research being carried out here at Princeton University.



Nan Yao, Director of the Imaging and Analysis Center



Craig B. Arnold, Director of PRISM

Imaging and Analysis Center

Recent IAC users include over 300 students and researchers from 18 departments and centers on campus. Undergraduates, graduate students, and post-docs are each provided with a unique opportunity to conduct research using the IAC's state-of-the-art instrumentation. Their research covers a diverse spectrum of topics including: improving photovoltaics, batteries, circuit-design, and cements; elucidating biochemical pathways, understanding the structures of biomolecular machines; and characterizing samples from aerodynamic wing models, pharmaceutical drug crystals, catalytic nanoparticles, and biofilms.



Nanomaterials

topological 2D materials, cathode coating for battery cells, lead free solder, catalysts etc.



Biomaterials

biofilms, hydrogel, dental implants, contact lenses, surgical mesh, etc.



Electronic Materials

light-emitting diodes, transistors, solar cells, etc.



Ceramics and Glasses

cement, rock, anti-corrosion coating, display panel, anti-reflection coating, etc.



Polymers

bolck copolymer, food wrap, adhesives, paints, etc.



Metal Alloys

corrosion resistance supports, turbine blades, automobile chassis, etc.

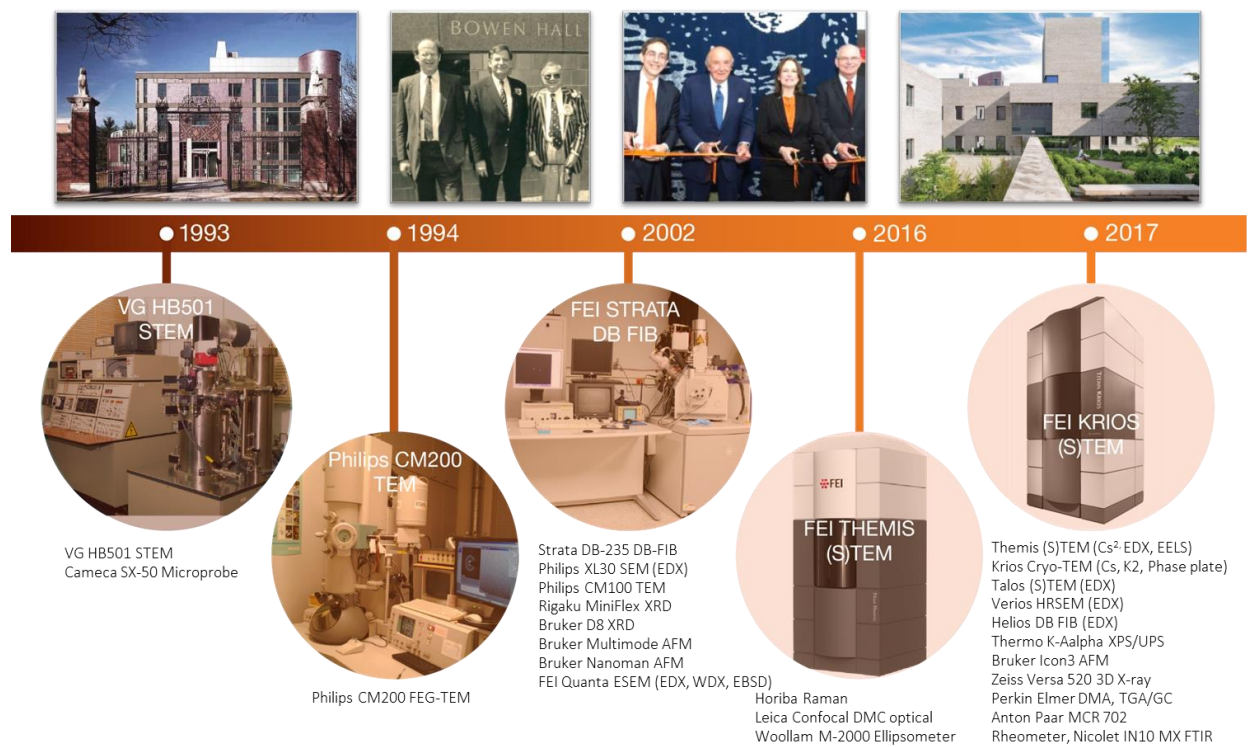


Pharmaceutical Materials

drug coating, toothpaste, molecular crystals, etc.

PRISM Imaging and Analysis Center (IAC)

IAC Background: Started in 1993 with one person, one microscope, and today has grown to seven staff and become a world-leading imaging and analysis center for the physical and life sciences.



IAC Facility layout:



* Total lab space is about 7500 sq. ft.

■ Labs/instruments ■ Supporting space

20'

IAC team members:



Nan Yao John Schreiber Paul Shao Dan McNesby Dan Gregory Yao-Wen Yeh Kevin Lamb

IAC faculty users from Princeton:

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Minjie Chen
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Chemical & Biological Eng.

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Catherine Peters
Z. Jason Ren
George Scherer
Claire White

Ecology & Evolutionary Biology

Henry Horn
David Stern

Electrical Engineering

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Claire Gmachl
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Tullis Onstott
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Bess Ward
Sarah White

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Thomas Conlan
Susan Naquin

Institute for Integrative Genomics

Elizabeth Gould
Stanislav Shvartsman

Lewis Center for the Arts

Fia Backstrom

Lewis-Sigler Institute

Joshua Shavevitz

Mechanical & Aerospace Eng.

Craig Arnold
Marcus Hultmark
Yiguang Ju
Jeremy Kasdin
Maksim Mezhericher
Wole Soboyejo
Daniel Steingart
Howard Stone

Molecular Biology

Bonnie Bassler
Zemer Gitai
Fred Hughson
Martin Jonikas
Alexei Korennykh
Sabine Petri
Jean Schwarzbauer
Nieng Yan

Physics

Robert Austin
Frank Calaprice
M. Zahid Hasan
Phuan Ong
Jason Petta
Suzanne Staggs
Paul Steinhardt
Chris Tully
Sanfeng Wu
Ali Yazdani

Plasma Physics

Andrew Carpe
Philip Efthimion
Charles Skinner
Yevgeny Raitses

Princeton Neuroscience Institute

Sebastian Seung

PRISM

Nan Yao

IAC outside users from industry and other universities:



IAC major outreach event:

natureconferences

Princeton University, PRISM, *Nature Communications*, *Nature Materials*, *Nature Structural & Molecular Biology* present:

**Princeton - Nature Conference:
Frontiers in Electron Microscopy
for the Physical and Life Sciences**

July 11-13, 2018 |
Princeton University, Princeton, NJ, USA

#fempl18
@Natureconf

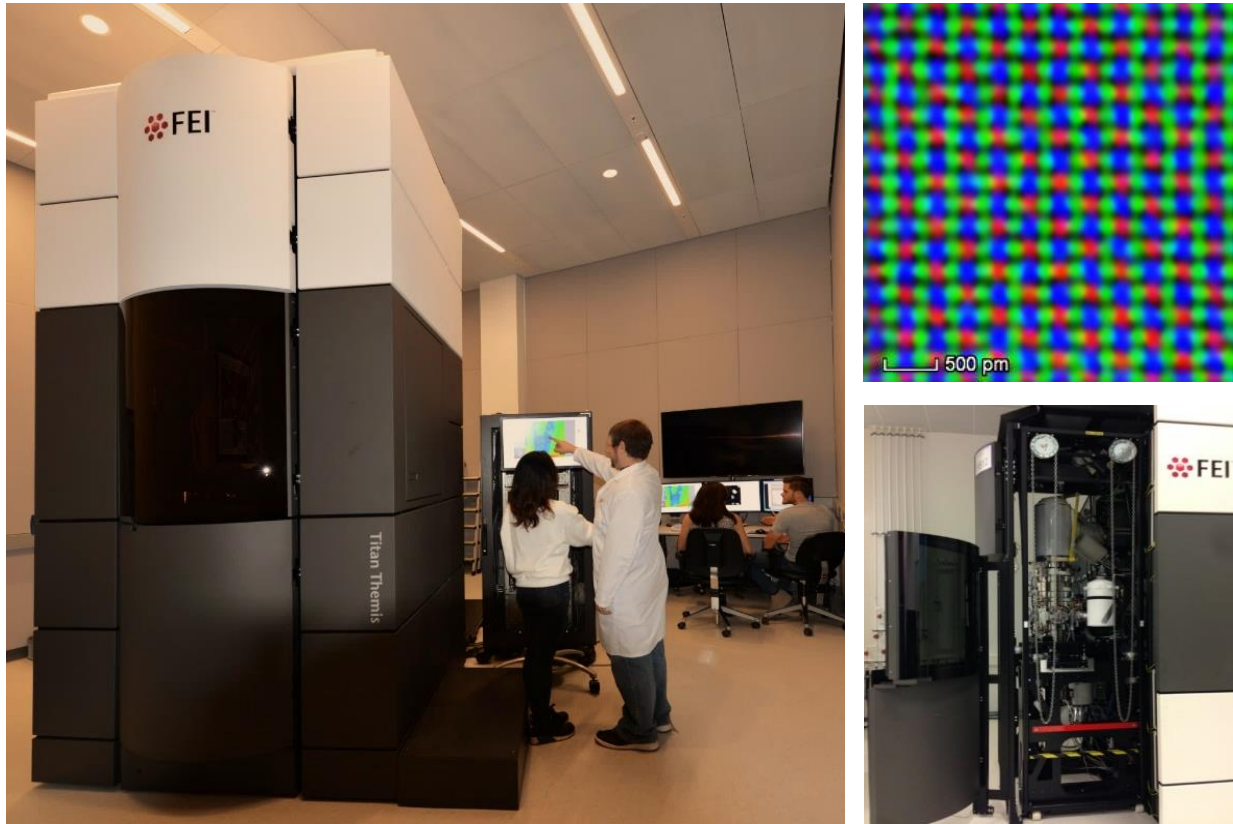
natureresearch

<https://www.nature.com/natureconferences/fempl2018/index.html>

IAC organized the inaugural Princeton-Nature Conference, a biennial international conference held at Princeton.

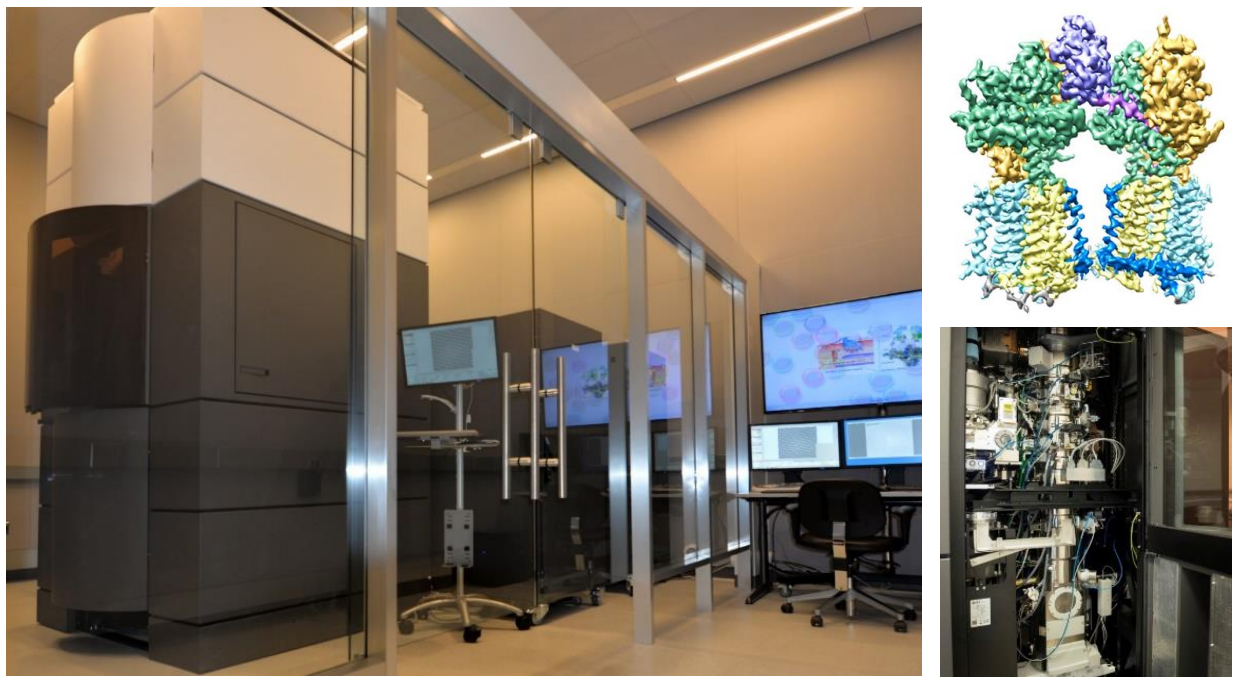
IAC new instrumentation highlights:

(1) Titan Themis Double Cs-corrected Scanning/Transmission Electron Microscope



(In operation, February 2017)

(2) Titan Krios G3 Cryo-Transmission Electron Microscope



(In operation, October 2018)

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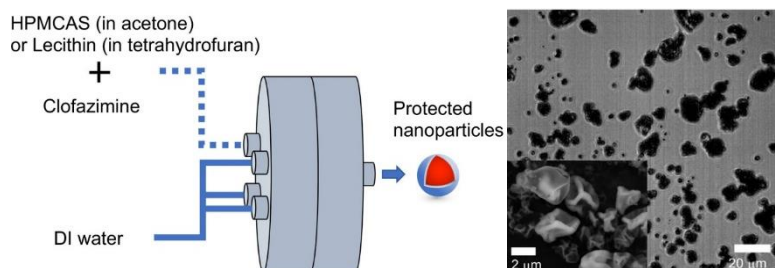
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Department of Chemical and Biological Engineering

Rapid Recovery of Clofazimine-Loaded Nanoparticles with Long-Term Storage Stability as Anti-Cryptosporidium Therapy

Jie Feng,¹ Yingyue Zhang,¹ Simon A. McManus,¹ Kurt D. Ristroph,¹ Hoang D. Lu,¹ Kai Gong,² Claire E. White,^{2,3} and Robert K. Prud'homme¹

¹Department of Chemical and Biological Engineering, ²Department of Civil and Environmental Engineering, and ³Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08544, United States



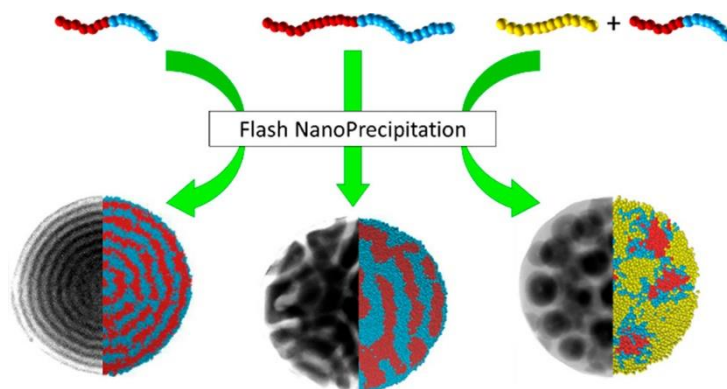
Herein we combined flash nanoprecipitation (FNP) and spray-drying as a nanofabrication platform for NP formulation and recovery without compromising the dissolution kinetics of the active ingredient. Clofazimine was chosen to be the representative drug, which has been recently repurposed as a potential treatment for cryptosporidiosis. Clofazimine was encapsulated in NPs with low-cost surface coatings, hypromellose acetate succinate (HPMCAS) and lecithin, which were required by the ultimate application to global health. Spray-drying and lyophilization were utilized to produce dried powders with good long-term storage stability for application in hot and humid climatic zones. The particle morphology, yield efficiency, drug loading, and clofazimine crystallinity in the spray-dried powders were characterized. The *in vitro* release kinetics of spray-dried NP powders were compared to analogous dissolution profiles from standard lyophilized NP samples, crystalline clofazimine powder, and the commercially available formulation Lamprene. The spray-dried powders showed a supersaturation level of up to 60 times the equilibrium solubility and remarkably improved dissolution rates. In addition, the spray-dried powders with both surface coatings showed excellent stability during aging studies with elevated temperature and humidity, in view of the dissolution and release *in vitro*. Considering oral delivery for pediatric administration, the spray-dried powders show less staining effects with simulated skin than crystalline clofazimine and may be made into minitables without additional excipients. These results highlight the potential of combining FNP and spray-drying as a feasible and versatile platform to design and rapidly recover amorphous NPs in a solid dosage form, with the advantages of satisfactory long-term storage stability, low cost, and easy scalability.

Status: published work at ACS Appl. Nano Mater. 2018, **1**, 2184-2194

Rapid Production of Internally Structured Colloids by Flash Nanoprecipitation of Block Copolymer Blends

Lorena S. Grundy,¹ Victoria E. Lee,¹ Nannan Li,¹ Chris Sosa,¹ William D. Mulhearn,¹ Rui Liu,² Richard A. Register,^{1,4} Arash Nikoubashman,³ Robert K. Prud'homme,³ Athanassios Z. Panagiotopoulos,¹ and Rodney D. Priestley^{1,4}

¹Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States; ²Ministry of Education Key Laboratory of Advanced Civil Engineering Materials, School of Materials Science and Engineering and Institute for Advanced Study, Tongji University, Shanghai 201804, China; ³Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany; ⁴Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08544, United States



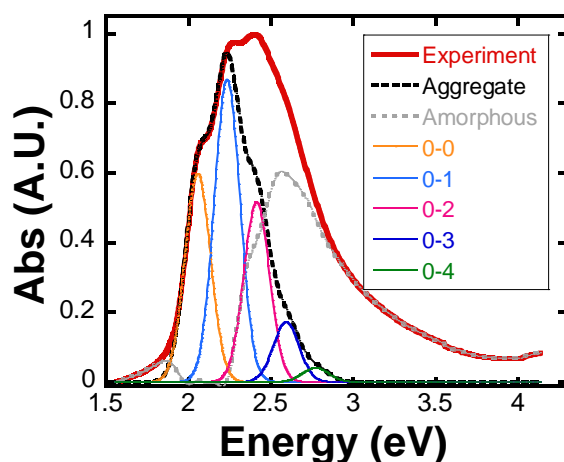
Colloids with internally structured geometries have shown great promise in applications ranging from biosensors to optics to drug delivery, where the internal particle structure is paramount to performance. The growing demand for such nanomaterials necessitates the development of a scalable processing platform for their production. Flash nanoprecipitation (FNP), a rapid and inherently scalable colloid precipitation technology, is used to prepare internally structured colloids from blends of block copolymers and homopolymers. As revealed by a combination of experiments and simulations, colloids prepared from different molecular weight diblock copolymers adopt either an ordered lamellar morphology consisting of concentric shells or a disordered lamellar morphology when chain dynamics are sufficiently slow to prevent defect annealing during solvent exchange. Blends of homopolymer and block copolymer in the feed stream generate more complex internally structured colloids, such as those with hierarchically structured Janus and patchy morphologies, due to additional phase separation and kinetic trapping effects. The ability of the FNP process to generate such a wide range of morphologies using a simple and scalable setup provides a pathway to manufacturing internally structured colloids on an industrial scale.

Status: published work at ACS Nano 2018, **12**, 4660-4668

Quantitative Assessment of Tie Chains for Charge Transport in Conjugated Polymers

Kaichen Gu¹, Chad R. Snyder², Jonathan Onorato³, Christine K. Luscombe³, August W. Bosse⁴, Yueh-Lin Loo^{1,5}

¹ Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ; ² Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD; ³ Materials Science and Engineering Department, University of Washington, Seattle, WA; ⁴ Corporate Strategic Research, ExxonMobil Research and Engineering Company, Annandale, NJ; ⁵ Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA



Owing to their chemical versatility, solution processability and compatibility with flexible substrates, conjugated polymers are promising candidates for next-generation electronic devices for sensing, display and energy applications. To understand the structural parameters that govern charge transport in these semicrystalline polymers, we applied a classical polymer-physics framework to quantitatively elucidate the effect of tie-chain connectivity on the electrical properties of a model conjugated polymer. We found a critical tie-chain fraction of 10^{-3} , below which intercrystallite connectivity limits macroscopic charge transport, and above which intracrystallite disorder is the bottleneck.¹

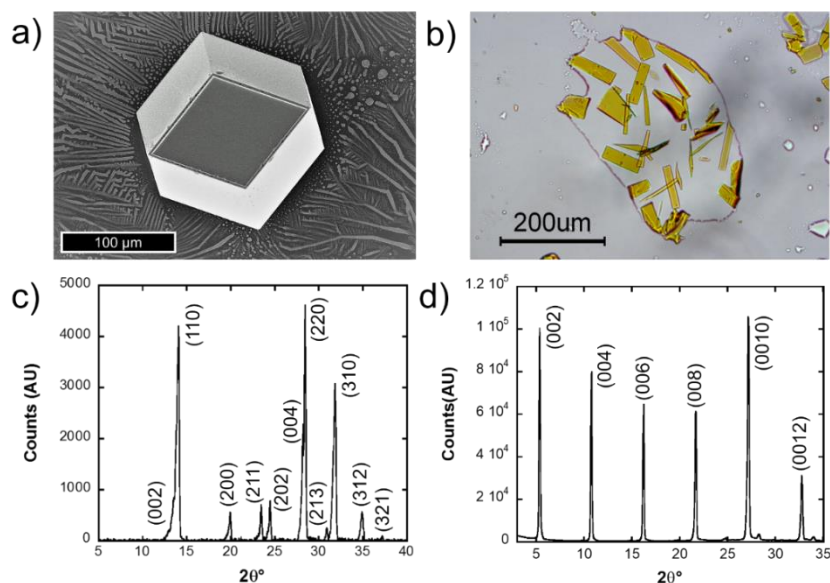
The access to a host of powerful characterization tools was critical to establish the structure-property relationships of these functional materials. In our project, we accessed the UV-VIS spectrometer to understand polymer aggregation, the differential scanning calorimeter to obtain polymer crystallite size and crystallinity, as well as the atomic force microscope to probe surface morphology.

Status: published work at ACS Macro Lett. 2018, **7**, 1333–1338.

Growth and structural characterization of hybrid organic-inorganic single crystals

J. Clay Hamill,¹ J. Schwartz,² and Yueh-Lin Loo^{1,3}

¹Department of Chemical and Biological Engineering, Princeton University, ²Department of Chemistry, Princeton University, ³Andlinger Center for Energy and the Environment, Princeton University



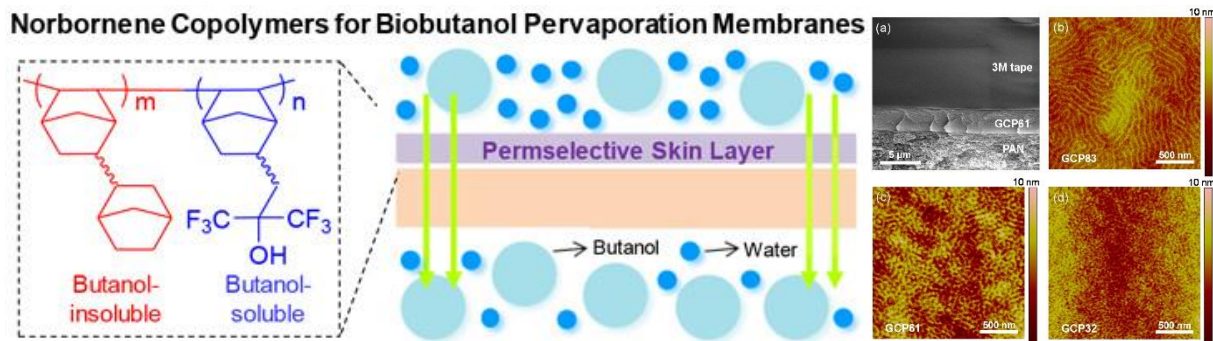
Solution-processed hybrid organic-inorganic perovskites (HOIPs) have demonstrated great promise as absorbing materials in high-efficiency, next-generation solar photovoltaics (PVs). By employing solvents with a lower electron-donating ability relative to those conventionally used to form stable inks for HOIP deposition and thin-film formation, we found a facile route to grow single crystals of the HOIP methylammonium lead iodide (a) and phenethylammonium lead iodide (b). The growth of HOIP single crystals allows the study of intrinsic properties of the material, such as photoluminescence, ferroelectricity, electronic band structure, and photoresponse.

Using the Bruker Discover D8 high-resolution X-ray diffractometer available in the Imaging and Analysis Center (IAC), we were able to obtain powder X-ray diffraction (XRD) patterns of the resulting single crystals of methylammonium lead iodide (c) and phenethylammonium lead iodide (d). When compared to calculated traces of their respective materials, the experimental diffraction patterns allowed us to verify the structure of the crystals and to determine the degree of phase purity of crystals grown by our solution-growth method. Future work further utilizes the XRD capabilities available in the IAC to determine the crystal structure and phase purity of thin-films of HOIP materials.

Status: published work at ACS Energy Lett. 2017, 3, 92–97

Vinyl Addition Copolymers of Norbornylnorbornene and Hydroxyhexafluoroisopropylnorbornene for Efficient Recovery of *n*-Butanol from Dilute Aqueous Solution via Pervaporation

Beom-Goo Kang, Dong-Gyun Kim, and Richard A. Register
Department of Chemical and Biological Engineering, Princeton University, NJ, USA



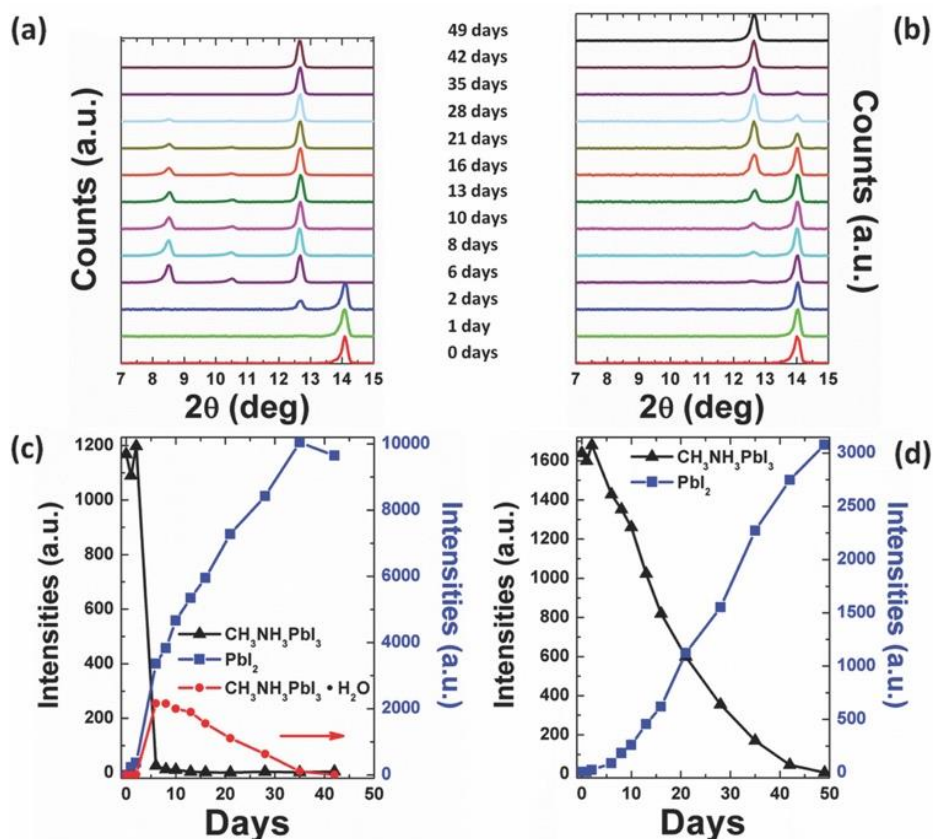
The high energy cost to recover heavier alcohols, such as *n*-butanol, from dilute aqueous solution is a significant practical barrier to their large-scale bioproduction. Membrane pervaporation offers an energy-efficient alternative, provided membrane materials can be developed which provide both good alcohol selectivity and high flux. Previous work has revealed that vinyl addition polynorbornenes bearing substituents—especially hydroxyhexafluoroisopropyl—with an affinity for *n*-butanol have potential in this application, as their high glass transition temperature allows the formation of thin but mechanically robust selective layers in thin-film composite (TFC) membranes. In the present work, we synthesize both microphase-separated gradient copolymers, and homogeneous random copolymers, of hydroxyhexafluoroisopropylnorbornene (HFANB) with norbornylnorbornene (NBANB) and evaluate their *n*-butanol/water pervaporation performance. Compared with analogous copolymers of HFANB and *n*-butylnorbornene (BuNB), the greater *n*-butanol permeability and selectivity of PNBANB vs PBU NB lead to a more-than-2-fold increase in membrane selectivity for *n*-butanol transport; the best HFANB–NBANB copolymers show *n*-butanol selectivities and fluxes which compare favorably with those of the best commercial TFC membranes, which contain cross-linked polydimethylsiloxane selective layers. Moreover, vinyl addition copolymers offer a straightforward route to further flux enhancement, simply by reducing the selective layer thickness.

Status: published work at *Macromolecules* 2018, **51**, 3702-3710

Precursor Solution Annealing Forms Cubic-Phase Perovskite and Improves Humidity Resistance of Solar Cells

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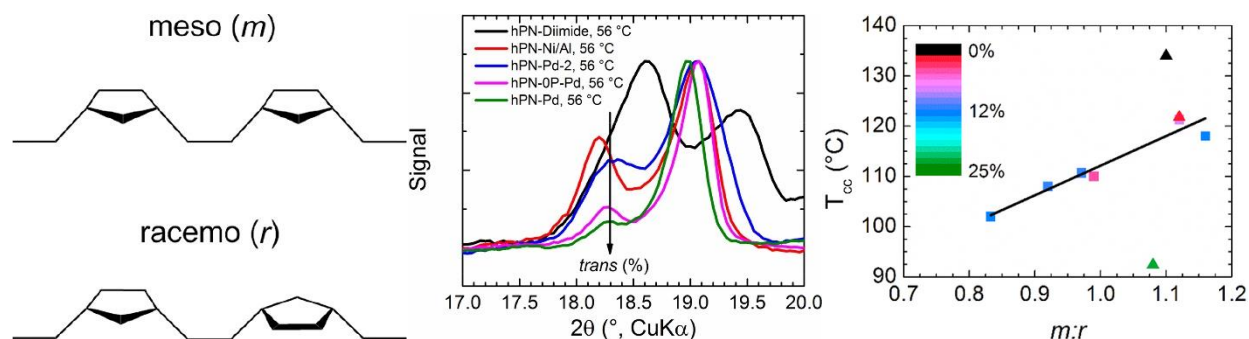
Using time-resolved wide-angle x-ray diffraction, we tracked the degradation of organic-inorganic hybrid perovskite thin films that were processed from unannealed and thermally annealed precursor solutions that are otherwise analogous. Unannealed solutions resulted in the formation of the conventional tetragonal phase that is susceptible to rapid degradation when exposed to moisture through the formation of a hydrate. Annealed solutions resulted in the thin films adopting a cubic phase that is substantially more resistant to degradation; its eventual degradation pathway to PbI_2 does not access any hydrate intermediates.

Status: published work at Adv. Func. Mater. 2018, **28**, 1801508

Tuning the phase behavior of semicrystalline hydrogenated polynorbornene via epimerization

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Hydrogenated polynorbornene (hPN) synthesized by ring-opening metathesis polymerization (ROMP) exhibits a thermoreversible change in crystal polymorph at a temperature T_{cc} below its melting point, T_m . The polymorphic transition corresponds to a sharp increase in rotational disorder around the chain axis as the temperature is increased above T_{cc} . Saturation of ROMP polynorbornene (PN) to hPN can be achieved through both catalytic and noncatalytic approaches. Here, three different hydrogenation routes were employed on the same precursor polymer: catalytic routes over either supported Pd0 or a Ni/Al complex, and noncatalytic saturation with diimide. The different hydrogenation routes result in hPNs with varying degrees of epimerization of the cyclopentylene ring (from cis to trans); these epimerized units are included in the hPN crystals. The crystal structure of the rotationally ordered hPN polymorph, observed below T_{cc} , changes sharply at low levels of epimerization and then is weakly influenced by further increases in trans content. The stability of the rotationally ordered hPN polymorph decreases with increasing epimerization, as reflected in a reduction of T_{cc} from 134 °C to 92 °C at 22% epimerization.

Status: published work at J. Polym. Sci. B. 2018, **50**, 1-8

Scalable Production of Internally-Structured and Surface-Active Polymer Colloids *via* Flash NanoPrecipitation

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¹*Department of Chemical and Biological Engineering, Princeton University, Princeton NJ, USA*

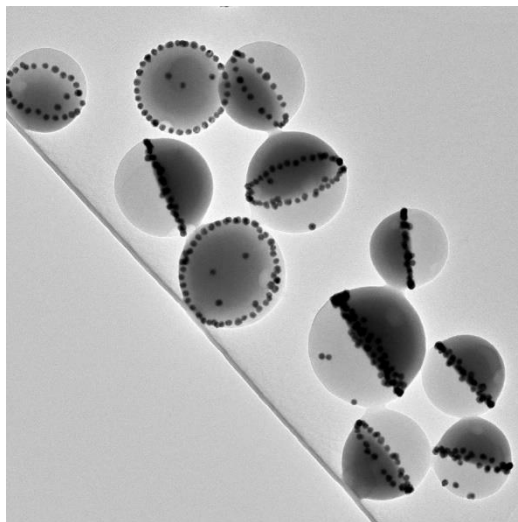


Figure: TEM image of polystyrene/polyisoprene Janus particles with gold nanoparticles selectively aligned in a ring at the polymer-polymer interface.

Production of polymer colloids with complex internal structures or anisotropic surface functionality on large scales has been a challenge which has hindered their implementation in applications from drug delivery and biosensing to oil and gas recovery. We have developed Flash NanoPrecipitation (FNP) as a scalable process which can be used to generate kilograms of such polymer colloids per day. Complex morphologies can be achieved using this low-cost equipment by taking advantage of the phase separation of chemically distinct polymers. Janus, core-shell, patchy, and lamellar morphologies have been produced by incorporating a blend of homopolymers or block copolymers into the system, and hydrophilic coronas can be generated *via* the use of amphiphilic block copolymers. Such amphiphilic Janus colloids are surface-active in oil-water mixtures and show promise as Pickering emulsion stabilizers.

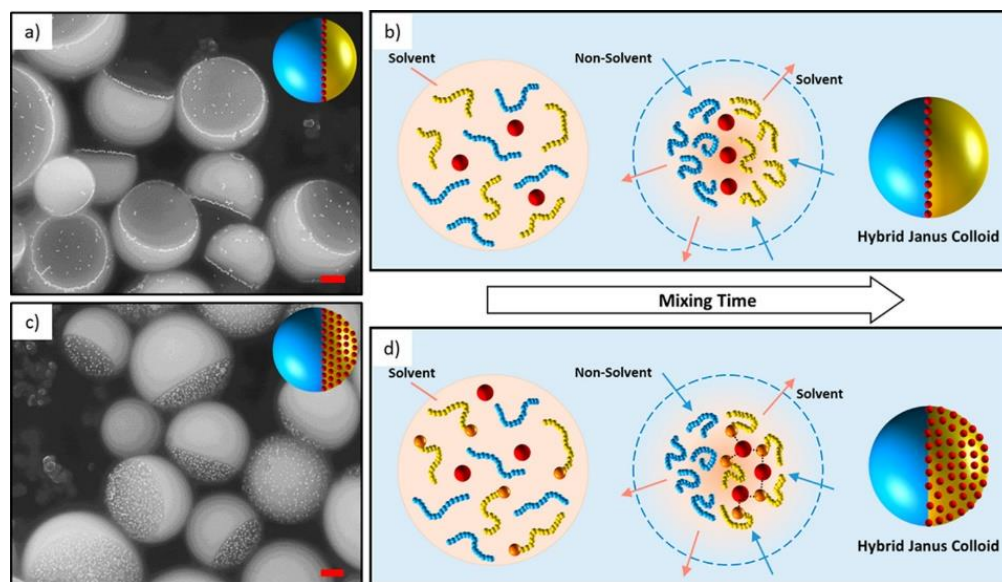
TEM allows us to analyze the colloid morphologies that are prepared with the FNP process in nanoscale detail. By selectively staining polymers and studying the colloid morphology, we gain insight into how the polymers interact with one another and the solvent environment and how the confinement of a colloid affects their behavior. The nanometer resolution of the TEM instruments in the IAC also allows us to look at the crystallinity and placement of inorganic nanoparticles incorporated into our polymeric colloids which can enable biphasic catalysis and enhanced biosensing capabilities.

Status: ongoing research project

Scalable Platform for Structured and Hybrid Soft Nanocolloids by Continuous Precipitation in a Confined Environment

Victoria E. Lee,¹ Chris Sosa,¹ Rui Liu,³ Robert K. Prud'homme,¹ and Rodney D. Priestley^{1,2}

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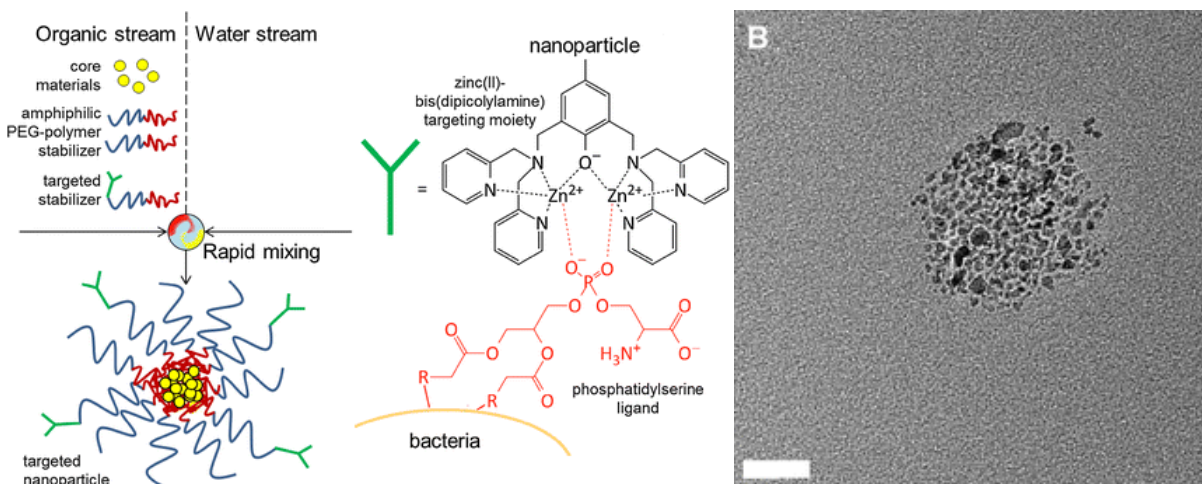
Geometrically structured polymer nanocolloids, including Janus nanocolloids, have been widely investigated for their unique properties, which are derived from their anisotropy. Controlled surface decoration with inorganic nanoparticles could induce another level of functionality into structured nanocolloids that could enable applications in fields ranging from rewriteable electronics to biphasic catalysis. Here, we demonstrate flash nanoprecipitation (FNP) as a one-step, scalable process platform for manufacturing hybrid polymer–inorganic nanocolloids in which one phase is selectively decorated with a metal nanocatalyst by tuning the molecular interactions between the feed ingredients during the process. For instance, by modifying the polymer end-group functionality, we document the ability to tune the location of the metal nanocatalyst, including placement at the nanocolloid circumference. Moreover, the addition of molecular additives is shown to transform the Janus nanocolloid structure from spherical to dumbbell or snowman while maintaining the ability to control the nanocatalyst location. In considering the flexibility and continuous nature of the FNP process, it offers an industrial-scale platform for the manufacturing of nanomaterials that are anticipated to impact many technologies.

Status: published work at *Langmuir* 2017, **33**, 3444–3449

Nanoparticle Targeting of Gram-Positive and Gram-Negative Bacteria for Magnetic-Based Separations of Bacterial Pathogens

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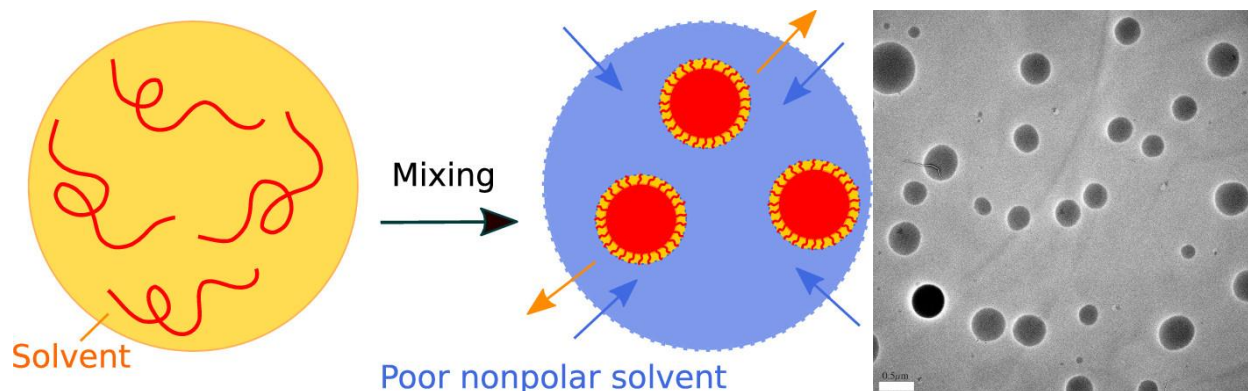
Antimicrobial resistance is a healthcare problem of increasing significance, and there is increasing interest in developing new tools to address bacterial infections. Bacteria-targeting nanoparticles hold promise to improve drug efficacy, compliance, and safety. In addition, nanoparticles can also be used for novel applications, such as bacterial imaging or bioseparations. We here present the use of a scalable block-copolymer-directed self-assembly process, Flash NanoPrecipitation, to form zinc(II)-bis(dipicolylamine) modified nanoparticles that bind to both Gram-positive and Gram-negative bacteria with specificity. Particles have tunable surface ligand densities that change particle avidity and binding efficacy. A variety of materials can be encapsulated into the core of the particles, such as optical dyes or iron oxide colloids, to produce imageable and magnetically active bacterial targeting constructs. As a proof-of-concept, these particles are used to bind and separate bacteria from solution in a magnetic column. Magnetic manipulation and separation would translate to a platform for pathogen identification or removal. These magnetic and targeted nanoparticles enable new methods to address bacterial infections.

Status: published work at *Appl. Nanosci.* 2017, **7**, 83-93

On the Stability of Polymeric Nanoparticles Fabricated through Rapid Solvent Mixing

Tatiana I. Morozova,¹ Victoria E. Lee,² Athanassios Z. Panagiotopoulos,² Robert K. Prud'homme,² Rodney D. Priestley,² Arash Nikoubashman¹

¹*Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany,* ²*Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States*



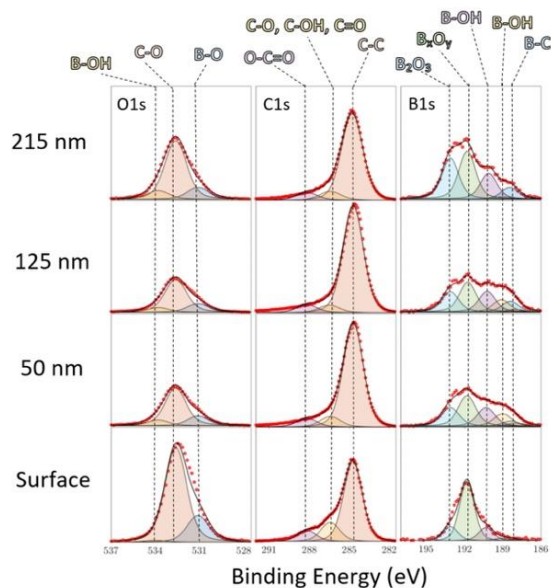
We study the stability of polymeric nanoparticles fabricated through the rapid mixing of polymers in a good solvent with a poor solvent that is miscible with the good solvent. In previous experiments where water was used as the poor solvent, a negative surface charge was measured on the precipitated nanoparticles, which led to the long-time stability of the dispersion. It was argued that these charges originate presumably from either water or hydroxide adsorption at the hydrophobic nanoparticle surface or from impurities in the feed streams that preferentially adsorb on the precipitated nanoparticles. To elucidate the origin of this stabilization mechanism, we performed experiments wherein we replaced water with a nonpolar poor solvent. The polymers aggregated into stable nanoparticles for a range of processing parameters. We investigated theoretically three possible explanations for this stability, i.e., electrostatic stabilization, conditional thermodynamic equilibrium, and steric stabilization. Our experiments and considerations suggest that steric stabilization is the most likely candidate.

Status: published work at *Langmuir* 2019, **35**, 709-717

Chemical Changes Induced by Ion and Cluster Depth Profiling of Boronized Graphite

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HR-XPS signal evolution with depth after 1 keV, high current ion sputtering.

Understanding plasma-materials interactions is an integral part of improving the performance of magnetic confinement devices such as tokamaks. The elemental and chemical state of the top 250-300 nm of a boronized ATJ graphite tile sample from the NSTX-U tokamak was measured with high-resolution X-ray photoelectron spectroscopy (HR-XPS) at the IAC. Depth profiling was performed by sputtering the sample with monatomic argon ions and argon gas cluster ions from a MAGCIS™ source. Depth profiling with monatomic argon ions was found to significantly alter the chemical state of the NSTX-U samples. Atomic concentrations from XPS analysis measured by cluster ion sputtering showed higher oxygen concentrations by a factor of two and higher boron concentrations by up to 1.5 times than with monatomic ion sputtering. The preferential removal of oxygen by monatomic argon ion sputtering resulted in the growth of new features at low binding energies in the B1s XPS spectra as boron-oxygen bonding was reduced. This artifact, indicating less B-O bonding, obscures boron's performance as an oxygen getter and its subsequent chemistry in erosion, redeposition, and hydrogen retention in tokamak environments.

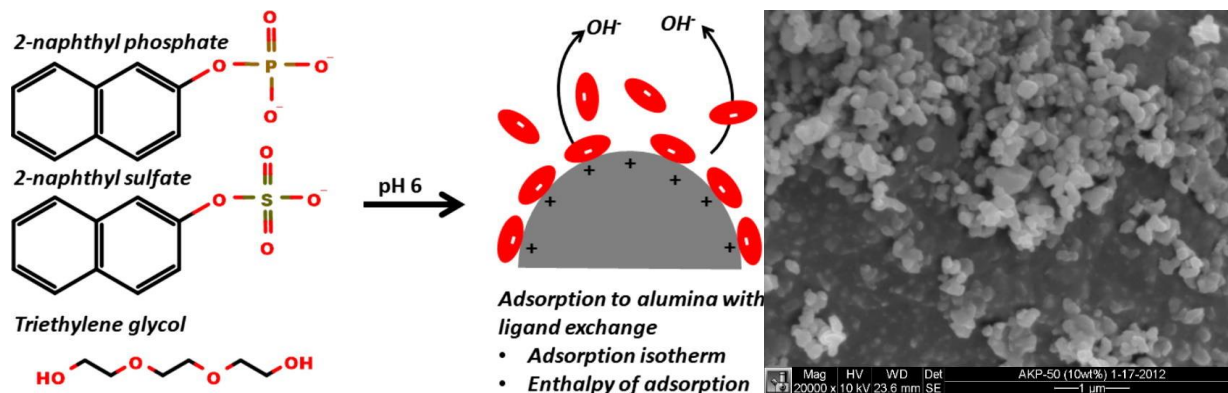
Status: ongoing research project

Adsorption Characteristics of Charged and Nonionic Small Molecules to Colloidal Alumina

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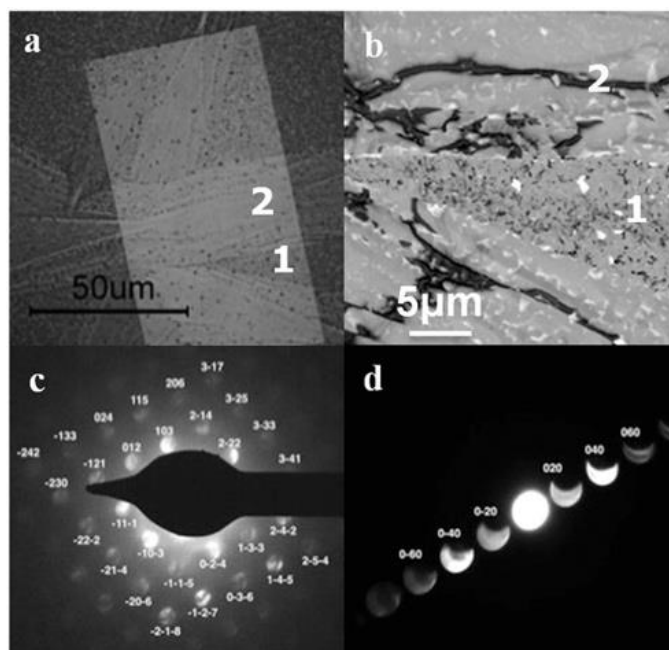
Dense fluorescent pigments used for inkjet printing of UV and IR-readable non-photobleaching security features require stabilizers to prevent aggregation/sedimentation and inkjet head clogging at high resolution. A study of small molecule adsorption to α -alumina, a model system for security pigments, is presented. Alumina is dispersed by two methods yielding different zeta potentials but identical isoelectric points. Essentially complete dispersion is obtained in water at pH 3 but aggregation occurs at pH 6 where the surface charging is lower. Adsorption studies focus on the naphthyl-phosphate, -sulfate, and hydroxyl (triethylene glycol) groups. Phosphate adsorption was strongest with a 1.2 molecules/nm² plateau, close to the titratable exchange capacity of 1.3 OH groups/nm² on the alumina surface with $\Delta H_{\text{adsorption}} = -7.58 \pm 1.63$ kJ/mol determined by calorimetry. Sulfate adsorption was weaker with a more linear adsorption isotherm. The adsorption/exchange process yields a rise in pH that is correlated with the binding strength. Hydroxyl binding is weakest, being driven by hydrogen bonding, and showed no rise in pH during adsorption. A polyphosphate-poly (ethylene glycol) block copolymer is expected to be advantageous for the dispersion of such inkjet colloids.

Status: published work at J. Coll. Int. Sci. 2018, **512**, 29-38

Polymorphic Transformations in Core-Chlorinated Naphthalene Diimide Thin Films

Geoffrey E. Purdum¹, Nan Yao², Arthur Woll³, Thomas Gessner⁴, R. Thomas Weitz⁴ and Yueh-Lin Loo^{1,5}

¹Department of Chemical and Biological Engineering, Princeton University, Princeton NJ, USA; ²Princeton Institute for Science and Technology of Materials, Princeton University, Princeton NJ, USA; ³Cornell High Energy Synchrotron Source, Cornell University, Ithaca NY, USA; ⁴BASF SE, Ludwigshafen, Germany; ⁵Andlinger Center for Energy and the Environment, Princeton University, Princeton NJ, USA

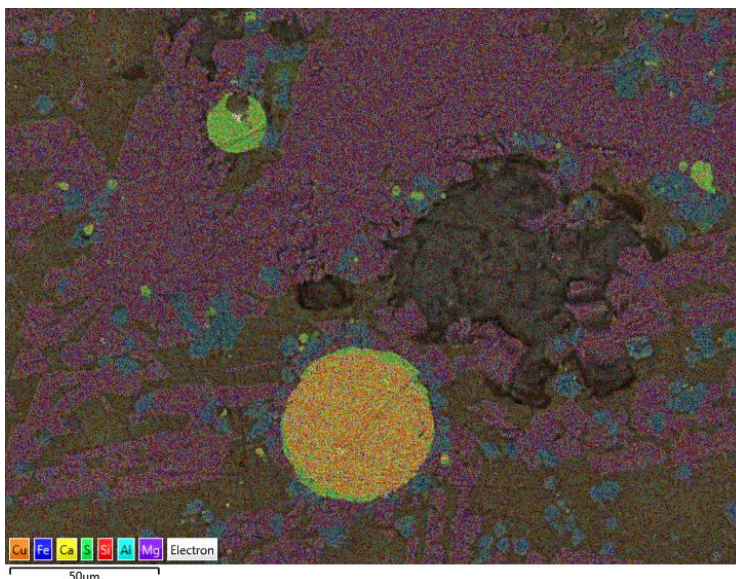


A molecular semiconductor of core-chlorinated naphthalene tetracarboxylic diimide, relevant as active channels in organic thin-film transistors, exhibit independent crystal structures of the monoclinic and triclinic forms. In polycrystalline thin films, these forms are reversibly accessed through post-deposition annealing. Figure (a) above shows an optical micrograph of a thin film of this material, with 1 and 2 denoting the triclinic and monoclinic forms, respectively, with (b) showing a bright-field transmission electron micrograph of the same film, capturing its polymorphic transformation from the triclinic to the monoclinic forms. Figures (c) and (d) are selected-area electron diffraction patterns obtained from regions 1 and 2, with reflections indexed to the triclinic and monoclinic crystal structures, respectively. Given the molecular packing in the triclinic crystal structure, it exhibits smaller in-plane charge transport anisotropy compared to the monoclinic form. This study implicates the importance of understanding packing polymorphs and their associated transformation in maximizing charge transport in polycrystalline thin films.

Status: published work at *Adv. Func. Mater.* 2016, **26**, 2357, 2016; featured on inside cover.

From Slags to Riches: Using Materials Characterization Methods to Investigate Changes in Japanese Copper Smelting from 700 to 2000 C.E.

Rachel S. Selinsky¹, Farhat Alam^{5*}, Alex Jiang^{2*}, Howard Stone³, Nan Yao⁶, Thomas Conlan⁴
¹Departments of Chemical and Biological Engineering, ²Molecular Biology, ³Mechanical and Aerospace Engineering, & ⁴East Asian Studies and History, Princeton University Princeton, NJ, USA; ⁵Department of Materials Science & Engineering, University of California, Berkeley, Berkeley, CA, USA; ⁶Princeton Institute for the Science and Technology of Materials, Imaging and Analysis Center, Princeton University, Princeton, NJ, USA.* Undergraduate researchers



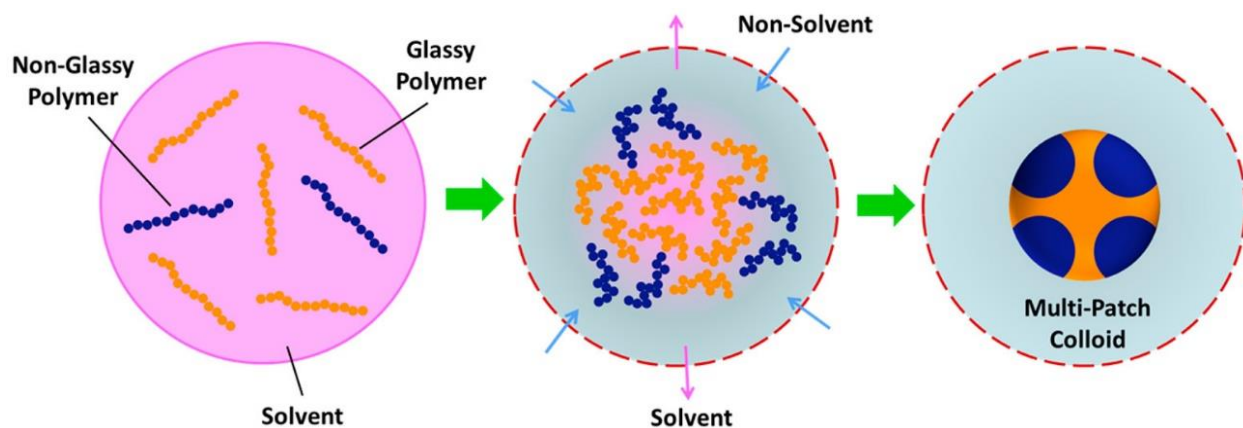
Copper slag, the impurities that float to the top when copper ore is smelted, are undesirable by-products that have been unceremoniously discarded over centuries of copper refining. However, the chemical composition and physical characteristics of this rocky refuse result directly from the smelting process undergone. The Japanese copper mine at Naganobori operated, largely continuously, from the 8th to 20th centuries. We have obtained accurately dated copper slag samples over the full time range. Working at the intersection of history and materials science, we utilized materials characterization techniques including X-ray fluorescence spectrometry (XRF), Raman spectroscopy, and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX, as shown above for a Naganobori copper slag sample from the early 15th century) on these copper slag samples to elucidate understanding of the conditions under which they were smelted. The project is the result of an David A. Gardiner '69 Magic Project Humanities Innovation Grant: *The Story of Slag: Creating a Chronology of Copper Smelting for Japan 700-2000*, that was awarded to Thomas Conlan, Howard Stone, and Nan Yao for the 2018-2019 academic years.

Status: published work at Research at Princeton 2018-2019 (2019) 14

Combining Precipitation and Vitrification to Control the Number of Surface Patches on Polymer Nanocolloids

Chris Sosa,¹ Victoria E. Lee,¹ Lorena S. Grundy,¹ Mary J. Burroughs,¹ Rui Liu,² Robert K. Prud'homme,¹ and Rodney D. Priestley^{1,3}

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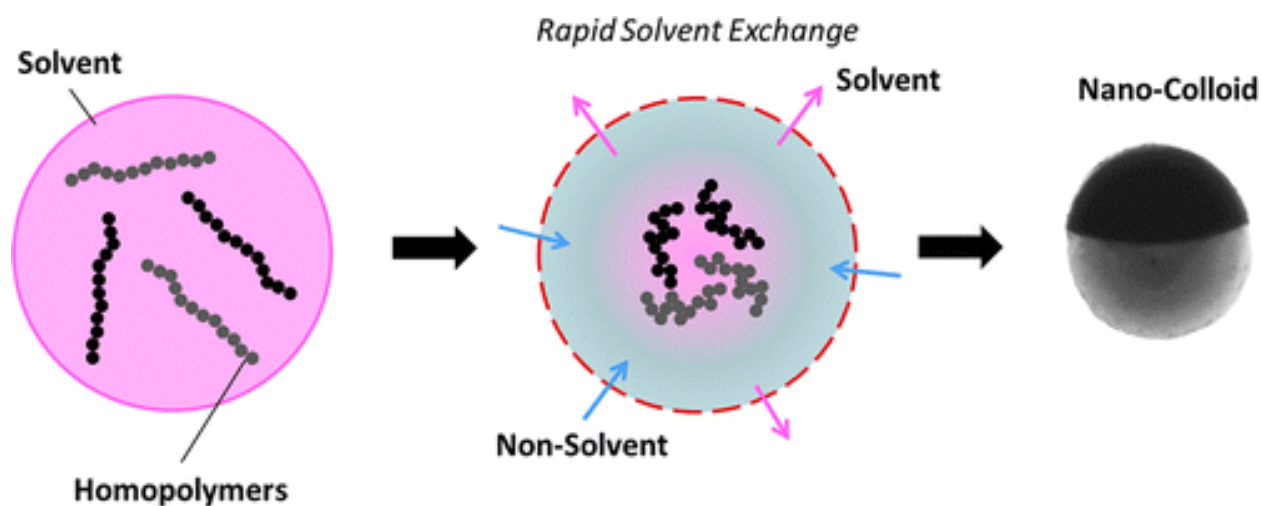
In an effort to incorporate increasingly higher levels of functionality into soft nanoparticles, heterogeneously structured particles stand out as a simple means to enhance functionality by tailoring only particle architecture. Various means exist for the fabrication of particles with specific structural configurations; however, the tunability of particle morphology is still a challenging and often laborious task, especially in self-assembled systems where a single equilibrium configuration dominates. Improved strategies for multipatch particle assembly are therefore needed to allow for the tailoring of particle structure via a single, continuous assembly route. One means of accomplishing this is through kinetic trapping of particle morphologies along the path to the final equilibrium configuration in precipitation-induced, phase-separating polymer blends. Here, we demonstrate this capability by using rapid nanoprecipitation to control the overall size, composition, and patch distribution of soft colloids. In particular, we illustrate that polymer feed concentration, blend ratio, and polymer molecular weight can all serve as functional handles with which to consistently alter particle patch distributions in a self-assembling homopolymer system without redesigning the starting materials. We furthermore delineate the role of polymer vitrification in the determination of particle structure.

Status: published work at Langmuir 2017, **33**, 5835-5842

Soft Multifaced and Patchy Colloids by Constrained Volume Self-Assembly

Chris Sosa[†], Rui Liu[†], Christina Tang[†], Fengli Qu^{†‡}, Sunny Niu[†], Martin Z. Bazant^{§||}, Robert K. Prud'homme^{*†}, and Rodney D. Priestley^{*† ⊥}

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Soft colloidal particles with multiple surface patches of differing composition are critical to the development of complex macroscopic structures that can serve as interfacial catalysts, macroscale surfactants, electronically responsive materials, and drug delivery vehicles. Here, we present a continuous process for the scalable formation of soft colloidal particles with multiple surface domains that employs well-established principles of polymer precipitation and phase separation to controllably shape particle architectures. Our results illustrate the broad range of particle morphologies, including Janus and Cerberus structures, and surface compositions accessible to our versatile solution-based assembly system. We also identify polymer diffusion, precipitation, and vitrification as the primary determinants of particle structure for the first time.

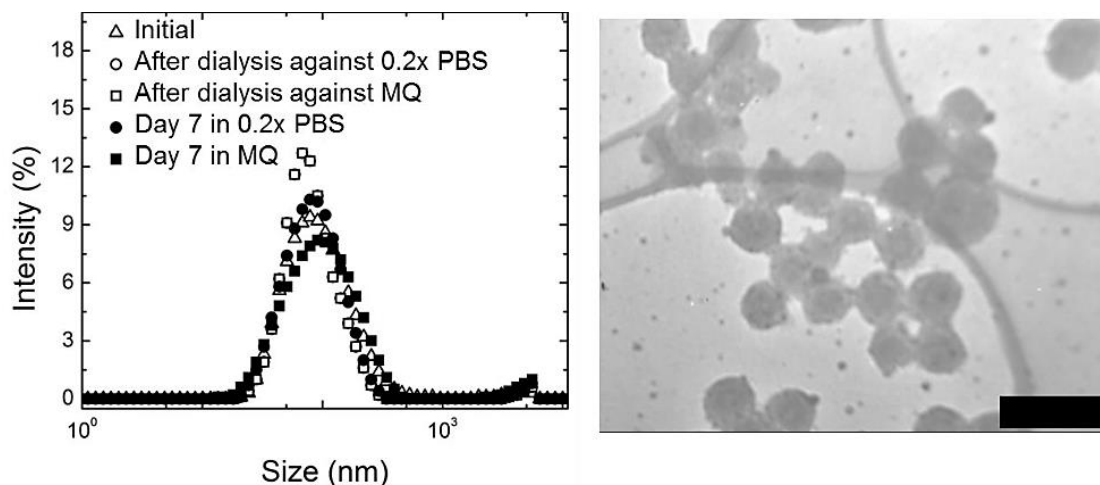
Status: published work at *Macromolecules* 2016, **49**, 3580-3585

Preparation of PEGylated Iodine-Loaded Nanoparticles via Polymer-Directed Self-Assembly

Christina Tang,^{1,2} Adam W. York,² John L. Mikitsh,³ Alexander C. Wright,³ Ann-Marie Chacko,³ Drew R. Elias,⁴ Yaodong Xu,⁴ Heng-Keang Lim,⁴ Robert K. Prud'homme²

¹Department of Chemical and Life Science Engineering Virginia Commonwealth University Richmond, VA 23284 USA; ²Department of Chemical and Biological Engineering Princeton University Princeton, NJ 08544 USA;

³Department of Radiology Division of Nuclear Medicine and Clinical Molecular Imaging University of Pennsylvania Perelman School of Medicine Philadelphia, PA 19104 USA; ⁴Janssen Research & Development LLC Spring House, PA



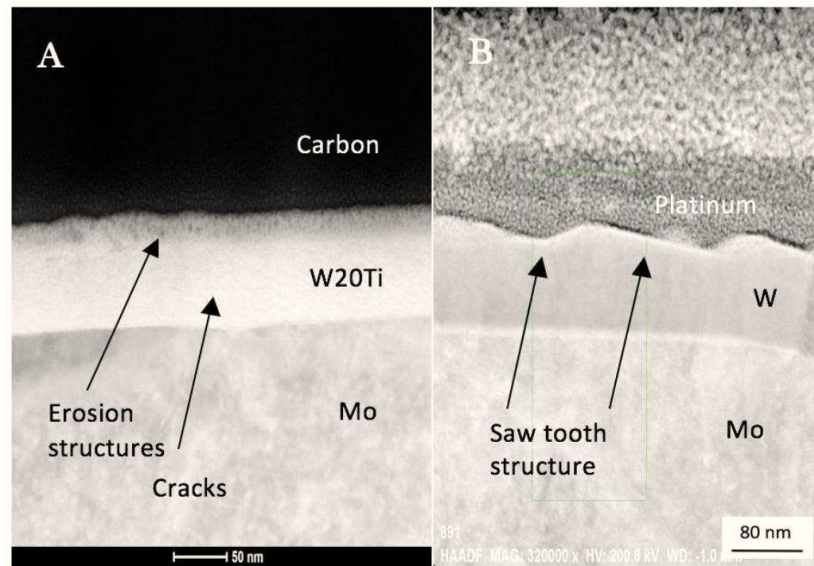
The preparation of size-tunable PEGylated, iodine-loaded nanoparticles is investigated for biomedical applications. Di-iodination of polyvinyl phenol and encapsulation of the iodinated polymer via directed self-assembly with an amphiphilic polyethylene glycol-based diblock copolymer are reported. Nanoparticles with iodine loadings up to 45 wt% are achieved using a rapid, scalable process. The size of the nanoparticles can be readily tuned between 35 and 130 nm by increasing the ionic strength of the antisolvent used during nanoparticle self-assembly. The resulting PEGylated iodine-loaded nanoparticles have potential applications in nanomedicine for 1) quantitative biodistribution analysis via inductively coupled plasma mass spectrometry (ICP-MS) or 2) X-ray contrast in biomedical imaging. For quantitative biodistribution studies using ICP-MS, a limit of detection of $2 \mu\text{g mL}^{-1}$ in mouse serum is achieved. For biomedical imaging, the X-ray attenuation rates are comparable to currently commercially available iodine-based contrast agents. Therefore, encapsulation of the iodinated polymer enables formulation of trackable, size tunable nanoparticles as a versatile platform for developing nanomedicines.

Status: published work at *Macromol. Chem. and Phys.* 2018, **219**, 1700592.

Deuterium and Helium Ion Irradiation of Nanograined Tungsten and Tungsten-Titanium Alloy Materials

Meagan Yeh and Bruce E. Koel

Class of 2018, Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA



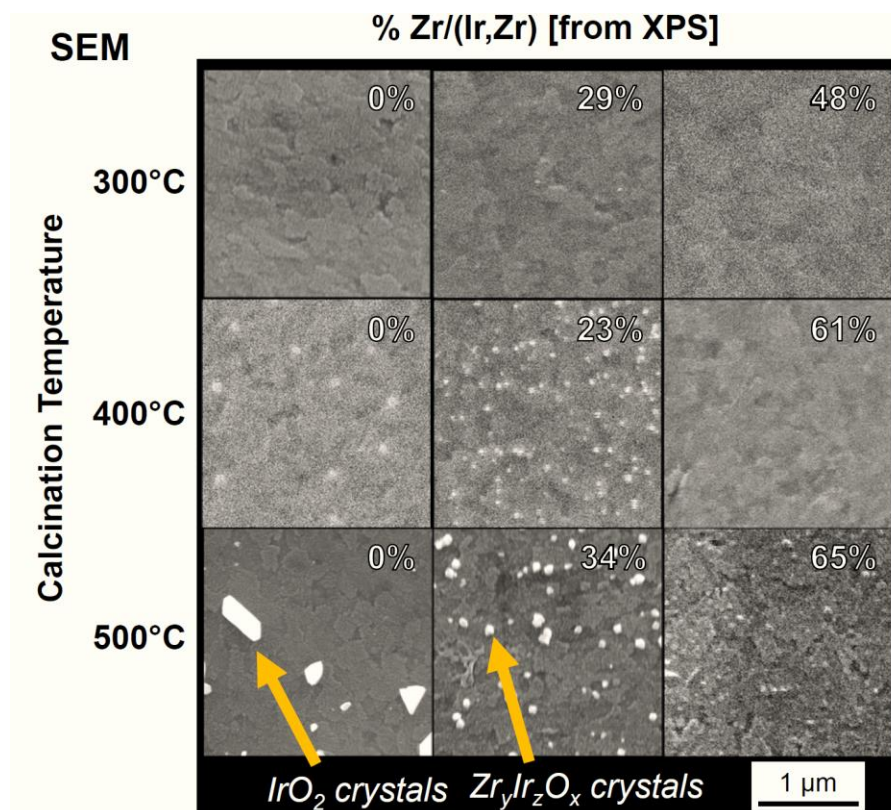
Tungsten has long been considered a primary candidate for the plasma-facing components of nuclear reactors due to its favorable thermal and mechanical properties such as high melting temperature, low erosion yield, and low fuel retention. It will be used in the divertor region of the International Thermonuclear Experimental Reactor (ITER). However, irradiation with energetic particles makes tungsten susceptible to cracks, blisters, bubbles, and other morphological changes. This thesis aimed to investigate two new materials, nanograined tungsten and a nanograined tungsten-titanium alloy, for potential use as plasma-facing materials by analyzing their deuterium and helium retention and morphological changes after plasma exposure. It was found that after plasma irradiation, nanograined tungsten had smaller blisters, was less prone to fuzz formation, and retained less helium than common polycrystalline tungsten. Additionally, a nanograined tungsten-titanium alloy showed a lower concentration of blisters on its surface than pure tungsten. Further research involving bulk samples rather than thin films and a broader range of plasma irradiation conditions is needed in order to accurately assess the capabilities of nanograined tungsten and nanograined tungsten-titanium alloys as plasma-facing materials.

Status: undergraduate senior thesis

Synthesis, physical, and electrochemical characterization of IrO₂-ZrO₂ electrocatalysts for the oxygen evolution in acidic media

Edward Zhang, Rachel Selinsky, Xiaofang Yang, and Bruce Koel

Class of 2019, Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA



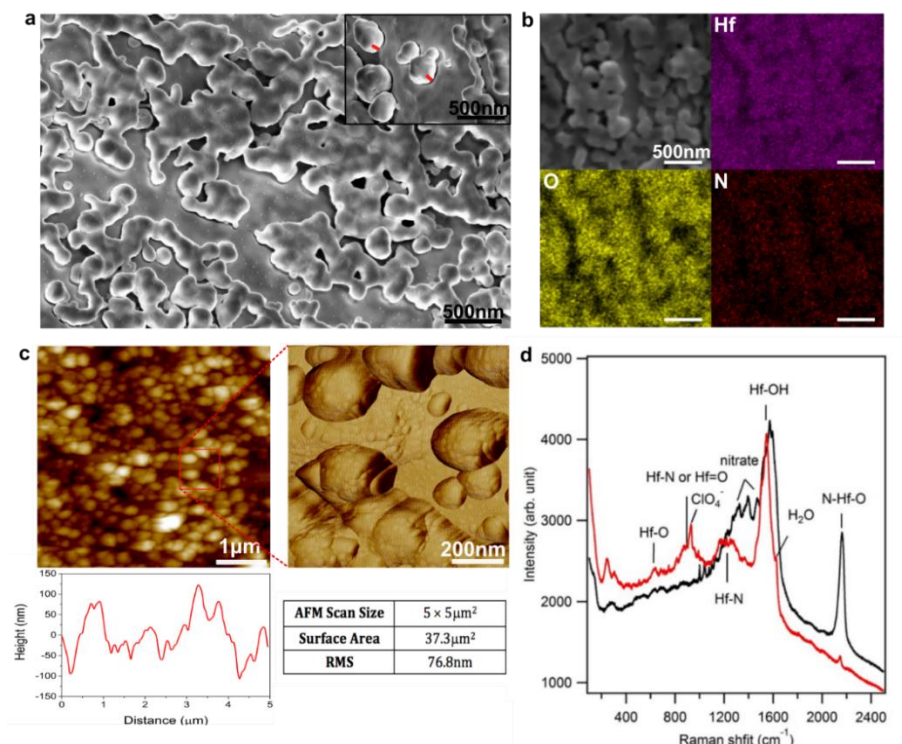
The kinetically sluggish oxygen evolution reaction (OER) is the limiting factor for the efficiency of water electrolyzers, requiring highly active and expensive catalysts such as iridium oxide. We are examining the properties of zirconium-iridium mixed oxides as OER catalysts. Electrochemical techniques such as cyclic voltammetry and chronopotentiometry are applied to determine the catalytic activity and stability of these materials in acidic conditions. To gain insights into the electronic, morphological, and structural changes at the catalyst surface, we use techniques such as XPS, SEM, EDX, XRD, and operando Raman spectroscopy. These insights will speed up progress in the rational design of highly efficient, cost-effective, and durable OER catalysts.

Status: undergraduate senior thesis

N₂-Plasma Treated Hafnium Oxyhydroxide as an Efficient Acid-Stable Electrocatalyst for Hydrogen Evolution and Oxidation Reactions

Xiaofang Yang¹, Fang Zhao², Yao-Wen Yeh³, Rachel S. Selinsky¹, Zhu Chen¹, Nan Yao³, Christopher G. Tully², Yiguang Ju⁴ and Bruce E. Koel¹

¹Department of Chemical and Biological Engineering, ²Department of Physics, ³Princeton Institute for Science and Technology of Materials (PRISM), ⁴Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA



Surface characterization of a HfN_xO_y film on a roughened Au surface by SEM and AFM. Prof. Koel group reports that hafnium oxyhydroxide with incorporated nitrogen by treatment using an atmospheric N₂ plasma demonstrates unprecedented high catalytic activity and stability for both HER and HOR in strong acidic media for earth-abundant materials. a, SEM image after electrochemical measurements (250 CV scans, -0.2-1.3 V) for HER/HOR in H₂-purged 0.1 M HClO₄. Inset: 45°-tilted SEM image of the surface revealing surface morphology; height of the structures marked by red lines are 120 nm. b, SEM image and corresponding EDX images for Hf, O, and N; scale bars are 300 nm. c, AFM mapping showing (top left) a topography image, and (top right) a phase image of the red square area, and (lower left) line scan. An inset provides a table for the root mean square (RMS) roughness. d, the Raman spectrum for HfN_xO_y before (bottom or red spectra) and after (top or black spectra) electrochemical measurement in acidic media.

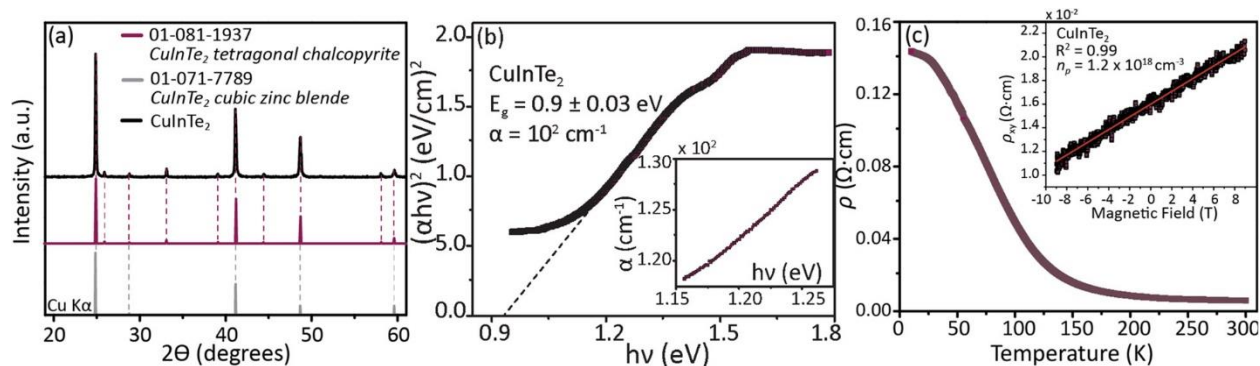
Status: accepted work at Nature Communications 2019

Department of Chemistry

Single-Crystal Growth and Characterization of the Chalcopyrite Semiconductor CuInTe₂ for Photoelectrochemical Solar Fuel Production

Jessica J. Frick¹, Andreas Topp², Sebastian Klemenz¹, Maxim Krivenkov³, Andrei Varykhalov³, Christian R. Ast², Andrew B. Bocarsly¹, and Leslie M. Schoop¹

¹Department of Chemistry, Princeton University, Princeton, NJ, USA, ²Max Planck Institute for Solid State Research, Stuttgart, Germany, ³Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

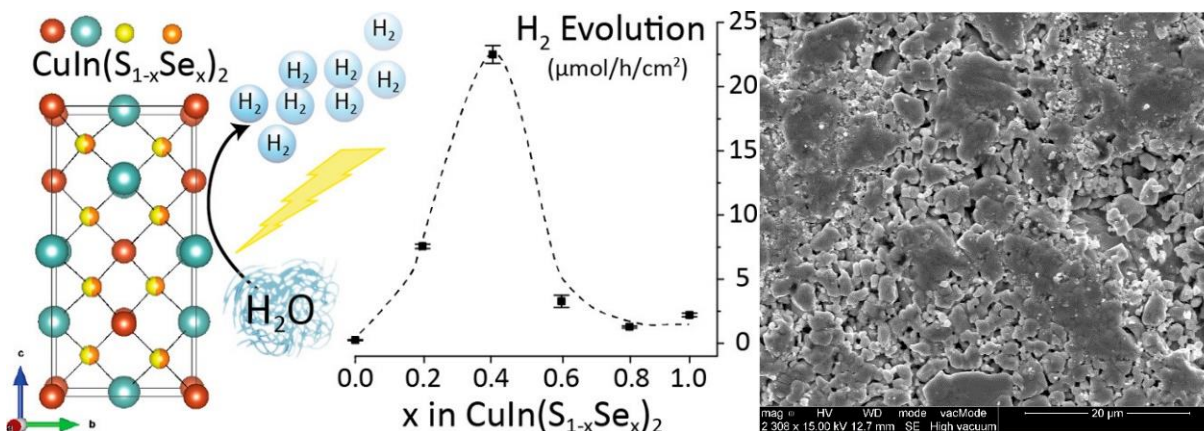


Transition-metal chalcogenides are a promising family of materials for applications as photocathodes in photoelectrochemical (PEC) H₂ generation. A long-standing challenge for chalcopyrite semiconductors is characterizing their electronic structure, both experimentally and theoretically, because of their relatively high-energy band gaps and spin-orbit coupling (SOC), respectively. In this work, we present single crystals of CuInTe₂, whose relatively small optically measured band gap of 0.9 ± 0.03 eV enables electronic structure characterization by angle-resolved photoelectron spectroscopy (ARPES) in conjunction with first-principles calculations incorporating SOC. ARPES measurements reveal bands that are steeply dispersed in energy with a band velocity of $2.5\text{--}5.4 \times 10^5$ m/s, almost 50% of the extremely conductive material graphene. Additionally, CuInTe₂ single crystals are fabricated into electrodes to experimentally determine the valence band edge energy and confirm the thermodynamic suitability of CuInTe₂ for water redox chemistry. The electronic structure characterization and band edge position presented in this work provide kinetic and thermodynamic factors that support CuInTe₂ as a strong candidate for water reduction.

Status: published work at J. Phys. Chem. Lett. 2018, **9**, 6833

Chalcopyrite $\text{CuIn}(\text{S}_{1-x}\text{Se}_x)_2$ for Photoelectrocatalytic H_2 Evolution: Unraveling the Energetics and Complex Kinetics of Photogenerated Charge Transfer in the Semiconductor Bulk

Jessica J. Frick, Robert J. Cava, and Andrew B. Bocarsly
Department of Chemistry, Princeton University, Princeton, NJ, USA



$\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CIGS) chalcopyrites and their derivatives are potential candidates for use in photoelectrochemical (PEC) H_2 generation because of their well-matched solar absorption properties and agreeable band positions relative to the water reduction redox potential. In this work, we present the photoelectrochemical characterization and H_2 evolution performance of the highly tunable anion CIGS derivative series $\text{CuIn}(\text{S}_{1-x}\text{Se}_x)_2$. The photocathodes were subjected to Mott–Schottky analysis and chopped-light irradiation to determine their flat band potential. With excellent agreement between the two techniques, the flat band potentials were determined to increase successively with increasing x in $\text{CuIn}(\text{S}_{1-x}\text{Se}_x)_2$, with all band positions possessing appropriate energetics for the thermodynamic requirement of reducing H_2O to H_2 . The photocathodes were then subjected to identical bulk H_2 evolution conditions for 10–12 h, maintaining $\sim 90\%$ faradaic efficiency. The rates of photoelectrocatalysis were found to vary significantly within the $\text{CuIn}(\text{S}_{1-x}\text{Se}_x)_2$ series, ranging over 2 orders of magnitude using a constant light intensity of $100 \text{ mW}/\text{cm}^2$. Carrier transport behavior beyond the space charge region where charge diffusion dominates is suggested as a limiting factor for the H_2 evolution rate of these p-type materials through the indirect influence of the majority carrier concentration.

Status: published work at Chem. Mater. 2018, **30**, 4422-4431

The Search for Topological States and Anomalous Electronic Behaviors in In- and Mn-doped GeTe

Eric N. Fung and Robert J. Cava

Class of 2018, Department of Chemistry, Princeton University, Princeton, New Jersey, USA

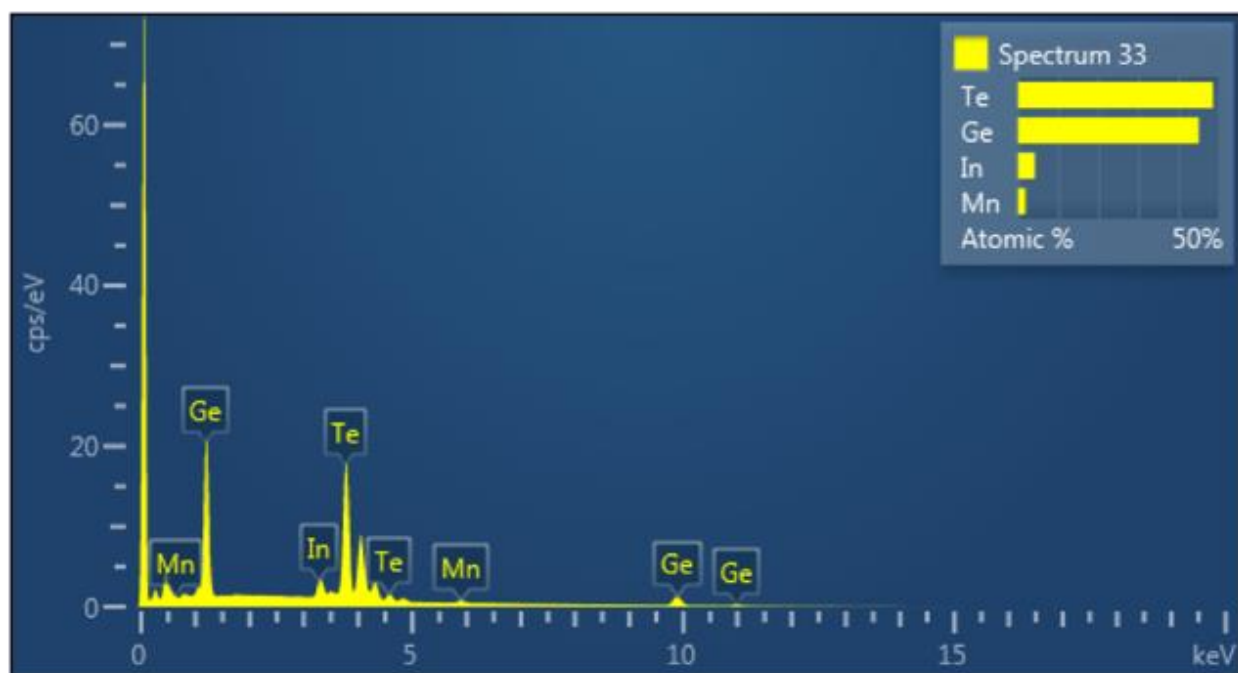


Figure: Representative EDX spectra of $\text{Ge}_{0.86}\text{In}_{0.14-x}\text{Mn}_x\text{Te}$

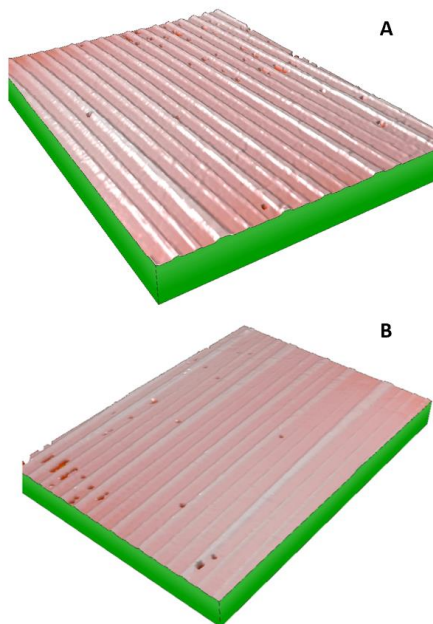
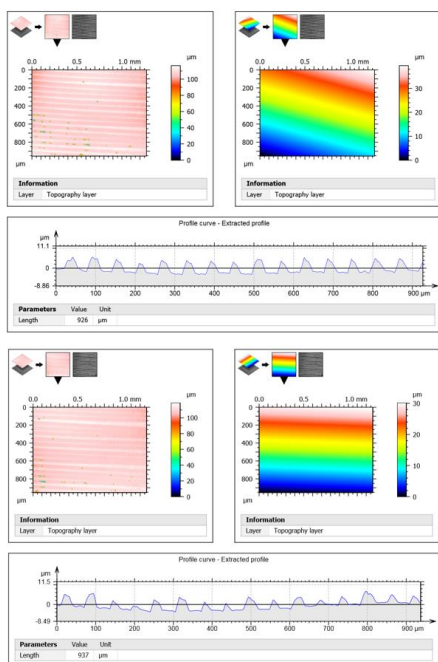
Recently, researchers predicted and showed experimentally that GeTe exhibits novel physics, such as giant Rashba effect, so the potential of this semiconductor to exhibit additional novel physics phenomena, such as topological electronic states, motivates a resurgence in its study. Due to its consistently metallic and strong p -type behavior, however, it is very difficult to observe electronic states that may lie above the Fermi level. Here, I report and describe a series of single crystal samples that I grew by a modified Bridgman technique in both the $\text{Ge}_{1-x}\text{In}_x\text{Te}$ and $(\text{GeTe})_{1-x}(\text{In}_{2/3}\text{Te})_x$ systems, in which I found anomalous highly insulating behavior at 14 at. % In content in the normally highly metallic and conducting GeTe system. Additionally, I report my characterization of a series of In- and Mn-co-doped GeTe crystals that show ferromagnetic behavior with increasing Curie temperature as a function of increasing Mn content as well as an anomalous Hall effect. While I have not yet gathered direct evidence for topological electronic states in these two systems, I have found anomalous behaviors in doped GeTe and, as a result, have laid the groundwork for future study that may lead to the discovery and characterization of additional novel physics phenomena in doped GeTe.

Status: undergraduate senior thesis

Towards Topographical and Chemical Patterning of Tecoflex Polyurethane: A Novel Polymer for Tissue Engineering Devices

Jessica Li, Kelly Lim and Jeffrey Schwartz

Class of 2018, Department of Chemistry, Princeton University, Princeton, NJ, USA



Using our new patterning apparatus, we observed major improvements in the consistency of groove depths going from the periphery to the center of polymer. In places of “minor grooves,” we observed flat bases. **A.** Taken from the top left quadrant, grooves in this area consistently displayed a depth of 8-10 μm as seen in the profile curve. **B.** Similarly, taken from the center of the polymer, grooves in this area, though marginally diminished in depth, are still mostly consistent and have a depth of 6-8 μm .

In opening a new frontier of tissue engineering, the Schwartz group previously developed methods for a diverse array of materials to spatially control the cell growth, which in turn self-assembled extracellular matrix that can be harvested for guided tissue regeneration. However, despite these successes, many of the materials studied – PET, PCLF, and PEEK – are mechanically and biochemically incompatible with cell surfaces. As such, Tecoflex Polyurethane, a shape memory elastomer, was explored as a compatible biomaterial to translate the Schwartz method. This present study aims to first, establish on Tecoflex surfaces the reproducibility of topographical patterns that provide environmental cues. Secondly, this study demonstrates the feasibility of depositing upon the pattern polymer a zirconium oxide/self-assembled mono-phosphonate (SAMP) layer with cell-recruiting ability. Patterns were assessed through confocal microscopy, SEM, among other imaging techniques. In showing the replicability of topographical and chemical patterns on Tecoflex, this study presents the elastomer as a novel, effective material for translational medicine that seeks to reconstruct cellular architecture in damaged soft tissues.

Status: undergraduate senior thesis

Crystal growth of quantum spin liquid candidate $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$

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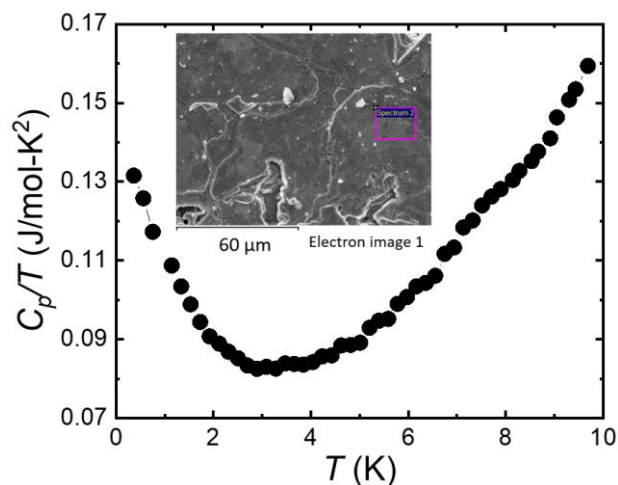


Figure: Low temperature molar heat capacity divided by temperature for $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$. The inset shows the SEM/EDS image (with the help of Dr. Zhong in Cava lab) of the crystal.

Third law of Thermodynamics states that all systems must freeze at zero Kelvin and the entropy remains constant. However, quantum spin liquid (QSL) state is highly entangled state, in which spins remain dynamic and do not order due to quantum fluctuations, even at absolute zero. Potential applications for quantum computer intrigue researchers to look for new QSL materials. Here, we synthesize $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$, crystallized in a 12-layer hexagonal perovskite unit cell with the $R-3m$ space group. Magnetic susceptibility measurements show no magnetic ordering down to 1.8 K despite the Curie-Weiss temperature of -13 K. The specific heat (C_p) was measured down to 0.35 K shows no indication of magnetic ordering and fitting a power law to C_p vs. T below 2 K yields the power $\alpha = 3/4$. Low temperature molar heat capacity divided by temperature for $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$ shows the linear upturn at the lowest temperature, implying a large amount of residual entropy still retained. These evidences suggest that $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$ is a candidate QSL.

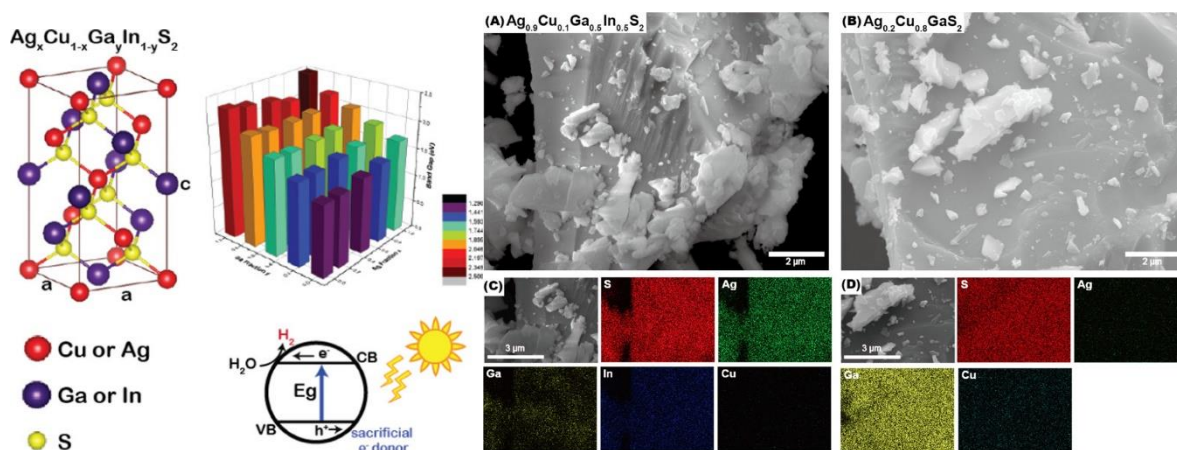
To confirm the QSL state in this material, μSR measurement and inelastic neutron diffraction are needed and they both require crystals. We grow crystals of $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$ by flux growth method. SEM/EDS shows layer structure and justifies the elemental ratio. This simple work is especially important because the flux can be doped, or the compound decomposes and forms different substances during the growth. We grow and prepare about 2g crystals of $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$, probed by SEM/EDS and verified QSL state by μSR measurement and inelastic neutron diffraction.

Status: published work at Phys. Rev. Mater. 2018, 2, 054414

Improved H₂ Evolution in Quaternary SCIGS Chalcopyrite Semiconductors

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Department of Chemistry, Princeton University, Princeton, NJ, USA



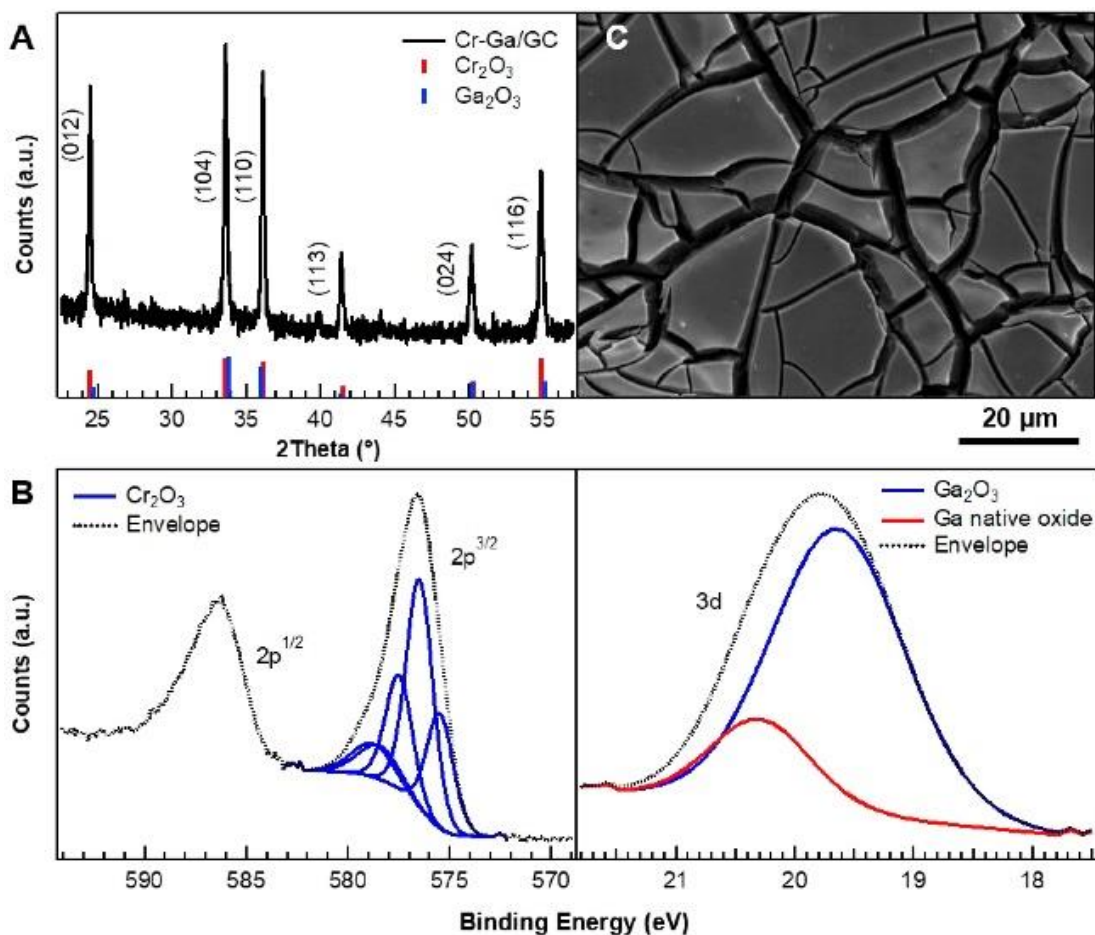
In a search for improved photocathode materials for fuel-producing photoelectrochemical cells, quaternary $\text{Ag}_x\text{Cu}_{1-x}\text{Ga}_y\text{In}_{1-y}\text{S}_2$ ($0 \leq x \leq 1.0$, $0 \leq y \leq 1.0$) p-type, chalcopyrite semiconductors (SCIGS) were prepared and tested for photochemical hydrogen evolution. The study reported here is based on the preparation of bulk phases of the quaternary system. In contrast to thin-film studies of this system, this approach enables enhanced control of the materials' chemical, structural, and electronic properties. Compared to ternary CIGS electrode materials, the quaternary SCIGS materials provide improved photoelectrochemical and electrocatalytic properties. The quaternary system allows for adjustment of the band structures and photocatalytic abilities to a finer degree than is possible in the $\text{Ag}_x\text{Cu}_{1-x}\text{GaS}_2$ or $\text{Ag}_x\text{Cu}_{1-x}\text{InS}_2$ ternaries, and several of the quaternary $\text{Ag}_x\text{Cu}_{1-x}\text{Ga}_y\text{In}_{1-y}\text{S}_2$ compositions are found to show better water-splitting capability than the ternaries, even when a platinum co-catalyst is present in the ternary systems. Our work on quaternary compounds has led to finding unexpected optoelectric properties in ternary compounds of composition $\text{Ag}_x\text{Cu}_{1-x}\text{GaS}_2$. Specifically, a “V-shaped” plot of semiconductor composition versus band gap is observed, which is not easily correlated with the observed variation in semiconductor structure. Even more interesting is the observation that the silver-rich branch of this “V” produces obviously higher H₂ evolution rates than observed with the copper-rich branch.

Status: published work at J. Phys. Chem. C 2019, **122**, 24512-24519

High-Efficiency Conversion of CO₂ to Oxalate in Water Is Possible Using a Cr-Ga Oxide Electrocatalyst

Aubrey R. Paris and Andrew B. Bocarsly

Department of Chemistry, Princeton University, Princeton, NJ, USA

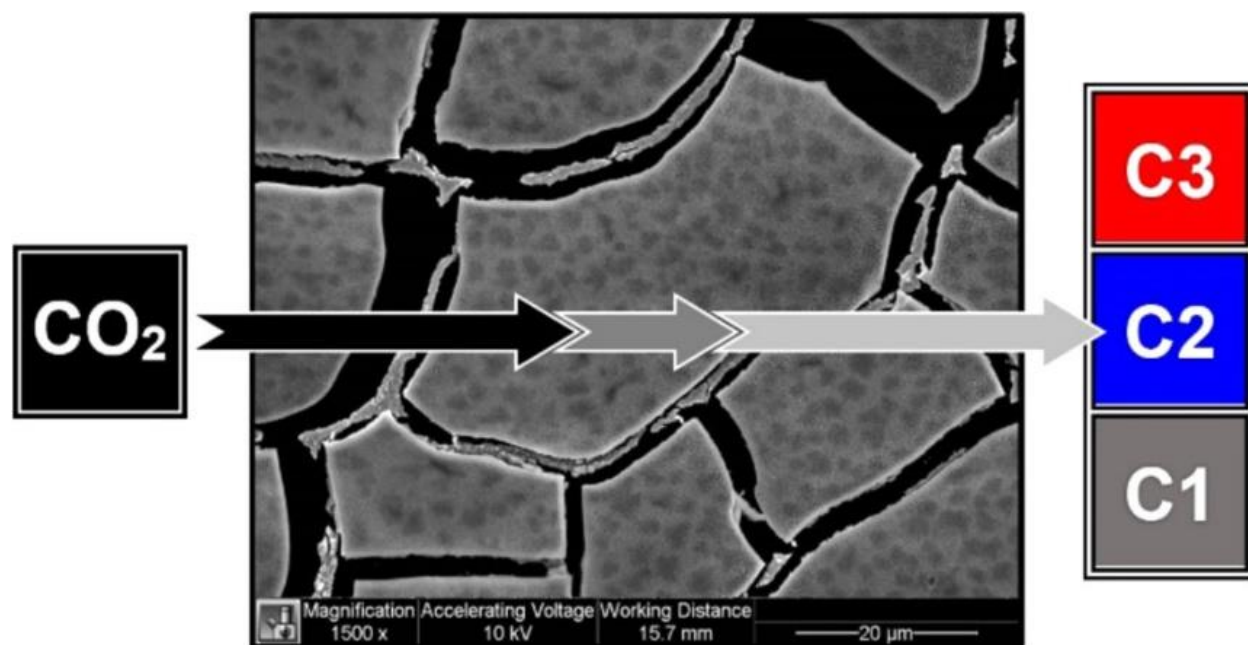


Electrochemical transformation of CO₂ into commodity chemicals such as oxalate is a strategy for profitably remediating high atmospheric CO₂ levels. Electrocatalysts for oxalate generation, however, have required prohibitively large applied potentials, forcing the use of nonaqueous electrolytes. Here, a thin film comprised of alloyed Cr and Ga oxides on glassy carbon is shown to electrocatalytically generate oxalate from aqueous CO₂ with high Faradaic efficiencies at 690 mV overpotential. Oxalate is produced at a surface anion site via a CO-dependent pathway; the process is highly sensitive to the hydrogen-bonding environment and avoids the commonly invoked CO₂⁻ intermediate. Ultimately, this catalytic system accomplishes efficient CO₂ to oxalate conversion in protic electrolyte.

Status: published work at ACS Catalysis 2019, 9, 2324-2333

Ni–Al Films on Glassy Carbon Electrodes Generate an Array of Oxygenated Organics from CO₂

Aubrey R. Paris and Andrew B. Bocarsly
Department of Chemistry, Princeton University, Princeton, NJ, USA



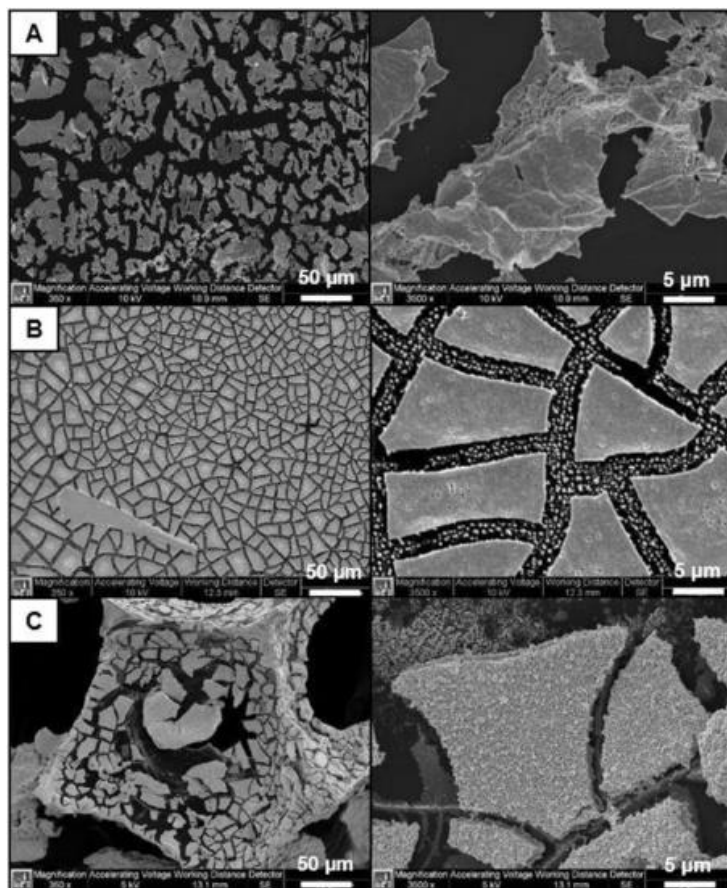
The transformation of CO₂ into chemical feedstocks or fuels is an attractive goal, but catalysts capable of generating useful, multicarbon products have been challenging to design. Here, thin films of the intermetallic Ni₃Al on glassy carbon are found to be electrocatalytic for aqueous CO₂ reduction. At -1.38 V vs Ag/AgCl, Ni₃Al films produce a range of C1, C2, and C3 oxygenated organic species including 1-propanol and methanol at Faradaic efficiencies that are competitive with single-metal electrodes reported in the literature. To the best of our knowledge, Ni₃Al on glassy carbon is the only noncopper-containing material shown to generate C3 products.

Status: published work at ACS Catalysis 2017, **7**, 6815-6820

Tuning the Products of CO₂ Electroreduction on a Ni₃Ga Catalyst Using Carbon Solid Supports

Aubrey R. Paris, An T. Chu, Conor B. O'Brien, Jessica J. Frick, Sonja A. Francis and Andrew B. Bocarsly

Department of Chemistry, Princeton University, Princeton, NJ, USA

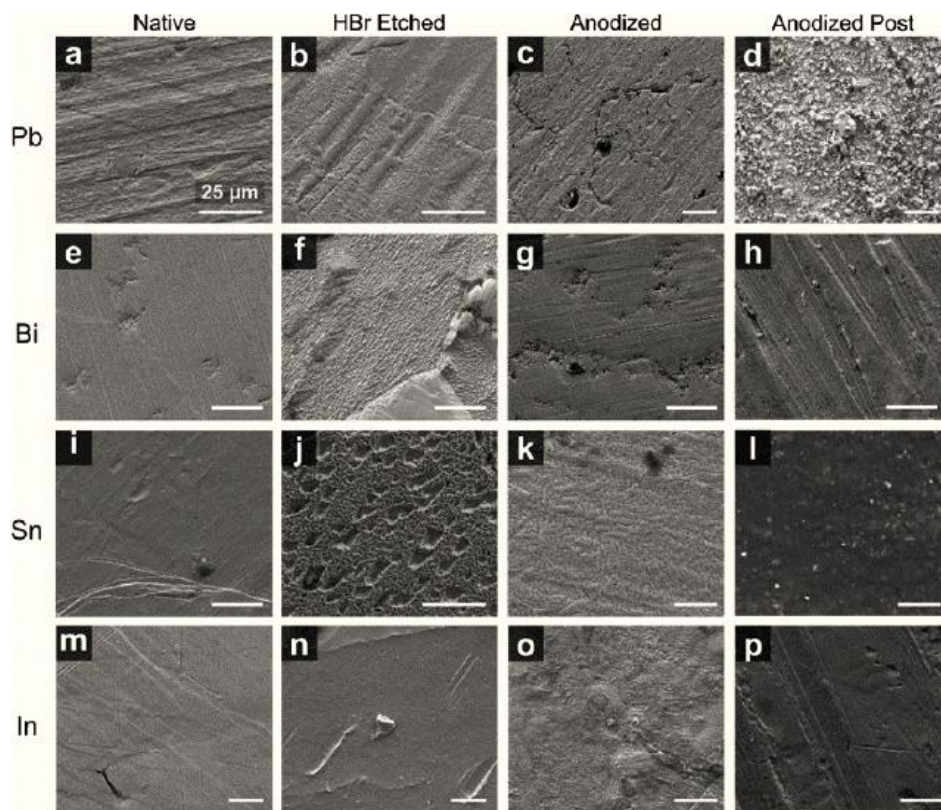


Certain alloys of nickel have recently been shown to reduce CO₂ to multi-carbon products electrochemically without the need for copper. Here we show that Ni₃Ga thin film electrocatalysts on carbon electrodes discriminate between CO₂ reduction pathways and products based on their surface morphologies, which are controlled by catalyst-carbon support interactions. It is also observed that unsupported, bulk Ni₃Ga reduces CO but not CO₂. With this understanding, a tandem electrocatalyst utilizing two variants of the Ni₃Ga material—one supported and one unsupported—was developed. In this two-electrode system, CO is generated from CO₂ on an electrode optimized for this process, and the CO is then further reduced to methanol in the same reactor. It appears that choice of carbon support impacts the morphology of Ni₃Ga during the synthesis of the catalyst, thereby influencing the electrolysis product distribution.

Status: published work at J. Electrochem. Soc. 2018, **165**, H385-H392

Probing the Mechanism of Aqueous CO₂ Reduction on Post-Transition-Metal Electrodes using ATR-IR Spectroelectrochemistry

James E. Pander III, Maor F. Baruch, and Andrew B. Bocarsly
Department of Chemistry, Princeton University, Princeton, NJ, USA

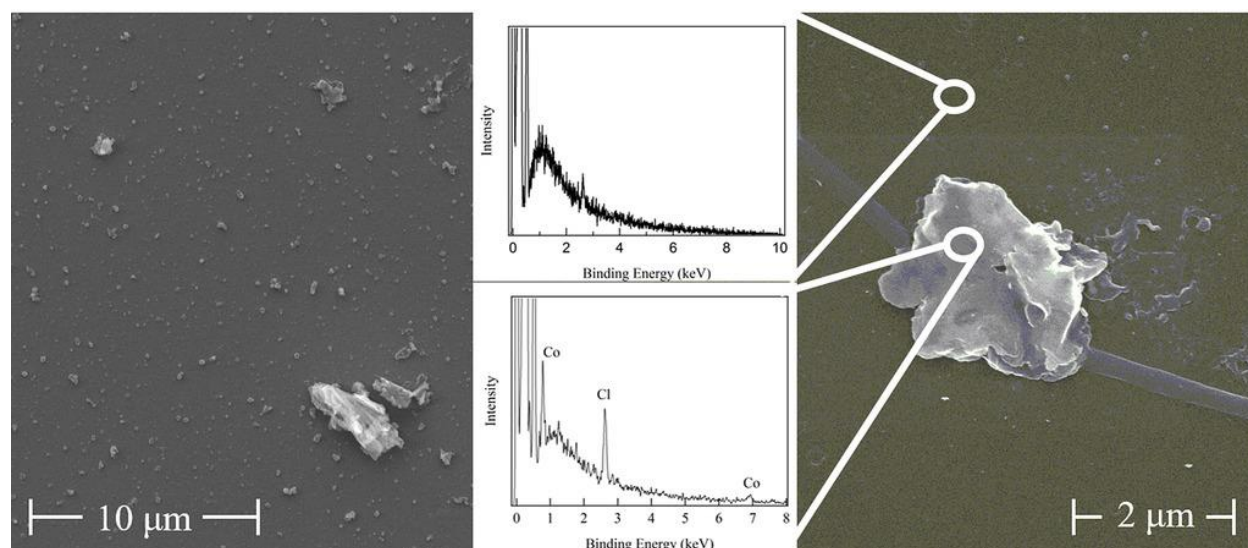


The role of metastable surface oxides in the reduction of CO₂ on lead, bismuth, tin, and indium electrodes was probed using in situ attenuated total reflectance infrared (ATR-IR) spectroelectrochemistry. The effect of the surface oxide on the Faradaic efficiency of CO₂ reduction to formic acid was studied by etching and anodizing the electrodes, and the results were correlated with respect to the observed spectroscopic behavior of the catalysts. A metastable oxide is observed on lead, tin, and indium cathodes under the electrochemical conditions necessary for CO₂ reduction. Spectroscopic evidence suggests that bismuth electrodes are fully reduced to the metal under the same conditions. The dynamics of the electroreduction of CO₂ at lead and bismuth electrodes appears to be different from that on tin and indium electrodes, which suggests that these catalysts act through different mechanistic pathways. The post-transition-metal block can be divided into three classes of materials: oxide-active materials, oxide-buffered materials, and oxide-independent materials, and the mechanistic differences are discussed.

Status: published work at ACS Catalysis 2016, **6**, 7824-7833

Utilization of Electropolymerized Films of Cobalt Porphyrin for the Reduction of Carbon Dioxide in Aqueous Media

James E. Pander III, Alex Fogg, and Andrew B. Bocarsly
Department of Chemistry, Princeton University, Princeton, NJ, USA



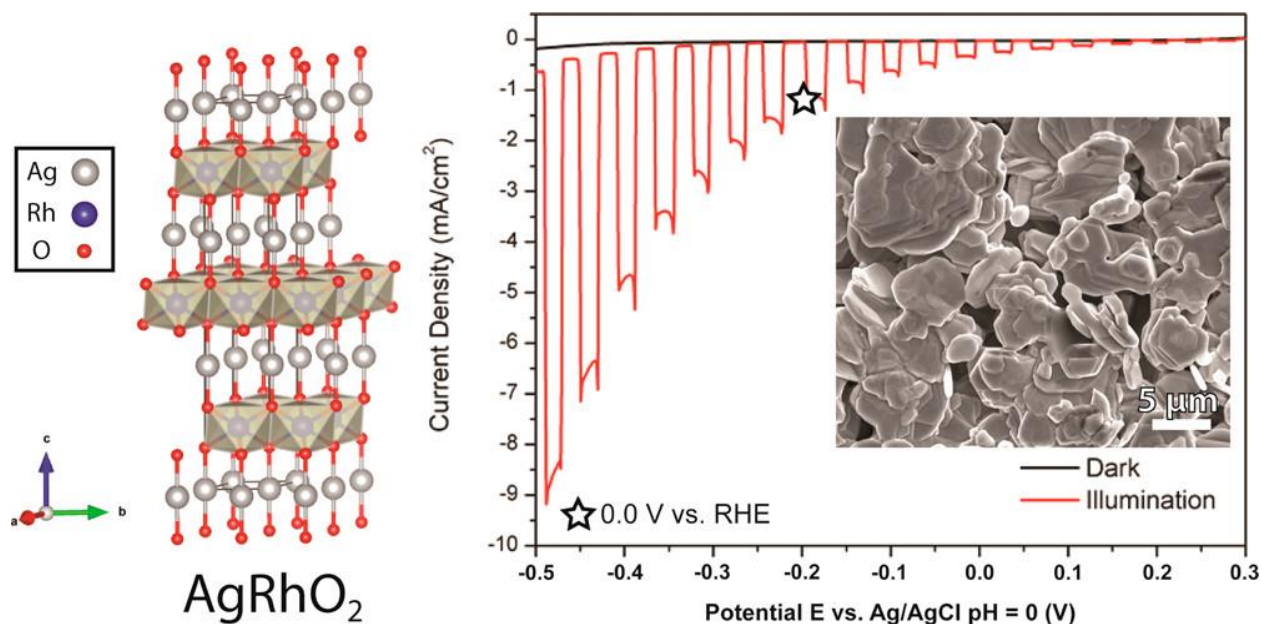
A facile electropolymerization process was utilized to prepare electrodes modified with thin films of cobalt protoporphyrin IX. These thin films exhibited a high Faradaic efficiency ($84 \pm 2\%$) for the reduction of CO_2 to CO in aqueous solutions near neutral pH with 450 mV of overpotential and a turnover frequency at zero overpotential ($\log(\text{TOF}_0)$) of -5.9 . The production of CO was stable over several hours at these modest potentials. The use of a $^{13}\text{CO}_2$ reactant led exclusively to ^{13}CO as the product. Polymeric films of the unmetalated porphyrin did not demonstrate catalysis for CO_2 reduction. UV/Vis spectroelectrochemical experiments indicate that the parent Co^{II} complex is reduced to Co^{I} at the electrode surface before interaction with CO_2 . It is proposed that the rate-determining step in the reduction of CO_2 is the initial reduction of the Co^{II} moiety to Co^{I} , which binds CO_2 and then undergoes a proton-coupled electron transfer and a loss of water to form CO. Additionally, a new metric for the evaluation of electrocatalysts, the catalytic efficiency, is proposed. The catalytic efficiency is the ratio of the power stored to power consumed for a given electrochemical reaction and can be used to describe both the kinetics and overpotential considerations of a given system.

Status: published work at Chem. Cat. Chem. 2016, **8**, 3536-3545

Stable Hydrogen Evolution from an AgRhO₂ Photocathode under Visible Light

James Eujin Park, Yuan Hu, Jason W. Krizan, Quinn D. Gibson, Uriel T. Tayvah, Annabella Selloni, Robert J. Cava, and Andrew B. Bocarsly

Department of Chemistry, Princeton University, Princeton, NJ, USA

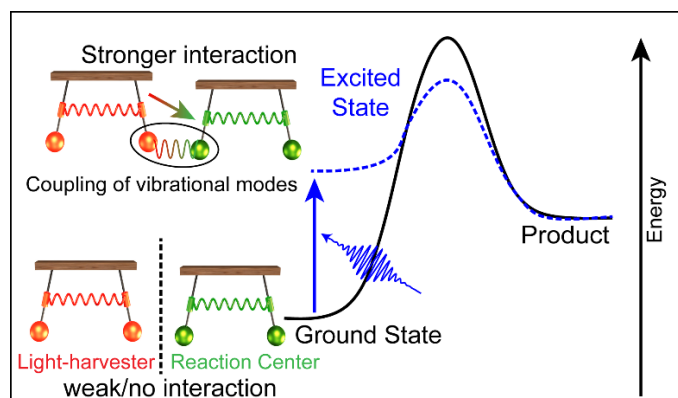


In the search for improved materials for photoelectrochemical water splitting, it has become important to identify new classes of semiconductor materials that may serve as improved photocathodes. To this end, p-type AgRhO₂ has been synthesized and tested as a photocathode for water splitting. The AgRhO₂ photocathode is found to exhibit excellent photocatalytic capability for reducing protons to H₂ across a wide range of pH values with nearly 100% faradaic efficiency and good photostability. Polycrystalline AgRhO₂ electrodes exhibit strong preferred *c*-axis orientation, resulting in anisotropic conductivity, evident from resistivity measurements. AgRhO₂ photocathodes are found to provide improved performance and photostability when compared to prior work using a p-CuRhO₂ electrode. Enhanced performance is in part attributed to the unusual degree of *c*-axis orientation found in this material. In addition, there is a significantly lower kinetic barrier for H₂ production at the AgRhO₂ interface.

Status: published work at Chem. Mater. **30**, (2018) 2574-2582

Coherence Spectroscopy Reveals a Quantum-Inspired Design Principle for Selective Bond Activation in Synthetic Chemistry

Shahnawaz Rafiq, Máté J. Bezdek, Paul J. Chirik, and Gregory D. Scholes
Department of Chemistry, Princeton University, NJ 08544 USA



The traditional view of a chemical change is inherently local and classical, relying on a mix of thermodynamic and kinetic parameters to control reactivity. Often, the thermodynamic stability of chemical bonds necessitates significant energy input for activation. One fundamental question is enticing and potentially transformative - can quantum mechanics open new opportunities for aiding selective bond activation? A possible answer lies in strategic input of quantum energy to reaction-specific nuclear motions. Towards this goal, our work describes the coupling of quantum motions via Fermi-resonance in a terpyridine-molybdenum transition metal complex hosting a highly nonreactive substrate—dinitrogen. Ultrafast coherence spectroscopies, augmented by resonance-Raman, and quantum calculations, were used to analyze the nuclear motions in the molybdenum dinitrogen complex. A striking vibrational coupling mechanism connecting in-plane breathing motion of the light-harvesting terpyridine ligands with the stretching motion of the spatially disparate dinitrogen bridge was identified. Notably, the coupling is significantly enhanced in the photoexcited state. This Fermi-resonance coupling indicates an energy conduit, driving the two oscillators in sync, and thereby amplifying vibrational energy exchange between the light-harvesting terpyridine and the dinitrogen molecule. Achieving selective substrate activation by bridging vibrations could present a quantum-inspired design principle in synthetic chemistry.

Status: published work at

[1] Chem 2018, DOI: doi.org/10.1016/j.chempr.2018.11.003

[2] J. Am. Chem. Soc. 2018, **140**, 6298-6307

Towards Chemical Exfoliation of a New Air-Stable Two-Dimensional Magnetic Material

Xiaoyu Song¹, Shiming Lei¹, Sebastian Klemenz¹, Yao-Wen Yeh², Daniel Weber³, Nan Yao² and Leslie M. Schoop¹

¹Department of Chemistry, Princeton University, Princeton, NJ, USA; ²Princeton Institute for Science and Technology of Materials, Princeton, NJ, 08544; ³Department of Chemistry, Ohio State University, Columbus, OH, USA

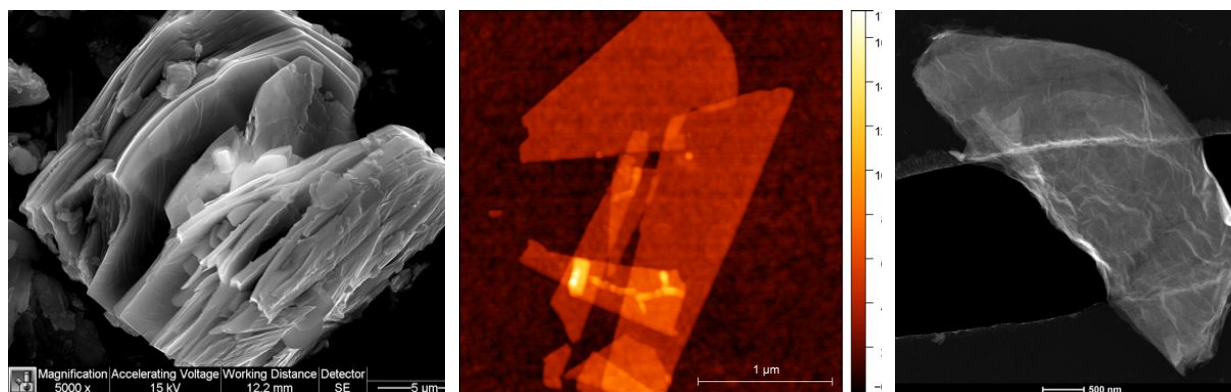


Figure: Left: A bulk material showing first signs of exfoliation as cracks can be seen among the layers. The image was taken by XL30; Middle: An AFM image of exfoliated nanosheets; Right: An image of exfoliated nanosheet taken with the Talos TEM.

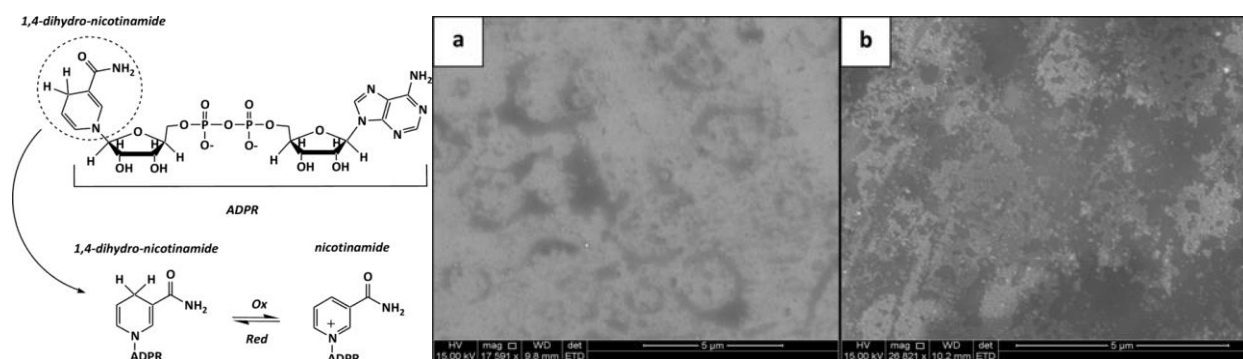
The emergence of high quality two-dimensional (2D) intrinsic magnetic materials is important for the development of the next generation's functional devices ^[1]. Over the past few years, several intrinsic 2D magnetic materials have been discovered, and the direct magnetic measurement on 2D materials were first performed on CrI₃^[2] and Cr₂Ge₂Te₆^[3], which were mechanically exfoliated from their van-der-Waals parent materials. However, none of the known 2D magnets are air-stable, and the relatively low yield of the micromechanical exfoliation method limits their practical applications. Currently, we are working on using chemical exfoliation methods to synthesize new air-stable 2D intrinsic magnetic materials.

We used SEM and EDX to characterize the surface morphology and chemical composition of the intermediate products. This information helped us to identify the degree of exfoliation, and we improved the synthesis conditions accordingly in order to obtain high-quality free-standing nanosheets. Once we confirmed the synthesis of nanosheets with AFM, we moved to the TEM to study their structure and chemical composition. With the ultra-high resolution of TEM, we were able to study those new materials atom by atom. The structural information serves as a cornerstone for us to understand the new materials we've made.

Status: ongoing research work

Photoelectrochemical NADH Regeneration using Pt-Modified p-GaAs Semiconductor Electrodes

Paolo Stufano, Aubrey R. Paris, Andrew Bocarsly
Department of Chemistry, Princeton University, Princeton, NJ, USA



Cofactor regeneration in enzymatic reductions is crucial for the application of enzymes to both biological and energy-related catalysis. Specifically, regenerating NADH from NAD⁺ is of great interest, and using electrochemistry to achieve this end is considered a promising option. Here, we report the first example of photoelectrochemical NADH regeneration at the illuminated ($\lambda > 600$ nm), metal-modified, p-type semiconductor electrode Pt/p-GaAs. Although bare p-GaAs electrodes produce only enzymatically inactive NAD², NADH was produced at the illuminated Pt-modified p-GaAs surface. At low overpotential (-0.75 V vs. Ag/AgCl), Pt/p-GaAs exhibited a seven-fold greater faradaic efficiency for the formation of NADH than Pt alone, with reduced competition from the hydrogen evolution reaction. Improved faradaic efficiency and low overpotential suggest the possible utility of Pt/p-GaAs in energy-related NADH-dependent enzymatic processes.

Status: published work at Chem. Electro. Chem. 2017, **4**, 1066-1073

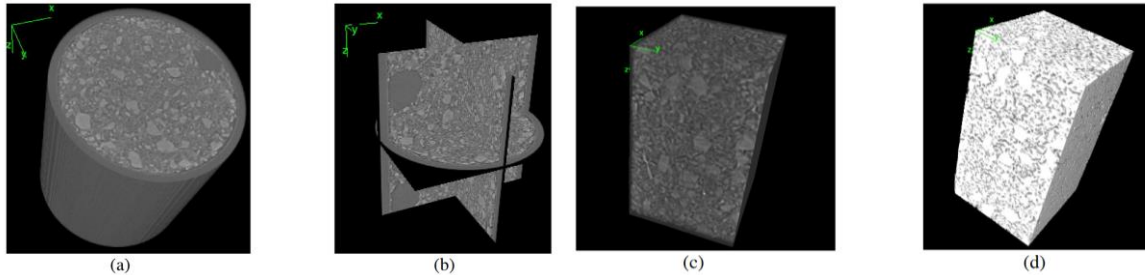
Department of Civil and Environmental Engineering

Characterizing the Effects of Magnesium Content and Carbonation on the Pore Structure of Alkali-Activated Slags

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This thesis is focused on characterizing the pore structure of alkali-activated slag paste (AAS, a sustainable cementitious material) and how its morphology changes with magnesium content and carbonation, a common concrete degradation process. Currently, ordinary Portland cement (OPC) is the most commonly used binder for concrete, but AAS offers a promising, sustainable alternative. However, little is known about its long-term durability, including its resistance to carbonation and interaction with CO₂. Recently, studies have shown that increasing the magnesium content in AAS, via different blast furnace slag sources, plays a role in resisting accelerated carbonation through the formation of a Mg-stabilized amorphous calcium carbonate (ACC). However, the effects of this ACC phase on AAS pore structure has yet to be elucidated. My thesis examines the pore size distribution and diffusion tortuosity of low- and high-magnesium content silicate-activated AAS through the techniques of nitrogen sorption, mercury intrusion porosimetry (MIP), and X-ray microtomography (μCT). Additionally, a random walker method is implemented in the reconstructed pore-space from μCT to calculate the diffusion tortuosity of the pastes. AAS is shown to be more resistant to pore structural degradation following carbonation than OPC, and increased Mg content in AAS is shown to further increase resistance to capillary pore formation and gel pore loss from decalcification due to carbonation.

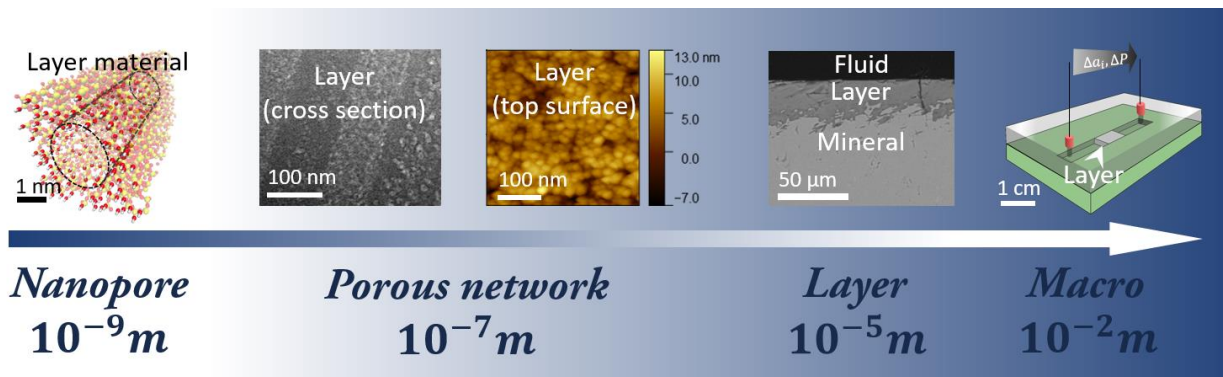
Status: undergraduate senior thesis work

Nanofluidic Controls on Silicate Alteration Kinetics

Bastien Wild¹, Claire E. White^{1,2}, and Ian C. Bourg^{2,3}

¹Andlinger Center for Energy and the Environment; ²Department of Civil and Environmental Engineering;

³Princeton Environmental Institute



The alteration rates and dissolution mechanisms of silicate materials have been prominent research fields over the past 50 years in relation to the long-term carbon cycle, the durability of urban infrastructure, and the feasibility of several low-carbon technologies including green cements and carbon capture and storage. In this project, we investigate the role of silica-rich nanoporous layers forming at reacting interfaces, which strongly influence the overall alteration process. We characterize the textural and structural properties of the nanoporous layers formed on model silicate materials including minerals, cements and glass by combining a series of complementary microscopy techniques including Electron Backscatter Diffraction, Focused Ion Beam, Transmission Electron Microscopy, Atomic Force Microscopy and Scanning Electron Microscopy. Furthermore, we use molecular dynamics simulations to track the effect of charges and pore size on the mobility of reactive species and dissolution products through the amorphous silica nanopores forming the layer. The temporal evolution of the nanoporous network within the layer as well as its apparent transport properties are probed *in-situ* using advanced beamline techniques such as synchrotron-based X-Ray Reflectivity and Grazing-Incidence Small-Angle X-ray scattering. The ultimate goal of this approach is to better bridge molecular-scale processes with the effect of nanoporous layers on alteration rates of silicate materials observed at the macroscopic scale.

Status: ongoing research project

Department of Electrical Engineering

Atomic Source of Single Photons in the Telecom Band

A. M. Dibos, M. Raha, C. M. Phenicie, S. Chen, and J. D. Thompson

Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544 USA

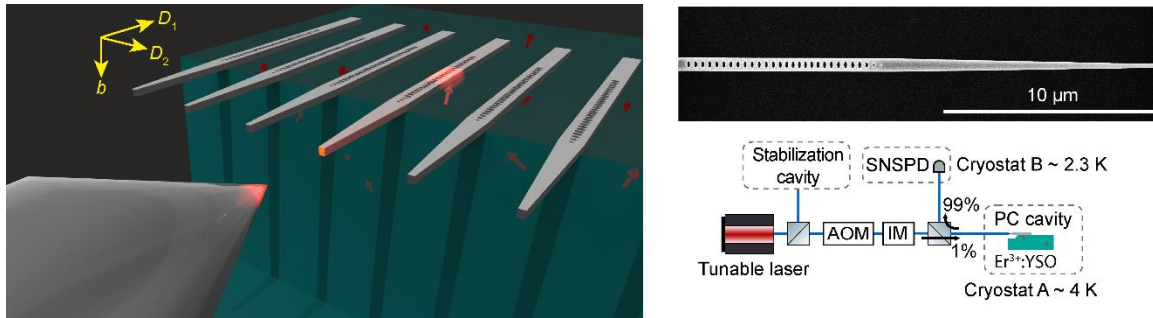
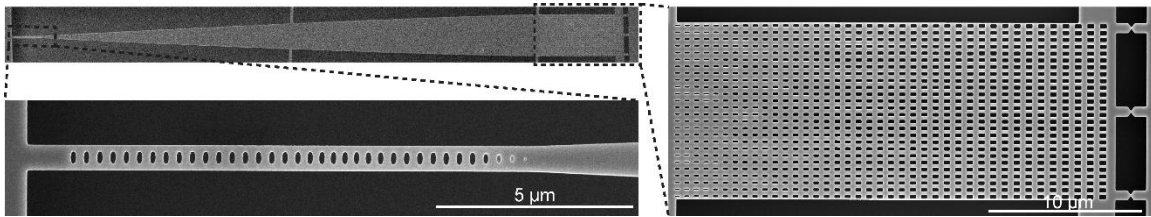


Figure 1. Experimental configuration for enhancing Er^{3+} emission with a silicon photonic crystal.



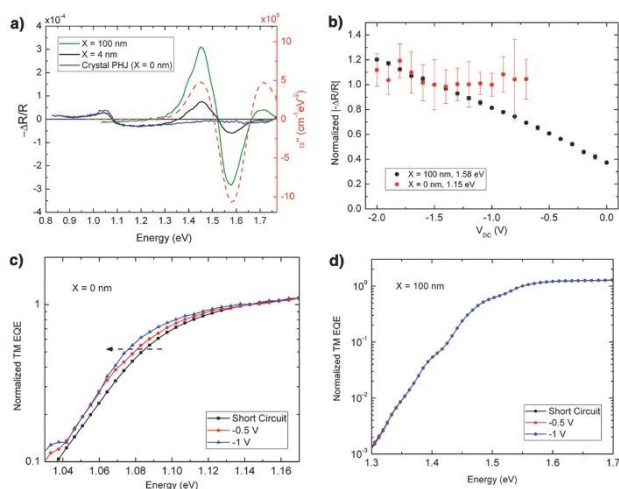
Single atoms and atom-like defects in solids are ideal quantum light sources and memories for quantum networks. However, most atomic transitions are in the ultraviolet-visible portion of the electromagnetic spectrum, where propagation losses in optical fibers are prohibitively large. Here, we observe for the first time the emission of single photons from a single Er^{3+} ion in a solid-state host, whose optical transition at $1.5 \mu\text{m}$ is in the telecom band, allowing for low-loss propagation in optical fiber. This is enabled by integrating Er^{3+} ions with silicon nanophotonic cavity structures, which results in an enhancement of the photon emission rate by a factor of more than 650. Dozens of distinct ions can be addressed in a single device, and the splitting of the lines in a magnetic field confirms that the optical transitions are coupled to the electronic spin of the Er^{3+} ions. These results are a significant step towards long-distance quantum networks and deterministic quantum logic for photons based on a scalable silicon nanophotonics architecture. The figures shows the 2D grating coupler for interfacing with the silicon photonic crystal.

Status: published work at Phys. Rev. Lett. **120** (2018) 243601.

Band-like Charge Photogeneration at a Crystalline Organic Donor/Acceptor Interface

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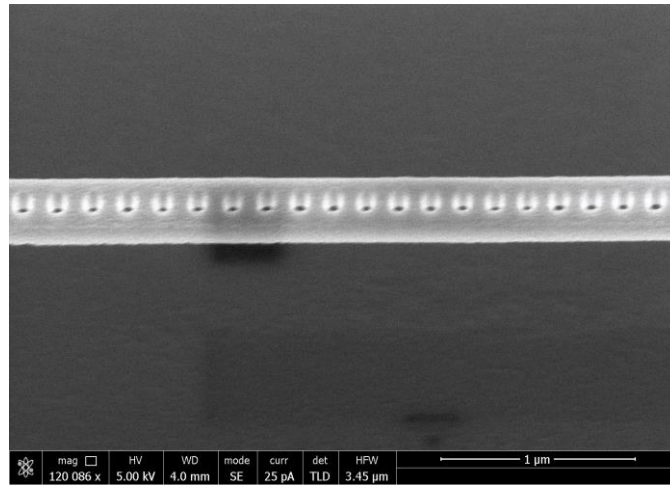


Organic photovoltaic cells possess desirable practical characteristics, such as the potential for low-cost fabrication on flexible substrates, but they lag behind their inorganic counterparts in performance due in part to fundamental energy loss mechanisms, such as overcoming the charge transfer (CT) state binding energy when photogenerated charge is transferred across the donor/acceptor interface. However, recent work has suggested that crystalline interfaces can reduce this binding energy due to enhanced CT state delocalization. Solar cells based on rubrene and C60 are investigated as an archetypal system because it allows the degree of crystallinity to be modulated from a highly disordered to highly ordered system. Using a postdeposition annealing method to transform as-deposited amorphous rubrene thin films into ones that are highly crystalline, it is shown that the CT state of a highly crystalline rubrene/C60 heterojunction undergoes extreme delocalization parallel to the interface leading to a band-like state that exhibits a linear Stark effect. This state parallels the direct charge formation of inorganic solar cells and reduces energetic losses by 220 meV compared with 12 other archetypal heterojunctions reported in the literature.

Status: published work at Adv. Energy Mater. 2018, **8**, 1701494

Nanophotonics for telecom quantum networks based on neutral silicon vacancy centers in diamond

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Department of Electrical Engineering, Princeton University, Princeton, NJ, USA



Quantum networks capable of distributing entanglement over long distances require long-lived quantum memories connected to photons at wavelengths that can travel efficiently in optical fiber. Although there are a number of theoretical schemes for long distance entanglement distribution based on atoms or atom-like defects in solids, physical implementation remains elusive. We recently demonstrated that a new color center in diamond, the neutral silicon vacancy center (SiV^0), has excellent optical coherence, as well as long spin coherence times at temperatures below 20 K, making it an ideal single-atom quantum memory. The integration of this new color center, SiV^0 , into nanophotonic circuits will enable efficient entanglement distribution over long distances. Such quantum networks will have an impact in secure communication, modular quantum computing, and distributed sensing.

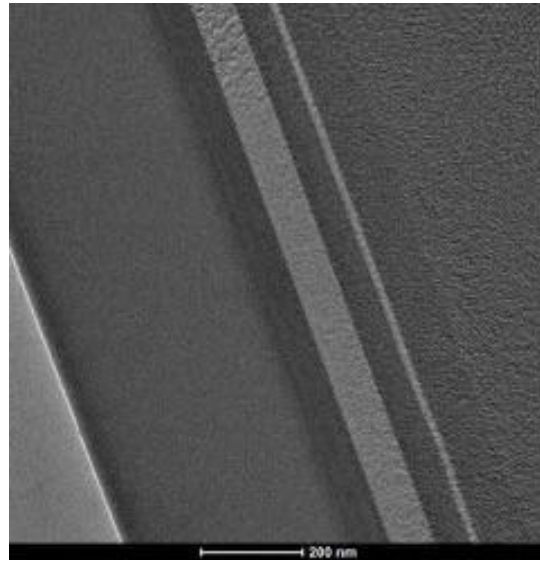
The figure shows a tilted (50°) SEM image of suspended GaAs photonic crystal cavity. The suspended cavity is obtained by etching a sacrificial layer of AlGaAs to let the patterned cavity becomes free-standing. The suspended GaAs device will later be transferred onto diamond for coupling with SiV^0 .

Status: ongoing research project

Si/SiGe 2DEGS Grown by UHVCVD for Quantum Computing Applications

Weiguang Huo and James Sturm

Department of Electrical Engineering, Princeton University, Princeton, NJ, USA



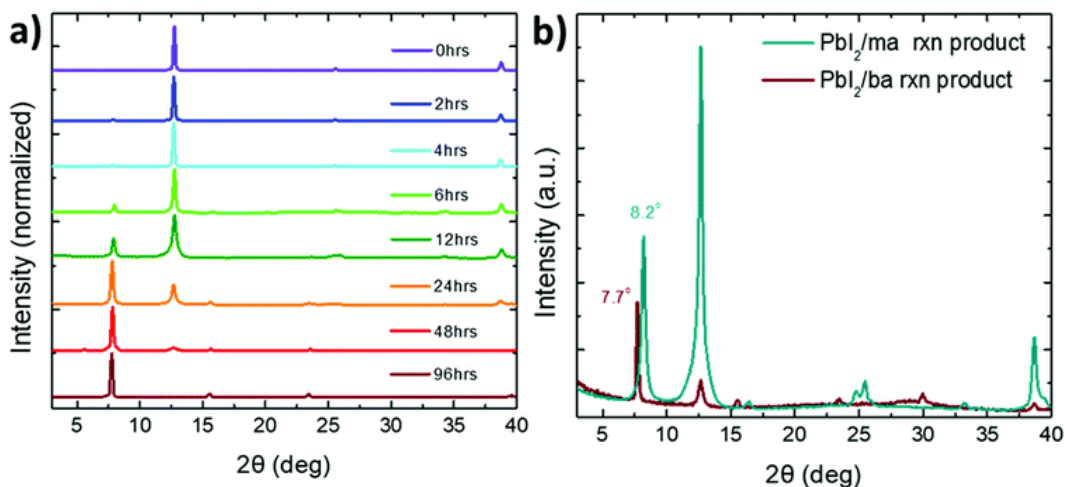
Two-dimensional electron gases (2DEGs) in Si/SiGe heterostructures have been considered as a potential platform to fabricate single electron quantum dots for spin manipulations because silicon has an inherently longer coherence time. The efforts to improve mobility of 2DEGs are the main focus of this project. We use Helios FIB to prepare the TEM sample and use Talos F2000 S/TEM to characterize the layer thickness, interface roughness and Ge composition of our sample. Then we will fabricate Hall bar devices to measure the density of electrons and mobility. The figure shows a TEM image of Si/SiGe heterostructure grown by Chemical Vapor Deposition (CVD). The darker layer is SiGe and the lighter layer is Si.

Status: ongoing research project

Amine Additive Reactions Induced by the Soft Lewis Acidity of Pb^{2+} in Halide Perovskites

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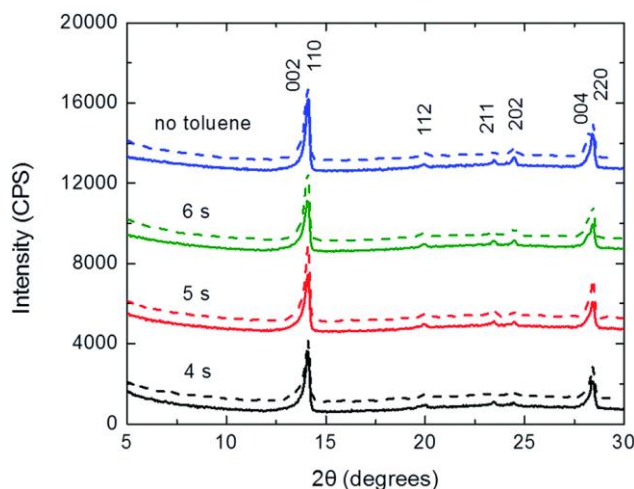
Metal halide perovskite materials (ABX_3) employed in optoelectronic devices have rapidly achieved high efficiencies. Their performance can be partially attributed to intrinsic defects being electronically benign. Despite the inertness of defects within the bulk, such as ion vacancies, solution processing additives and surface passivation have been shown to enhance material properties. Thus, detailed knowledge of additive chemistry is desirable to elucidate passivation mechanisms and facilitate further improvements. In particular, the soft Lewis acid nature of Pb^{2+} has been overlooked heretofore as a key feature of amine-lead chemistry in perovskite preparations. In Part I of this study, we demonstrate that acid–base reactions between PbI_2 and aliphatic amines yield alkylammonium and Pb–alkylamide species. The alkylammonium and alkylamide products are capable of occupying A-site cation and anion vacancies, respectively. These results reveal a new mechanism by which optoelectronic properties of perovskites can be chemically modified. Additionally, the general concept of acidification of organic molecules solvated to Pb^{2+} promoting unexpected reactions is applied to explain amine reactions with other additives, such as formic acid. Understanding acid–base reactions induced by PbI_2 complexing to protic molecules is useful to comprehend and predict defect/impurity chemistry in a wide variety of perovskite precursor formulations.

Status: published work at J. Mater. Chem. C 2019

Ultrasmooth Metal Halide Perovskite Thin Films via Sol–Gel Processing

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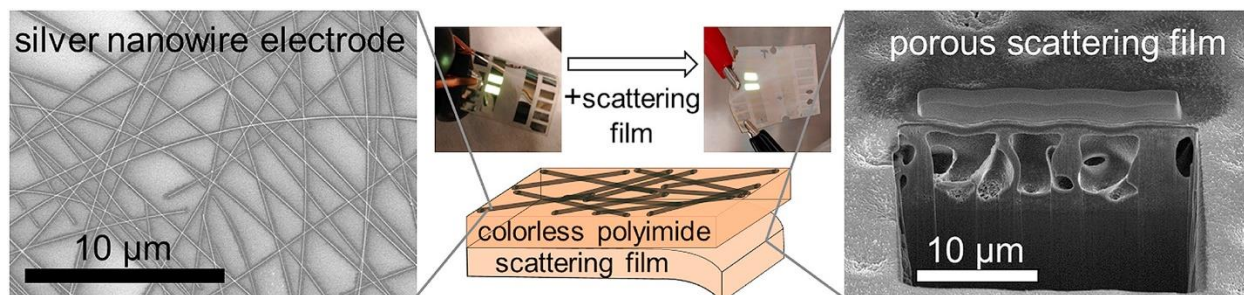


We demonstrate that lead halide perovskite thin film formation displays the characteristics of a sol–gel process. By performing a solvent exchange at different times, the stages of the sol–gel process are elucidated and their sensitivity to processing conditions are examined. For CH₃NH₃PbI₃, the reaction and aging kinetics are found to be extremely rapid, complete within 10 s, and a competing formation of a highly crystalline PbI₂:N,N-dimethylformamide (DMF) complex introduces additional complications relative to a well-behaved sol–gel process. Perovskite formation from strongly polar solvents can be described, in most cases, by the sol–gel processing of PbI₂ regarding other solution components as additives. Understanding the details of additive and environmental influences on the sol–gel properties allow us to exploit fundamental concepts of sol–gel engineering to direct solvent and surfactant choices to control particle size and demonstrate multiple widely employed lead halide perovskite films (CH₃NH₃PbI₃, CH₃NH₃PbBr₃, and CsPbBr₃) with unprecedented surface roughness of less than 2 nm.

Status: published work at J. Mater. Chem. A 2016, **4**, 8308

Enhanced Outcoupling in Flexible Organic Light-Emitting Diodes on Scattering Polyimide Substrates

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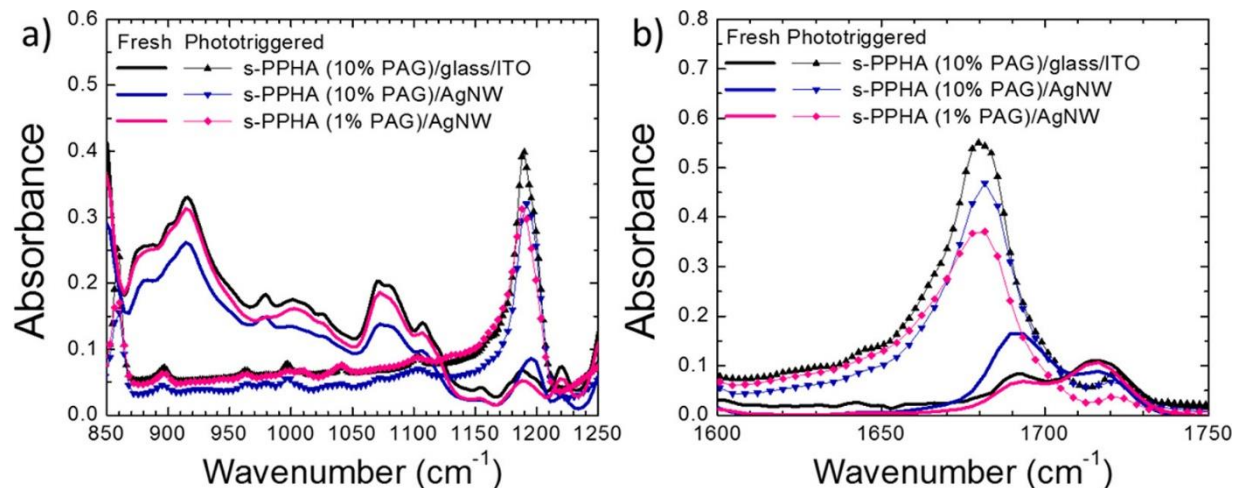


We demonstrate an upscalable approach to increase outcoupling in organic light-emitting diodes (OLEDs) fabricated on flexible substrates. The outcoupling enhancement is enabled by introducing a thin film of microporous polyimide on the backside of silver nanowire (AgNW) electrodes embedded in neat colorless polyimide. This porous polyimide film, prepared by immersion precipitation, utilizes a large index contrast between the polyimide host and randomly distributed air voids, resulting in broadband haze (>75%). In addition, the composite polyimide/AgNW scattering substrate inherits the high thermal (>360 °C), chemical, and mechanical stability of polyimides. The outcoupling efficiency of the composite scattering substrate is studied via optical characterization of the composite substrate and electron microscopy of the scattering film. The flexible scattering substrates compared to glass/indium tin oxide (ITO) allows for a 74% enhancement in external quantum efficiency (EQE) for a phosphorescent green OLED, and 68% EQE enhancement for a phosphorescent white OLED. The outcoupling enhancement remains unharmed after 5000 bending cycles at a 2 mm bending radius. Moreover, the color uniformity over viewing angles is improved, an important feature for lighting applications.

Status: published work at *Organic Electronics* 2017, **51**, 471-476

Phototriggered Depolymerization of Flexible Poly(phthalaldehyde) Substrates by Integrated Organic Light-Emitting Diodes

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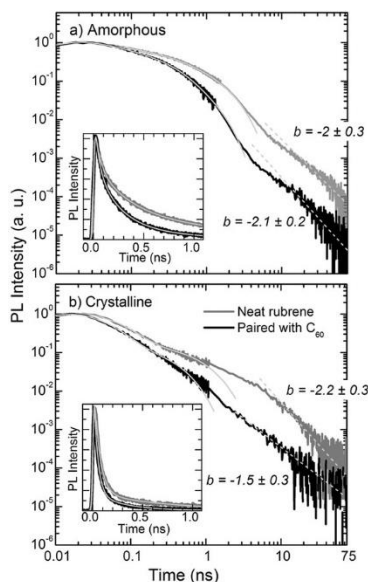
We demonstrate phototriggered depolymerization of a low ceiling temperature (T_c) polymer, poly(phthalaldehyde) (PPHA), via internal light emission from integrated organic light-emitting diodes (OLEDs) fabricated directly on flexible PPHA substrates with silver nanowire electrodes. The depolymerization of the PPHA substrates is triggered by absorption of the OLED emission by a sensitizer that activates a photoacid generator via energetically favorable electron transfer. We confirm with Fourier-transform infrared spectroscopy that the photon doses delivered by the integrated OLED are sufficient to depolymerize the PPHA substrates. We determine this critical dosage by measuring the operating lifetimes of the OLEDs whose failure is believed to be due to significant mechanical softening during the liquefaction of decomposed phthalaldehyde monomers.

Status: published work at ACS Appl. Mater. Interfaces 2018, **10**, 28062

Morphological Tuning of the Energetics in Singlet Fission Organic Solar Cells

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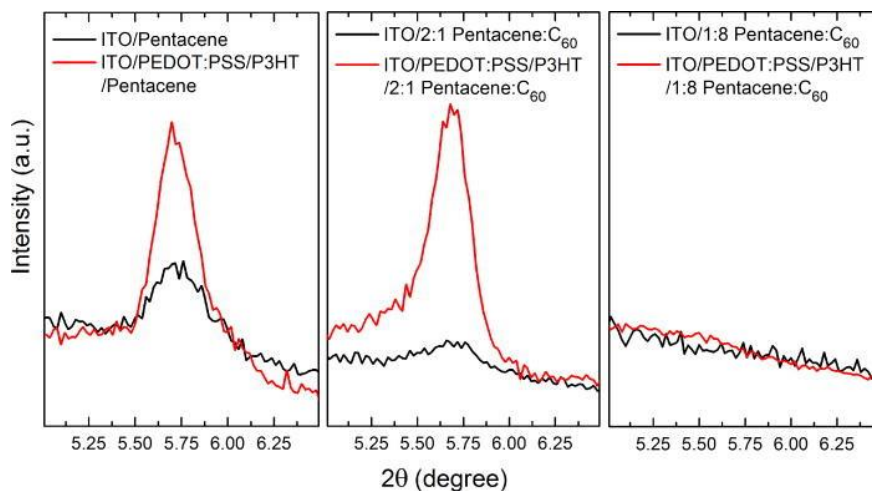
Effective singlet fission solar cells require both fast and efficient singlet fission as well as favorable energetics for harvesting the resulting triplet excitons. Notable progress has been made to engineer materials with rapid and efficient singlet fission, but the ability to control the energetics of these solar cells remains a challenge. Here, it is demonstrated that the interfacial charge transfer state energy of a rubrene/C60 solar cell can be modified dramatically by the morphology of its constituent films. The effect is so pronounced that a crystalline system is able to dissociate and collect triplets generated through singlet fission whereas an as-deposited amorphous system is not. Furthermore, a novel technique for studying the behavior of this class of devices using external quantum efficiency (EQE) measurements in the presence of a background light is described. When this method is applied to rubrene/C60 solar cells, it is shown that triplet–triplet annihilation makes significant contributions to photocurrent in the amorphous device—enhancing EQE by over 12% at relatively low intensities of background light (4 mW cm^{-2})—while detracting from photocurrent in the crystalline device. Finally, the conclusions on how the material system is affected by its morphology are strengthened by time-resolved photoluminescence experiments.

Status: published work at Adv. Funct. Mater. 2016, **26**, 6489

Variable Charge Transfer State Energies at Nanostructured Pentacene/C60 Interfaces

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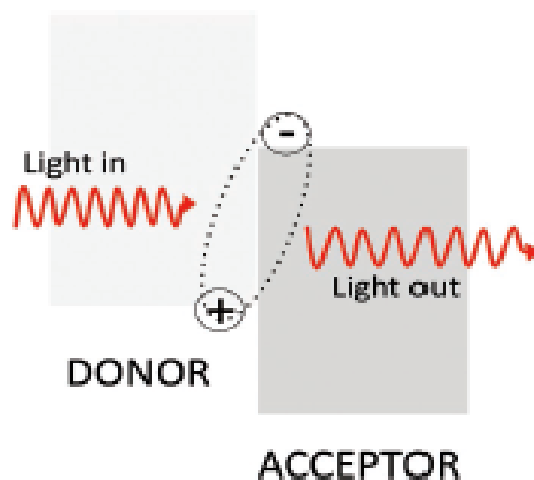
While it has recently been recognized that organic donor-acceptor charge transfer (CT) state energies can vary substantially under different interfacial morphologies, this behavior is under-appreciated in the context of organic singlet fission solar cells where a specific alignment between the triplet state of the fission material and the CT state of the donor-acceptor interface is necessary to the function of the device. In this work, we demonstrate that the CT state energy of a prototypical pentacene-C₆₀ singlet fission system is around 1 eV in most systems, but can vary over 300 meV depending on the composition and morphology of the interface. Moreover, we show that the inclusion of a poly(3-hexylthiophene-2,5-diyl) underlayer, which commonly serves as a triplet blocker and hole collector in pentacene/C₆₀ solar cells, helps promote active layer morphologies with stabilized, low energy CT states. These trends in the interfacial energetics are correlated with structural characterization of the films by atomic force microscopy and x-ray diffraction.

Status: published work at Appl Phys. Lett. 2018, **112**, 213302

The Impact of Local Morphology on Organic Donor/Acceptor Charge Transfer States

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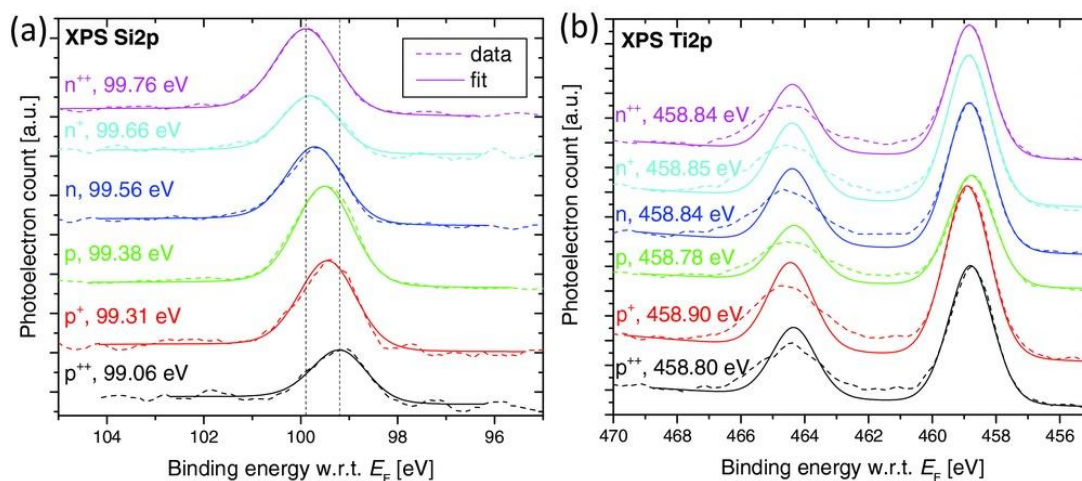
A major breakthrough in the field of organic photovoltaics (OPVs) was the development of the donor/acceptor heterojunction that aids in separating Coulombically bound excitons that are generated upon photoabsorption. Additionally, bound charge transfer (CT) states that result from the exchange of charge carriers across the donor/acceptor interface are believed to play an important role in charge generation. Though organic thin films are often disordered, enhancements to the local structural order at the donor/acceptor interface have recently been shown to greatly influence CT state energetics and the charge generation process. In this progress report, recent efforts to understand the role that donor/acceptor morphology plays in the behavior of CT states and the resulting implications on OPV function are presented. It is aimed to provide a survey of different experimental approaches and to present a balanced examination of current interpretations of key results, and to offer best practices for the fabrication and study of morphologically tunable donor/acceptor CT states.

Status: published work at Adv. Energy Mater. 2018, **8**, 1702816

Electronically Passivated Hole-Blocking Titanium Dioxide/Silicon Heterojunction for Hybrid Silicon Photovoltaics

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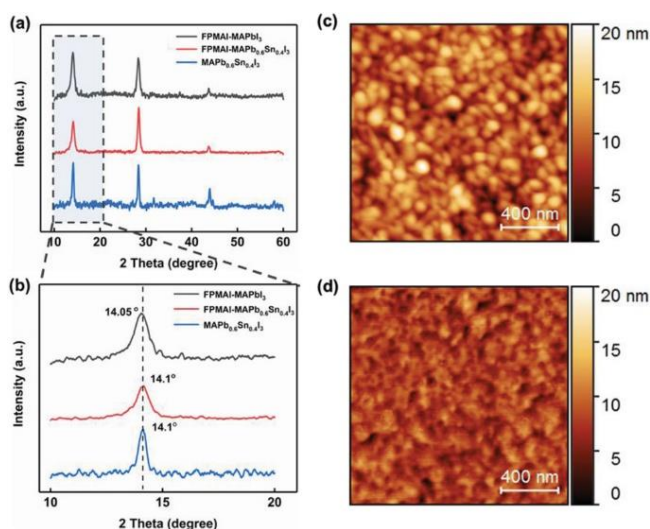
Carrier-selective heterojunctions are important for low-cost silicon-based photovoltaic applications. A low temperature (<100 °C) chemical vapor deposition technique is used here to deposit ultrathin (n-type) titanium dioxide (TiO_2) layers onto hydrogen-passivated surfaces of crystalline-silicon (c-Si). Energy level alignment and chemical composition at these abrupt, interfacial layer-free TiO_2/Si heterojunctions are investigated via ultraviolet, X-ray, and inverse photoemission spectroscopy, for c-Si doping ranging from $p^{++}(10^{19})$ to $n^{++}(10^{19})$. The interface Fermi level position and device-relevant TiO_2/Si band offsets are found to shift monotonically as a function of the Si doping, revealing the absence of Fermi level pinning at the c-Si interface and pointing to simple Fermi level equilibration as the driving mechanism behind the interface energy level alignment. Electrical transport measurements performed on TiO_2/Si -based diodes confirm the energy level alignment yielded by spectroscopic measurements and the hole-blocking properties of the TiO_2/Si heterojunction, exclude hole conduction in the TiO_2 as a transport mechanism, and show carrier recombination at the $\text{TiO}_2/p\text{-Si}$ heterojunction.

Status: published work at Adv. Mater. Interfaces 2016, **3**, 1600026

Mixed Lead–Tin Halide Perovskites for Efficient and Wavelength-Tunable Near-Infrared Light-Emitting Diodes

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Near-infrared (NIR) light-emitting diodes (LEDs), with emission wavelengths between 800 and 950 nm, are useful for various applications, e.g., night-vision devices, optical communication, and medical treatments. Yet, devices using thin film materials like organic semiconductors and lead based colloidal quantum dots face certain fundamental challenges that limit the improvement of external quantum efficiency (EQE), making the search of alternative NIR emitters important for the community. In this work, efficient NIR LEDs with tunable emission from 850 to 950 nm, using lead–tin (Pb–Sn) halide perovskite as emitters are demonstrated. The best performing device exhibits an EQE of 5.0% with a peak emission wavelength of 917 nm, a turn-on voltage of 1.65 V, and a radiance of 2.7 W Sr⁻¹ m⁻² when driven at 4.5 V. The emission spectra of mixed Pb–Sn perovskites are tuned either by changing the Pb:Sn ratio or by incorporating bromide, and notably exhibit no phase separation during device operation. The work demonstrates that mixed Pb–Sn perovskites are promising next generation NIR emitters.

Status: published work at Adv. Mater. 2019, 31, 1806105

Observation of an Environmentally Insensitive Solid-State Spin Defect in Diamond

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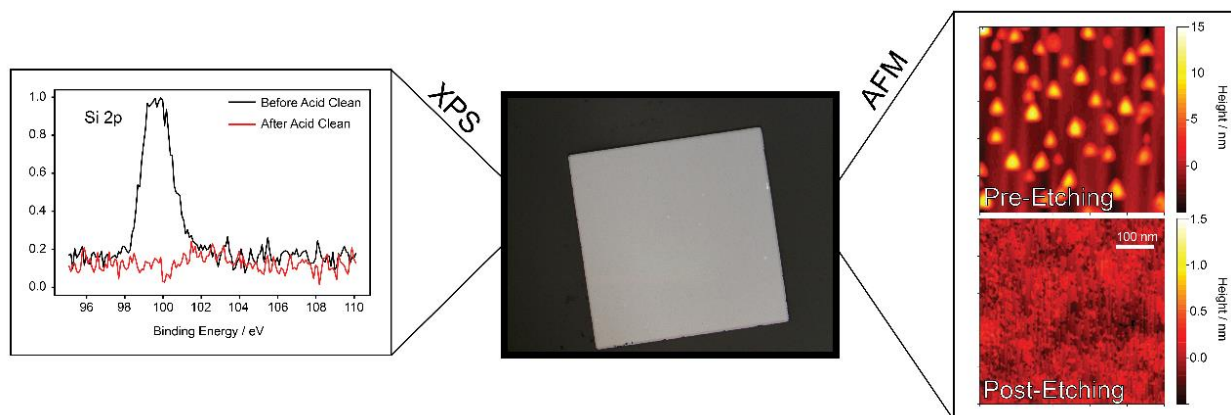


Figure 1 - (Left) Exemplar XPS spectra showing the detection of removal of Silicon contamination on the diamond surface. (Right) AFM spectra showing the effect of plasma etching on the surface smoothness.

Quantum communication requires hardware with capabilities fundamentally distinct from its classical analog. Color centers in diamond have shown great promise as communication nodes in a quantum network, yet much work remains to optimize these systems.

We have developed a recipe for the formation of the neutral silicon-vacancy color center in diamond, which has several desirable properties for a quantum node – long spin coherence times, narrow optical transitions and near infrared operation. The processing steps involve plasma etching and high temperature (1200°C) annealing. Monitoring the surface roughness (AFM) and contamination (XPS) is key for preventing the formation of silicon carbide and trapped charges, which have deleterious effects on the color center properties.

Status: published work at Science, 361, 60-63 (2018)

Excitonic Absorption in Ruddlesden-Popper phase Perovskites

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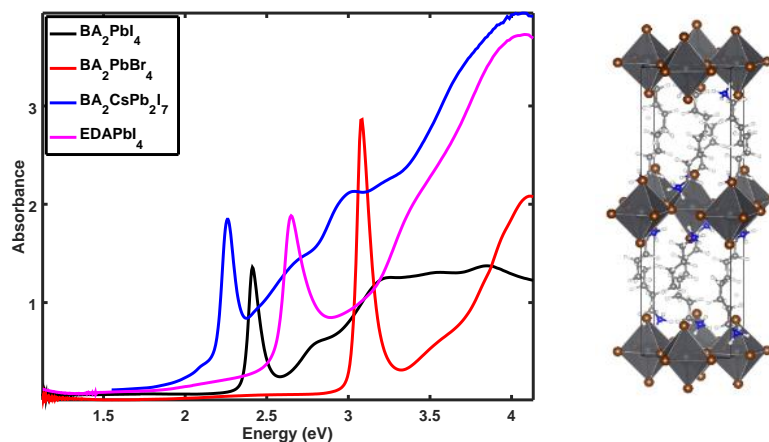


Figure: Absorption Spectra of the Ruddlesden-Popper phase perovskites including BA_2PbI_4 (BA = Butylammonium), BA_2PbBr_4 , and $EDAPbI_4$ (EDA = Ethylene diammonium) which each have one Pb -halide layer between organic layers ($n=1$) as well as $BA_2CsPb_2I_7$ which has two Pb -halide layers between organic layers. Inset is the structure of $n=1$ RPP showing the alternating layers.

Ruddlesden-Popper phase perovskites (RPPs) are promising candidates for the next generation of solar cells and LEDs due to their high absorbance, tunability, and environmental stability. RPPs self-assemble into quantum wells of Pb -halide layers separated by layers of insulating organic ligands creating a two-dimensional material. By modulating the organic ligand, cation, halide, and/or number of Pb -halide layers it is possible to modify the dimensions and energetics of the quantum well, which greatly affects the electronic properties of the film. In conjunction with Photoelectron spectroscopy measurements, absorption spectra enable us to determine the ionization energy, electron affinity, and exciton binding energy of RPPs to better understand the physics behind them and engineer optimized materials for each application.

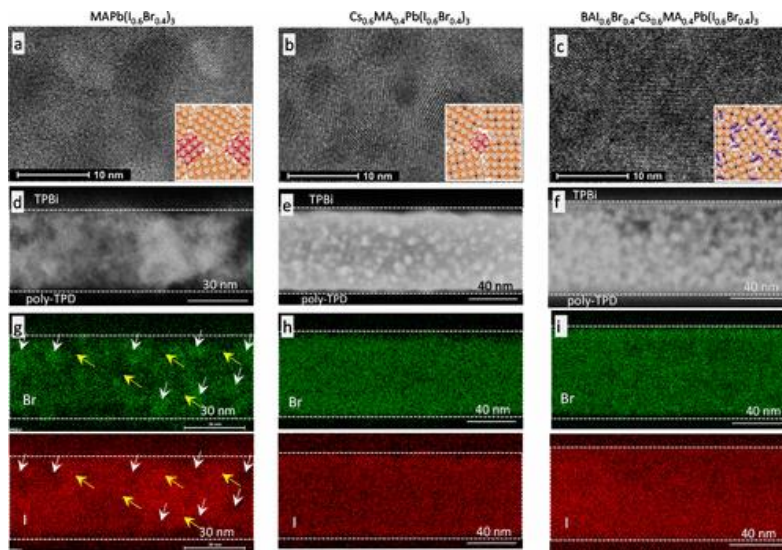
UV-Vis absorption spectroscopy is a quick technique that provides an abundance of characterization information. For multilayer RPPs, UV-Vis is good technique for evaluating the phase purity as well as measuring the optical band gap and excitonic absorption strength. The large exciton peaks in Figure 1 represent absorption due to bound electron-hole pairs, whereas the steady increase in absorption with increasing energy indicates the formation of free electrons and holes. Additionally, we can derive information about surface roughness, film thickness, and the joint density of states.

Status: ongoing research project

Mixed-Halide Perovskites with Stabilized Bandgaps

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¹Department of Electrical Engineering, ²Department of Chemistry, ³Princeton Institute for the Science and Technology of Materials, and ⁴Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA



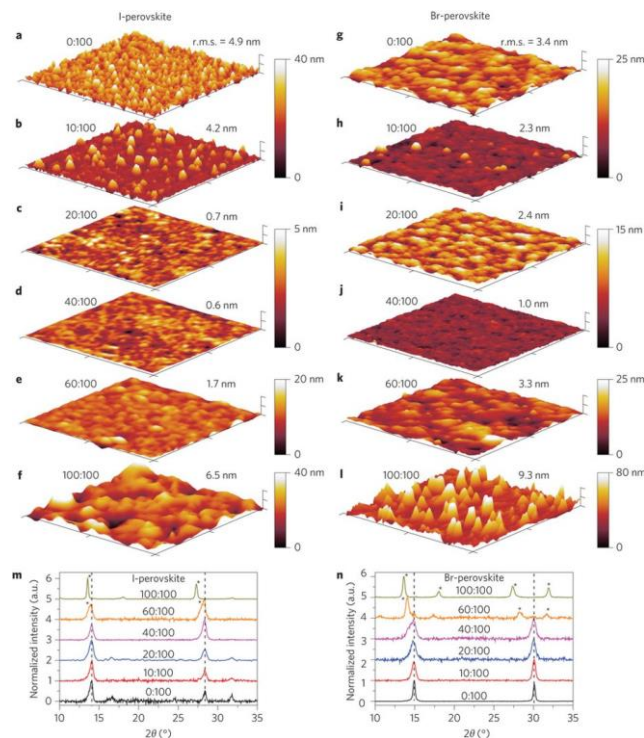
One merit of organic–inorganic hybrid perovskites is their tunable bandgap by adjusting the halide stoichiometry, an aspect critical to their application in tandem solar cells, wavelength-tunable light emitting diodes (LEDs), and lasers. However, the phase separation of mixed-halide perovskites caused by light or applied bias results in undesirable recombination at iodide-rich domains, meaning open-circuit voltage (V_{oc}) pinning in solar cells and infrared emission in LEDs. Here, we report an approach to suppress halide redistribution by self-assembled long-chain organic ammonium capping layers at nanometer-sized grain surfaces. Using the stable mixed-halide perovskite films, we are able to fabricate efficient and wavelength-tunable perovskite LEDs from infrared to green with high external quantum efficiencies of up to 5%, as well as linearly tuned V_{oc} from 1.05 to 1.45 V in solar cells.

Status: published work at Nano Lett. 2017, **11**, 6863

Efficient Perovskite Light-Emitting Diodes Featuring Nanometre-Sized Crystallites

Zhengguo Xiao¹, Ross A. Kerner¹, Lianfeng Zhao¹, Nhu L. Tran², Kyung Min Lee¹, Tae-Wook Koh¹, Gregory D. Scholes², and Barry P. Rand^{1,3}

Department of Electrical Engineering, Department of Chemistry, and Andlinger Center for Energy and the Environment, Princeton University, NJ, USA



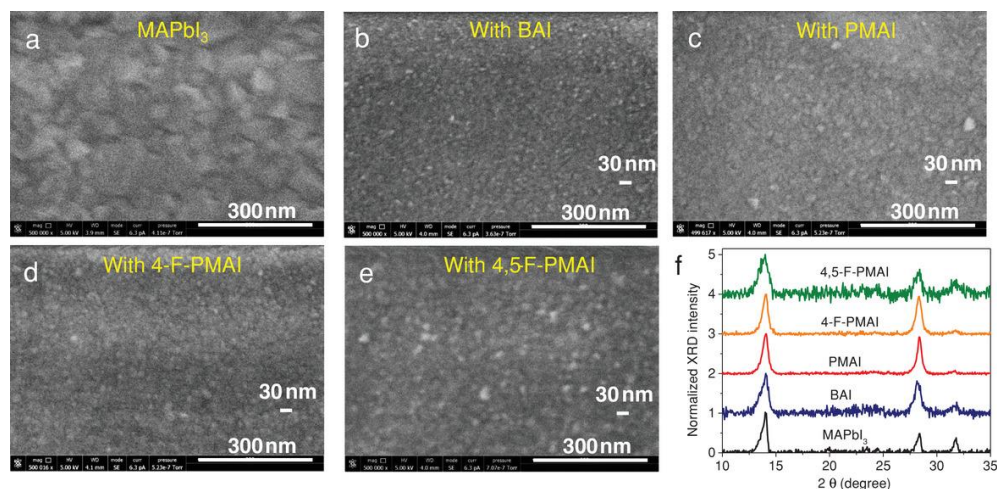
Organic–inorganic hybrid perovskite materials are emerging as highly attractive semiconductors for use in optoelectronics. In addition to their use in photovoltaics, perovskites are promising for realizing light-emitting diodes (LEDs) due to their high colour purity, low non-radiative recombination rates and tunable bandgap. Here, we report highly efficient perovskite LEDs enabled through the formation of self-assembled, nanometre-sized crystallites. Large-group ammonium halides added to the perovskite precursor solution act as a surfactant that dramatically constrains the growth of 3D perovskite grains during film forming, producing crystallites with dimensions as small as 10 nm and film roughness of less than 1 nm. Coating these nanometre-sized perovskite grains with longer-chain organic cations yields highly efficient emitters, resulting in LEDs that operate with external quantum efficiencies of 10.4% for the methylammonium lead iodide system and 9.3% for the methylammonium lead bromide system, with significantly improved shelf and operational stability.

Status: published work at Nat. Photonics 2017, **11**, 108

Engineering Perovskite Nanocrystal Surface Termination for Light-Emitting Diodes with External Quantum Efficiency Exceeding 15%

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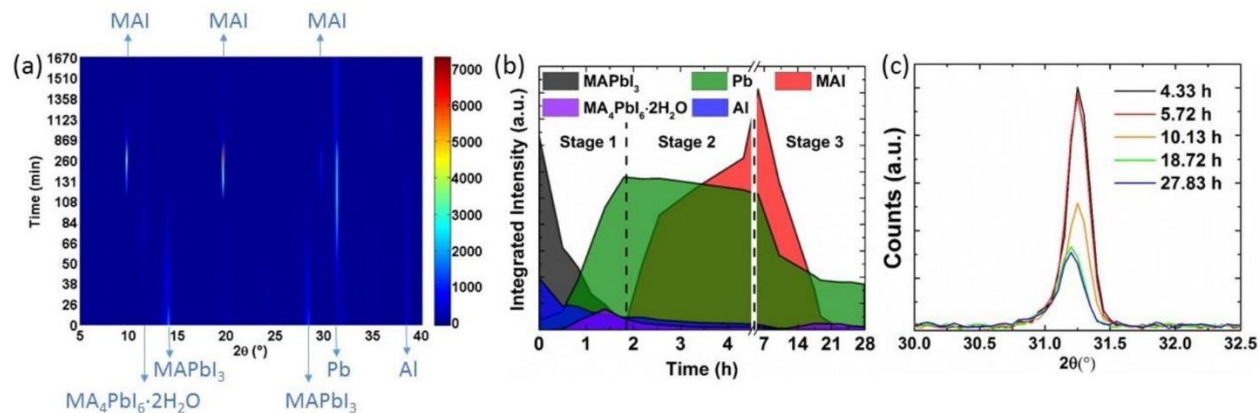
Hybrid organic–inorganic metal halide perovskites are particularly promising for light-emitting diodes (LEDs) due to their attractive optoelectronic properties such as wavelength tunability, narrow emission linewidth, defect tolerance, and high charge carrier mobility. However, the undercoordinated Pb and halide at the perovskite nanocrystal (NC) surface causes traps and nonradiative recombination. In this work, the external quantum efficiency of iodide-based perovskite LEDs is boosted to greater than 15%, with an emission wavelength at 750 nm, by engineering the perovskite NC surface stoichiometry and chemical structure of bulky organoammonium ligands. To the stoichiometric precursor solution for the 3D bulk perovskite, 20% molar ratio of methylammonium iodide is added in addition to 20% excess bulky organoammonium iodide to ensure that the NC surface is organoammonium terminated as the crystal size is decreased to 5–10 nm. This combination ensures minimal undercoordinated Pb and halide on the surface, avoids 2D phases, and acts to provide nanosized perovskite grains which allow for smooth and pinhole-free films. As a result of time-resolved photoluminescence (PL) and PL quantum yield measurements, it is possible to demonstrate that this surface modification increases the radiative recombination rate while reducing the nonradiative rate.

Status: published work at Adv. Funct. Mater. 2019, 1807284

Redox Chemistry Dominates the Degradation and Decomposition of Metal Halide Perovskite Optoelectronic Devices

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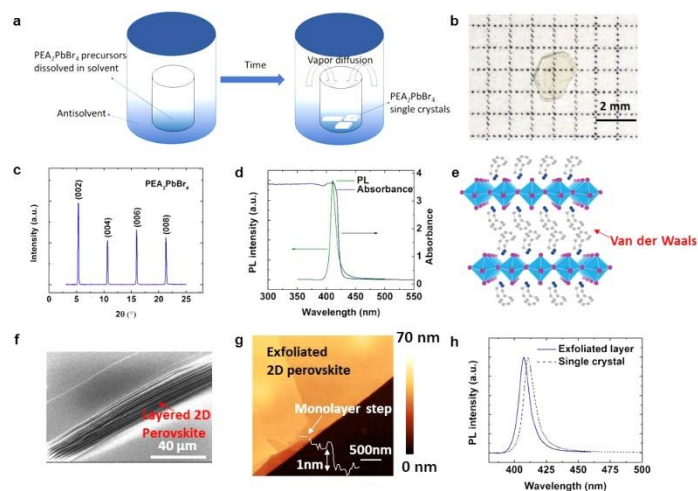
We report a comprehensive study of the chemistry of perovskite optoelectronic device degradation and show that redox reactions are fundamental to the degradation process for $\text{CH}_3\text{NH}_3\text{PbI}_3$, CsPbI_3 , and CsPbBr_3 perovskites with Ag, Al, Yb, or Cr contacts. Using in situ X-ray diffraction measurements, we study the chemistry of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite devices equipped with Al electrodes; we find that Al0 rapidly reduces Pb^{2+} to Pb^0 , converting $\text{CH}_3\text{NH}_3\text{PbI}_3$ first to $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ and then to $\text{CH}_3\text{NH}_3\text{I}$. In situ scanning electron microscopy measurements show that moisture enables continued reaction of the Al and perovskite layers by facilitating ion diffusion, before serving as a decomposition reagent for the perovskite film. Redox reactions follow what is expected based on standard electrochemical potentials for Al, Cr, and Yb; for Ag, the redox chemistry is enabled by the presence of iodide. We emphasize that critical chemical reactions can stem from intrinsic interfacial interactions between the layers in a device and not necessarily from external agents; degradation studies must consider the device as an entity, rather than focusing only on the stability of perovskite films.

Status: published work at ACS Energy Lett. 2016, **1**, 595

Extremely Low Operating Current Resistive Memory Based on Exfoliated 2D Perovskite Single Crystals for Neuromorphic Computing

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¹Institute of Microelectronics and Tsinghua National Laboratory for Information Science and Technology (TNList), Tsinghua University, Beijing, China, ²Department of Electrical Engineering, Princeton University, Princeton, NJ, USA, ³Princeton Institute for Science and Technology of Materials, Princeton University, Princeton, NJ, USA, ⁴Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA



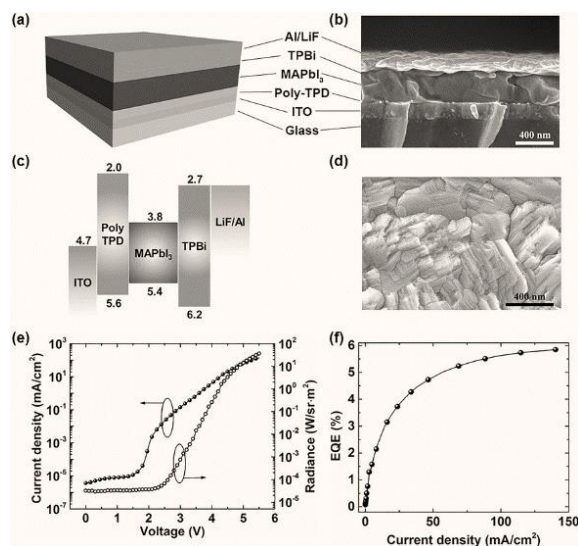
Extremely low energy consumption neuromorphic computing is required to achieve massively parallel information processing on par with the human brain. To achieve this goal, resistive memories based on materials with ionic transport and extremely low operating current are required. Extremely low operating current allows for low power operation by minimizing the program, erase, and read currents. However, materials currently used in resistive memories, such as defective HfO_x , AlO_x , TaO_x , etc., cannot suppress electronic transport (i.e., leakage current) while allowing good ionic transport. Here, we show that 2D Ruddlesden–Popper phase hybrid lead bromide perovskite single crystals are promising materials for low operating current nanodevice applications because of their mixed electronic and ionic transport and ease of fabrication. Ionic transport in the exfoliated 2D perovskite layer is evident via the migration of bromide ions. Filaments with a diameter of approximately 20 nm are visualized, and resistive memories with extremely low program current down to 10 pA are achieved, a value at least 1 order of magnitude lower than conventional materials. The ionic migration and diffusion as an artificial synapse is realized in the 2D layered perovskites at the pA level, which can enable extremely low energy neuromorphic computing.

Status: published work at ACS Nano 2017, **11**, 12247

Electrical Stress Influences the Efficiency of CH₃NH₃PbI₃ Perovskite Light Emitting Devices

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Organic–inorganic hybrid perovskite materials are emerging as semiconductors with potential application in optoelectronic devices. In particular, perovskites are very promising for light-emitting devices (LEDs) due to their high color purity, low nonradiative recombination rates, and tunable bandgap. Here, using pure CH₃NH₃PbI₃ perovskite LEDs with an external quantum efficiency (EQE) of 5.9% as a platform, it is shown that electrical stress can influence device performance significantly, increasing the EQE from an initial 5.9% to as high as 7.4%. Consistent with the enhanced device performance, both the steady-state photoluminescence (PL) intensity and the time-resolved PL decay lifetime increase after electrical stress, indicating a reduction in nonradiative recombination in the perovskite film. By investigating the temperature-dependent characteristics of the perovskite LEDs and the cross-sectional elemental depth profile, it is proposed that trap reduction and resulting device-performance enhancement is due to local ionic motion of excess ions, likely excess mobile iodide, in the perovskite film that fills vacancies and reduces interstitial defects. On the other hand, it is found that overstressed LEDs show irreversibly degraded device performance, possibly because ions initially on the perovskite lattice are displaced during extended electrical stress and create defects such as vacancies.

Status: published work at Adv. Mater. 2017, **29**, 1605317

In-Situ Preparation of Organic-Inorganic Hybrid Perovskite Nanocrystalline Thin Films

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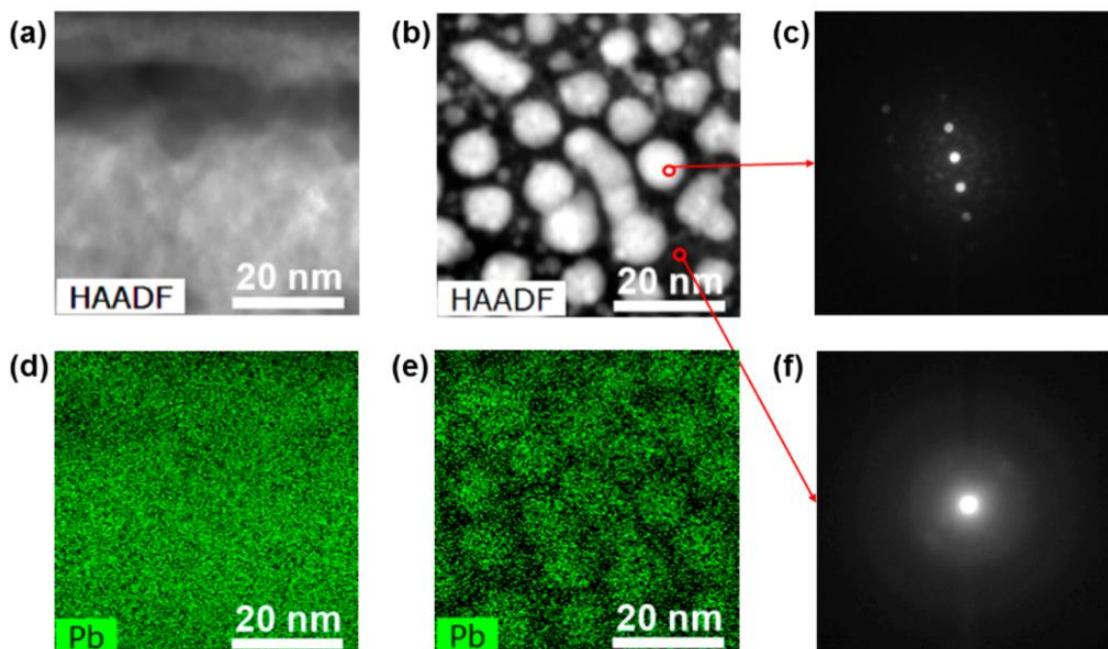


Figure: (a) Cross-sectional STEM image and (d) corresponding elemental EDS map showing the distribution of Pb for $\text{CH}_3\text{NH}_3\text{PbI}_3$ films without FPMAI additives. (b) Cross-sectional STEM image and (e) corresponding elemental EDS map showing the distribution of Pb for $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with FPMAI additives. Electron diffraction patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (c) nanocrystal and (f) matrix.

We demonstrate an *in-situ* strategy for the synthesis of metal halide perovskite nanocrystalline thin films. Rather than casting films from pre-prepared nanocrystal suspensions, we promote *in-situ* growth of perovskite nanocrystals during the film formation process by incorporating bulky organoammonium halides as additives into the starting precursor solution, which act to confine the crystal growth of 3D perovskites and passivate the surface of perovskite nanocrystals, increasing time-resolved photoluminescence (TRPL) decay lifetime and quantum yield (QY) significantly. Using this strategy, highly efficient methylammonium lead iodide and methylammonium lead bromide LEDs are demonstrated.

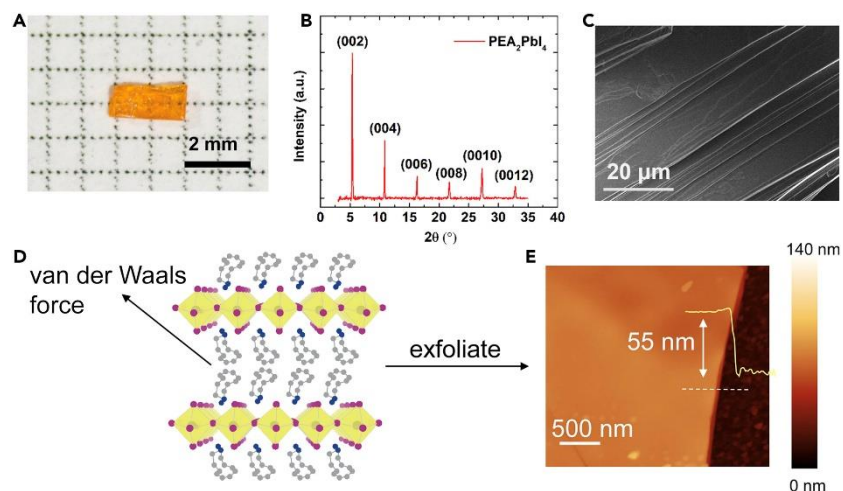
Status: published work at ACS Nano 2017, **11**, 3957

Ultrasensitive Heterojunctions of Graphene and 2D Perovskites Reveal Spontaneous Iodide Loss

Lianfeng Zhao^{1,3}, He Tian², Scott H. Silver¹, Antoine Kahn¹, Tian-Ling Ren² and Barry P. Rand^{1,3}

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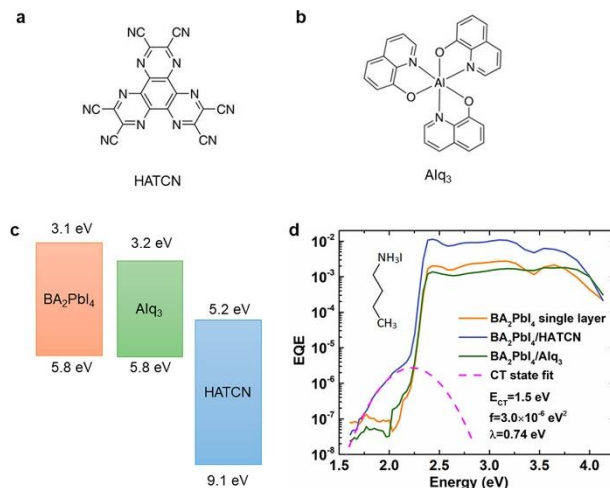
Despite the demonstrated high efficiency of perovskite solar cells and light-emitting devices, the understanding of the intrinsic stability of perovskites is far from complete. In this work, using an ultrasensitive, exfoliated 2D perovskite single-crystal sheet/graphene heterostructure device, we reveal spontaneous iodide loss as an important degradation pathway of 2D perovskite single crystals, which n-dopes the perovskite semiconductor by generating positively charged iodide vacancies. Furthermore, we show that covering perovskites with graphene can suppress the iodide loss, significantly improving perovskite stability. A perovskite phototransistor is demonstrated with a graphene/2D perovskite/graphene structure, which shows no degradation after 75 days. Our work not only provides important insights for future stable perovskite optoelectronic device development, but also demonstrates the potential of graphene as a promising sensitive diagnostic tool for device and material degradation studies.

Status: published work at Joule 2018, 2 2133

Donor/Acceptor Charge-Transfer States at Two-Dimensional Metal Halide Perovskite and Organic Semiconductor Interfaces

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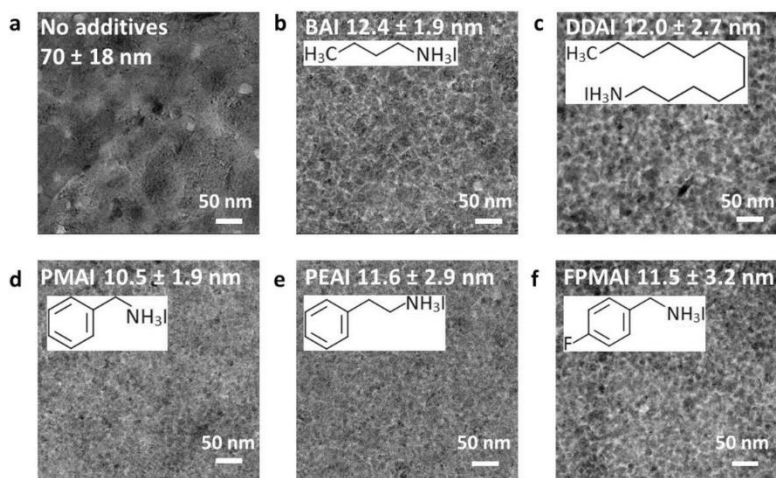
Metal halide perovskite semiconductors with small exciton binding energy have been widely used in perovskite solar cells and achieved rapid progress in terms of device performance. However, the strong excitonic nature of two-dimensional (2D) perovskites with small n values remains underexploited (n represents the number of inorganic monolayer sheets sandwiched between bulky organic cation layers). In this work, we report experimental evidence of donor/acceptor charge-transfer (CT) states formed at 2D metal halide perovskite/organic semiconductor heterojunctions, with a corresponding increase in photocurrent production for these excitonic materials. Furthermore, it is found that the size of the organic cation in the 2D perovskite layer plays a critical role in the CT process. The ability to dissociate excitons in 2D perovskites by interfacing with an organic semiconductor in a donor/acceptor configuration opens up new opportunities for exploiting the excitonic nature of low-dimensional perovskites in applications such as solar cells, photodetectors, light-emitting devices, and light–matter interactions.

Status: published work at ACS Energy Lett. 2018, **3**, 2708

Influence of Bulky Organo-Ammonium Halide Additive Choice on the Flexibility and Efficiency of Perovskite Light-Emitting Devices

Lianfeng Zhao¹, Nicholas Rolston², Kyung Min Lee¹, Xunhua Zhao³, Marcos A. Reyes-Martinez⁴, Nhu L. Tran³, Yao-Wen Yeh⁵, Nan Yao⁵, Gregory D. Scholes³, Yueh-Lin Loo⁴, Annabella Selloni³, Reinhold H. Dauskardt², Barry P. Rand^{1,6}

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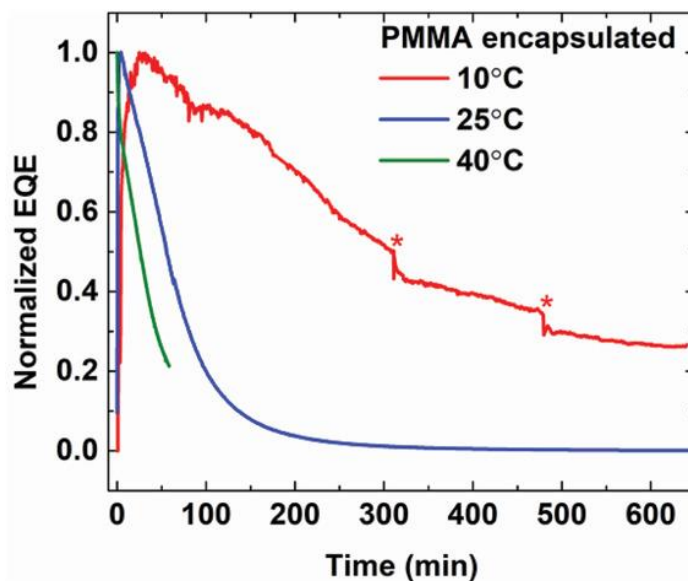
Perovskite light-emitting diodes (LEDs) require small grain sizes to spatially confine charge carriers for efficient radiative recombination. As grain size decreases, passivation of surface defects becomes increasingly important. Additionally, polycrystalline perovskite films are highly brittle and mechanically fragile, limiting their practical applications in flexible electronics. In this work, the introduction of properly chosen bulky organo-ammonium halide additives is shown to be able to improve both optoelectronic and mechanical properties of perovskites, yielding highly efficient, robust, and flexible perovskite LEDs with external quantum efficiency of up to 13% and no degradation after bending for 10 000 cycles at a radius of 2 mm. Furthermore, insight of the improvements regarding molecular structure, size, and polarity at the atomic level is obtained with first-principles calculations, and design principles are provided to overcome trade-offs between optoelectronic and mechanical properties, thus increasing the scope for future highly efficient, robust, and flexible perovskite electronic device development.

Status: published work at Adv. Funct. Mater. 2018, **28**, 1802060

Improved Outcoupling Efficiency and Stability of Perovskite Light-Emitting Diodes using Thin Emitting Layers

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Hybrid organic–inorganic perovskite semiconductors have shown potential to develop into a new generation of light-emitting diode (LED) technology. Herein, an important design principle for perovskite LEDs is elucidated regarding optimal perovskite thickness. Adopting a thin perovskite layer in the range of 35–40 nm is shown to be critical for both device efficiency and stability improvements. Maximum external quantum efficiencies (EQEs) of 17.6% for $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{2.8}\text{Br}_{0.2}$, 14.3% for $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃), 10.1% for formamidinium lead iodide (FAPbI₃), and 11.3% for formamidinium lead bromide (FAPbBr₃)-based LEDs are demonstrated with optimized perovskite layer thickness. Optical simulations show that the improved EQEs source from improved light outcoupling. Furthermore, elevated device temperature caused by Joule heating is shown as an important factor contributing to device degradation, and that thin perovskite emitting layers maintain lower junction temperature during operation and thus demonstrate increased stability.

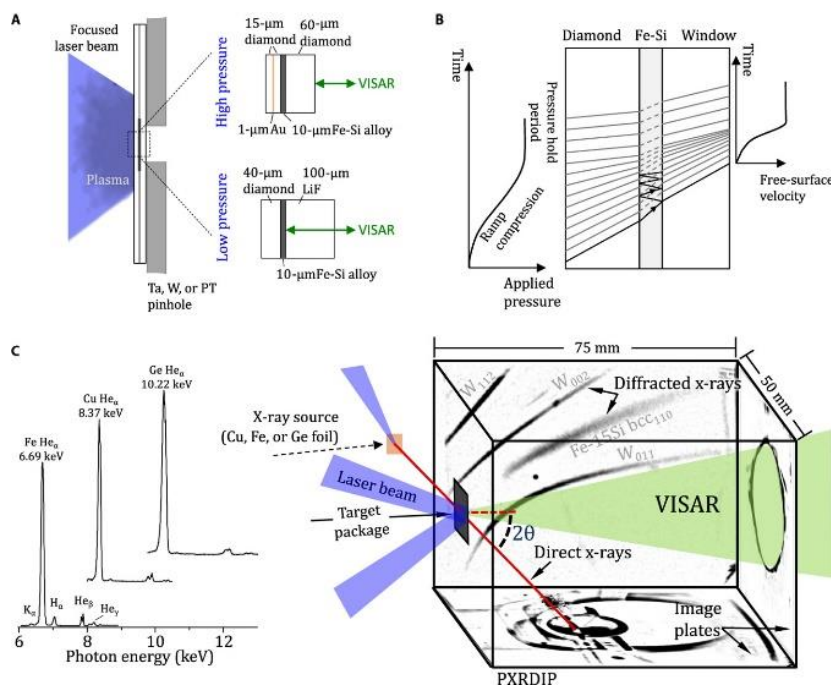
Status: published work at Adv. Mater. 2019, **31**, 1805836

Department of Geosciences

Crystal Structure and Equation of State of Fe-Si Alloys at Super-Earth Core Conditions

June K. Wicks^{1,2}, Raymond F. Smith³, Dayne E. Fratanduono³, Federica Coppari³, Richard G. Kraus³, Matthew G. Newman⁴, J. Ryan Rygg^{3,5}, Jon H. Eggert³, and Thomas S. Duffy¹

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The high-pressure behavior of Fe alloys governs the interior structure and dynamics of super-Earths, rocky extrasolar planets that could be as much as 10 times more massive than Earth. In experiments reaching up to 1300 GPa, we combine laser-driven dynamic ramp compression with in situ x-ray diffraction to study the effect of composition on the crystal structure and density of Fe-Si alloys, a potential constituent of super-Earth cores. We find that Fe-Si alloy with 7 weight % (wt %) Si adopts the hexagonal close-packed structure over the measured pressure range, whereas Fe-15wt%Si is observed in a body-centered cubic structure. This study represents the first experimental determination of the density and crystal structure of Fe-Si alloys at pressures corresponding to the center of a ~3-Earth mass terrestrial planet. Our results allow for direct determination of the effects of light elements on core radius, density, and pressures for these planets.

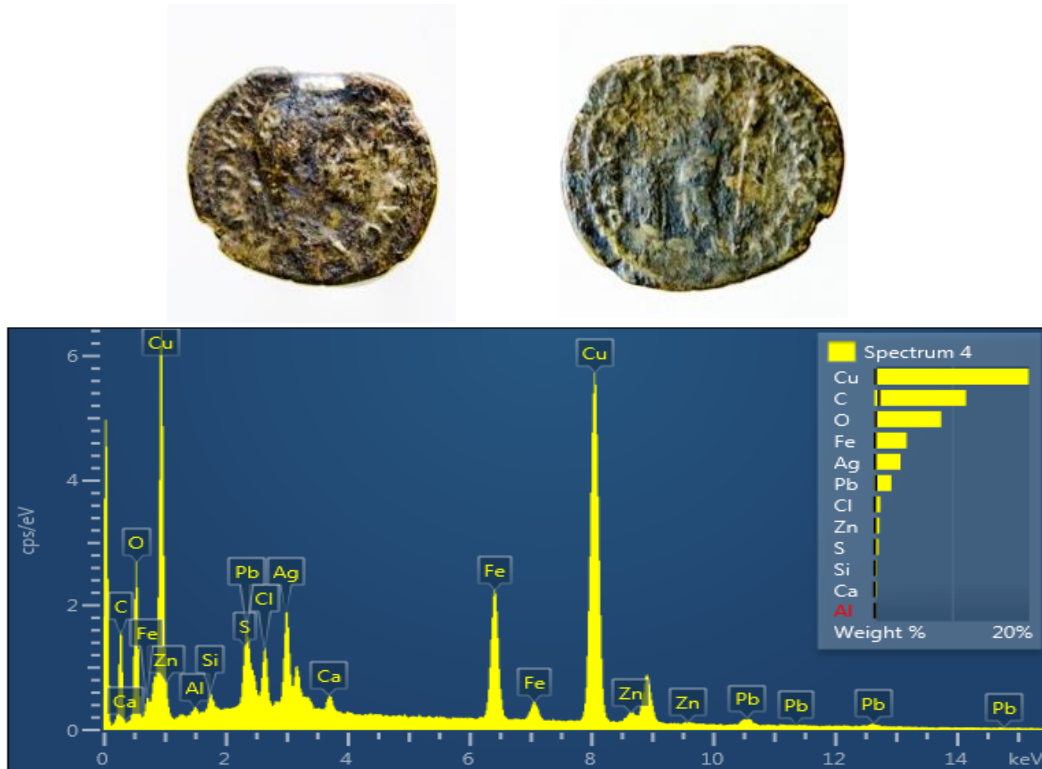
Status: published work at Sci. Adv. 2018, **4**, eaao5864

Department of History

Counterfeit Coins in Antioch Contextualized

Jennifer El-Fakir¹ and Alan M. Stahl²

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In her paper for CLA548, a graduate seminar in numismatic methodology, the author considered a coin in Princeton's Firestone Library excavated in Antioch-on-the-Orontes in 1938. The image and inscription were those of a fine silver denarius of the Roman emperor Caracalla datable to 206 CE. This specimen was, however, typical of most of the 32 such denarii found along with 22,000 bronze coins from the site in that it appeared to the eye to be mainly of copper rather than silver; it was described by the excavators at the time as either an extremely debased denarius or a contemporary bronze imitation. On the basis of SEM/EDX testing carried out by Princeton's Imaging and Analysis Center of three points on the coin's surface, it was determined that the coin was mainly copper, and therefore a contemporary counterfeit. Comparisons with finds from other excavations in the Eastern Mediterranean region suggest that the circulation of such counterfeits was common in the region.

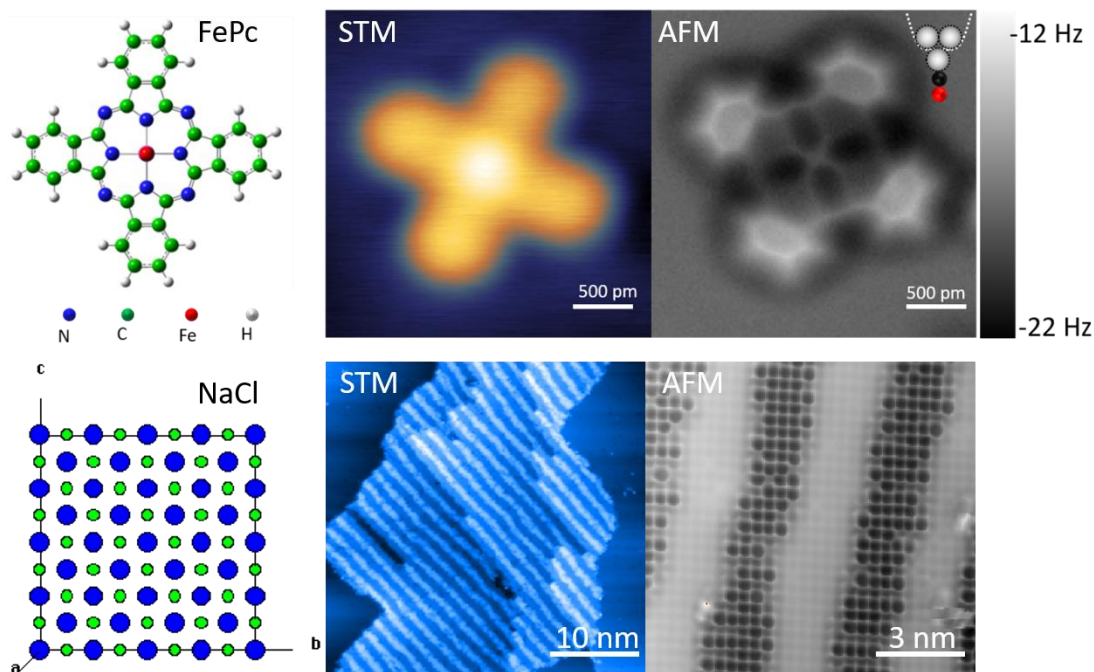
Status: undergraduate senior thesis

Imaging and Analysis Center

High-Resolution Atomic Force Microscopy of Organic Molecules and New 2D Materials

Pengcheng Chen and Nan Yao

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Princeton, New Jersey, USA.*

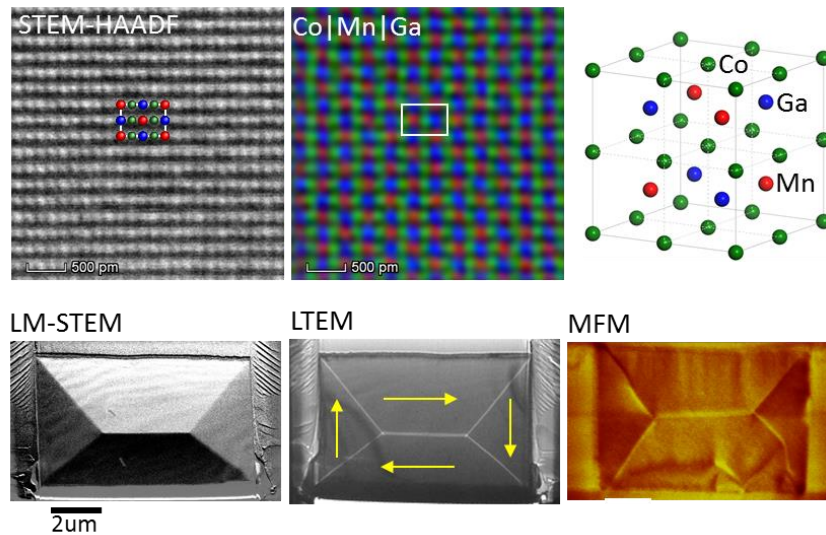


Under the condition of ultra-high vacuum (10^{-11} Torr) and liquid-helium temperature (4 K), we are able to grow organic molecules on single crystal surfaces. Using the CreaTec high-resolution non-contact atomic force microscope (nc-AFM) and scanning tunneling microscope (STM), with a carbon monoxide molecule probe tip, we have observed the chemical structure of single organic molecules. As shown in the images here (first row), the internal structure of single FePc molecules were resolved. By controlling the growth process, new 2D materials are grown with atomic precision. For example, above STM and AFM images (second row) show the single atomic layer insulating NaCl film grown on Cu (110) surface. Due to the variation of bonding strength induced by crystal lattice mismatch, strip like NaCl structure were formed. The AFM image on the right further revealed the internal NaCl crystal lattice at atomic resolution and conformed that the edges of film strips are polarized.

Status: ongoing research work

Magnetic Configurations in a Topological Magnet, Co_2MnGa

Guangming Cheng¹, Yao-Wen Yeh¹, Ilya Belopolski², M. Zahid Hasan² and Nan Yao¹
¹Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey, USA; ²Department of Physics, Princeton University, Princeton, New Jersey, USA



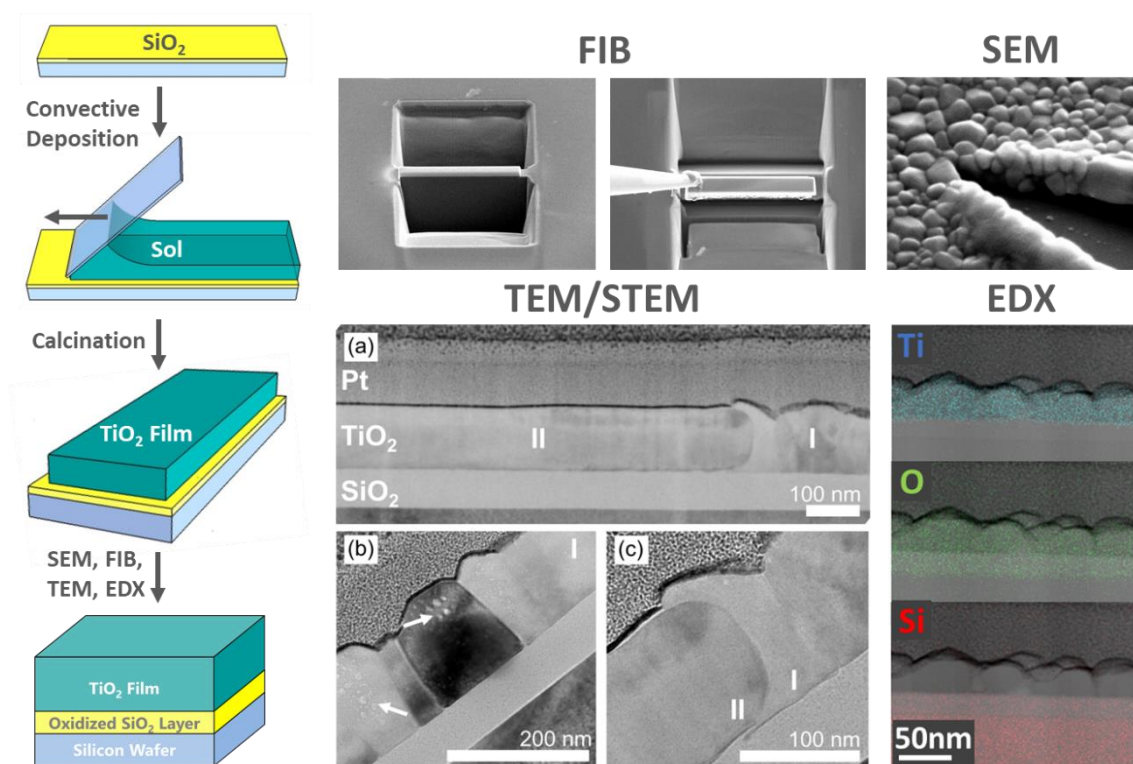
Single crystalline Co_2MnGa with a Heusler crystal structure ($L2_1$) was predicted to be a three dimensional magnet which can be topological with exotic surface states [1]. It is of great interest to find experimental approaches to verify its topological magnetic configurations. Co_2MnGa exhibits different crystal structures ($A2$, $B2'$ and $L2_1$) with the ordered or disordered occupancies of alloying elements. Here, the occupations of Co, Mn and Ga are identified in the $L2_1$ structure (ferromagnetic) by elemental mapping at atomic-level (STEM-HAADF). On the other hand, magnetic domains are the elements of the microstructure of magnetic materials that link the basic physical properties of a material with its macroscopic properties and applications. Magnetic domains can be identified in a bulk sample with large thickness (> 200 nm) via magnetic force microscopy (MFM). Magnetic domain walls can also be imaged in a thin lamellae (< 200 nm) under Lorentz transmission electron microscope (LTEM) mode and by differential phase contrast (DPC) imaging under low magnification STEM (LM-STEM). With the combination of electron microscopy and MFM, it will allow us to illustrate the magnetic domains in the samples with various thickness and further interpret the topological magnetic configurations in such material.

Status: ongoing research work

Thin Film Characterization via Complementary Electron Microscopy Techniques

Daniel Gregory and Nan Yao

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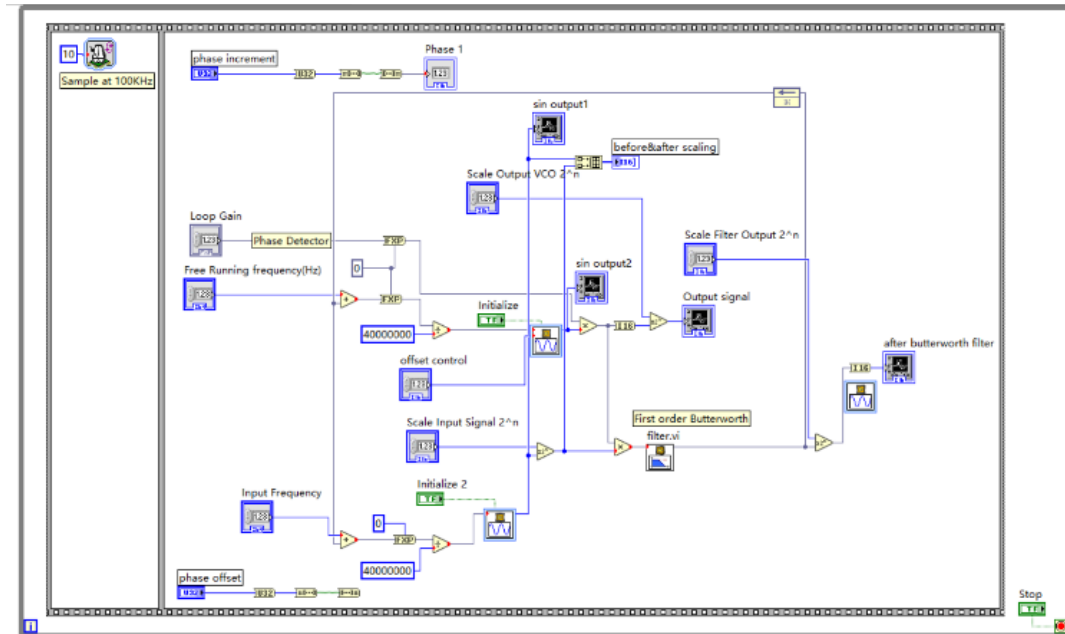
The application of complementary electron microscopy (EM) techniques offers a versatile approach for the characterization of thin films, semiconductors, and photovoltaics. In this study, a combination of FIB, SEM, TEM/STEM, and EDX were employed to study the polymorphic transformation of TiO₂ films, as prepared via convective deposition on oxidized silicon wafers. Focused Ion Beam lithography (FIB) was utilized to mill away portions of material from each film and subsequently lift-out a cross-sectional slice (*i.e.*, lamella), for direct examination of the underlying oxide layers. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were then utilized to characterize the thickness and morphology of each layer. Lastly, an energy-dispersive X-ray (EDX) spectrometer was used to map the elemental composition of the lamella. These complementary EM techniques demonstrated that the interface between the oxide layers was responsible for stabilization of the metastable anatase TiO₂ polymorph by restricting atomic mobility during calcination at temperatures >500 °C.

Status: published work at J. Phys. Chem. C 2017, **121**, 4434-4442

Phase Locked Loop Control for Q-Plus Non-Contact Atomic Force Microscope

Junrong Li¹ and Pengcheng Chen²

¹Department of Computer Science and Engineering, The Hong Kong University of Science and Technology, Hong Kong S.A.R., China; ²Imaging and Analysis Center, Princeton University, Princeton, New Jersey, USA



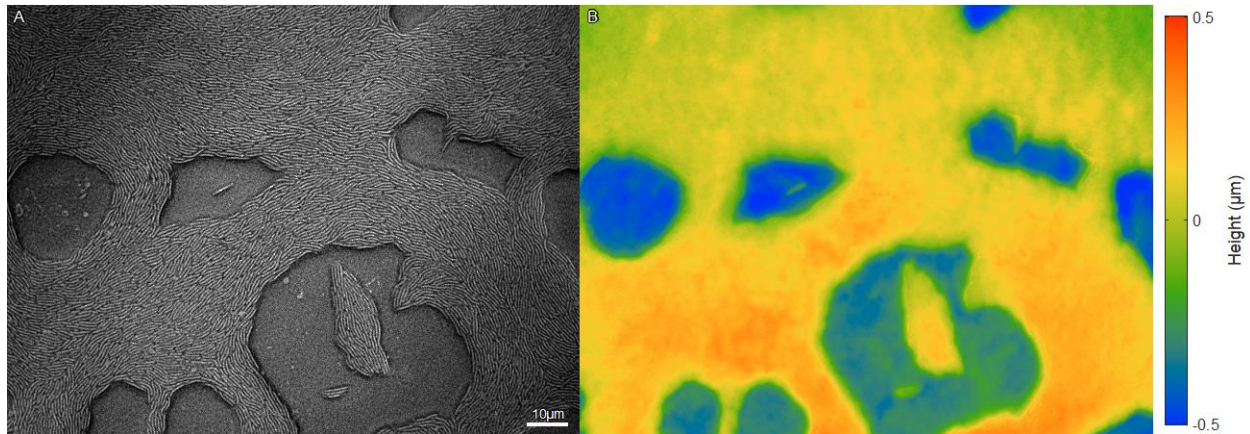
QPlus scanning technique can achieve a result with higher precision in imaging with a wider range of acceptable samples. There is an advanced atomic force microscope at the Imaging and Analysis Center which can attain distinguished precision. In order to save time and make a faster as well as more efficient approximation before the complete scan with this atomic force microscope, we can take the advantage of the q-Plus techniques to build up a scanning device and have a rough estimation of the samples. Then we should develop a software to realize the effective control on it. Based on the q-Plus techniques, control theory and model programs on the LabVIEW FPGA platform, I adapted the Phase Locked Loop method to lock the frequency of the Quartz tuning fork with respect to the tip frequency. This control program runs on the NI motherboard. It takes the oscillation frequency of the fork as input and regulates the frequency of the power source. Then it can make sure the power source can always follow the tip oscillation frequency. Consequently, the tuning fork will output the information more accurately from the detected surface.

Status: ongoing research work

Lewis-Sigler Institute of Integrative Genomics

Myxococcus Xanthus Swarms as an Active Material

Katherine Copenhagen, Cassidy Yang, Matthew Black and Joshua W. Shaevitz
Department of Physics and Lew-Sigler Institute, Princeton University, Princeton, NJ, USA



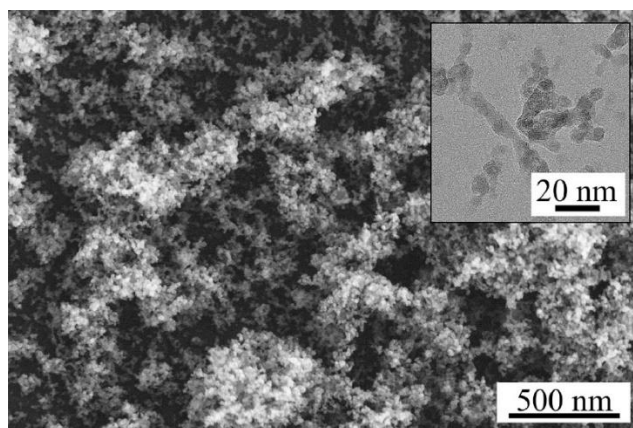
Statistical mechanics and thermodynamics are important tools for understanding how the properties of individual molecules in a material lead to its observable bulk properties, such as phase and magnetization. However, when a material is taken out of equilibrium by giving its molecules the ability to self-propel (as seen in bird flocks, fish schools, swarms of bacteria, and many other biological systems), they no longer follow the same laws as their equilibrium counterparts. Recent research on hydrodynamic and agent-based modeling of active materials has demonstrated a wide array of new properties that rely on the system being out of equilibrium. However, how these models apply to natural biological systems is not yet well understood. *Myxococcus xanthus* (*Myxo*) is a bacteria that lives in the soil and survives by existing in large cooperative groups. *Myxo* is an ideal experimental system for studying active materials, because the properties of individuals can be measured through microscopy and modified by genetic mutations, and its bulk, group properties are essential for survival. We use laser scanning confocal microscopy to look at the organization of cells within a sample while simultaneously measuring its 3D structure (see figure). Through timelapse imaging, we examine how details of cellular motion of individuals in different environments are connected to structural changes in the overall system, including monolayer to multilayer transitions and fruiting body formation under starvation.

Status: ongoing research work

Department of Mechanical and Aerospace Engineering

Flame Synthesis of Nanophosphors Using Sub-Micron Aerosols

Christopher Abram, Maksim Mezhericher, Frank Beyrau, Howard A. Stone, and Yiguang Ju
Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA, Lehrstuhl für Technische Thermodynamik, Otto-von-Guericke-Universität Magdeburg, Germany



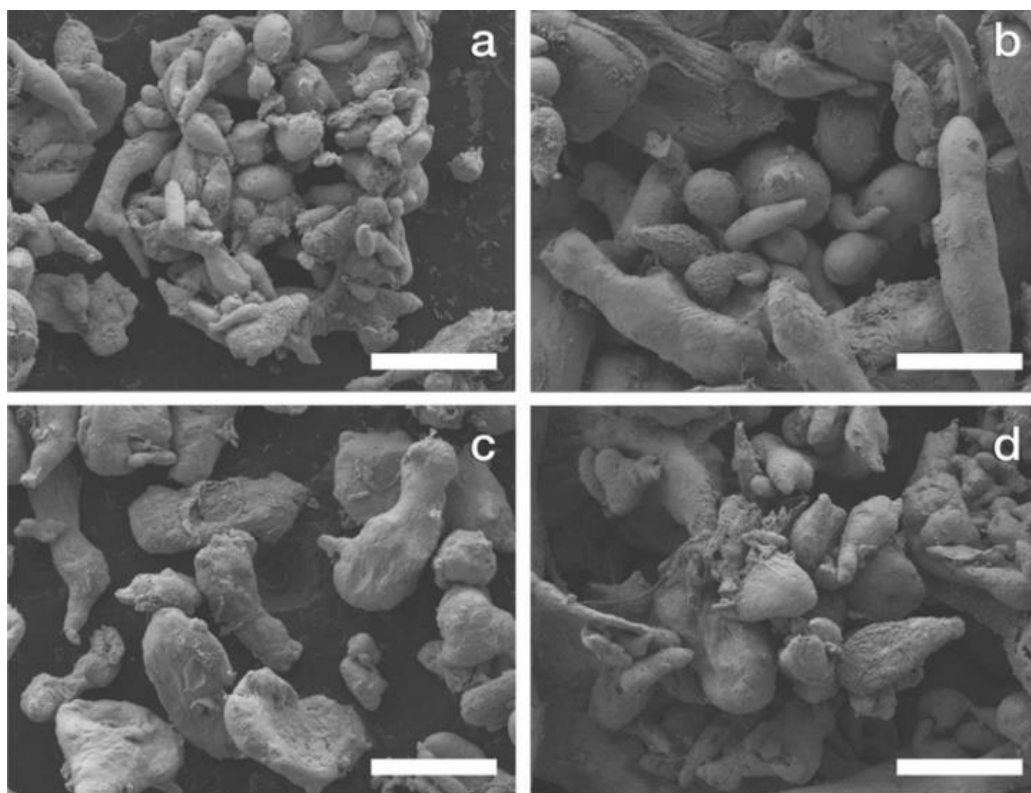
A flame synthesis approach is described for producing metal oxide nanoparticles. It is based on a novel microjet atomisation technique, which generates solution aerosol droplets in the sub-micron range with a mean diameter of 200 nm. Here, luminescent Eu-doped Y_2O_3 nanophosphors are successfully synthesised from aqueous metal nitrate precursors delivered to non-premixed $\text{CH}_4/\text{N}_2\text{-O}_2$ flames. The effect of droplet size and synthesis temperature on the particle formation route is experimentally investigated by comparison with micron-size droplets (mean diameter 3.5 μm) produced by ultrasonic atomisation. Depending on the synthesis temperature, the results show that particles are formed via two different mechanisms: gas-to-particle and droplet-to-particle. Using sub-micron droplets at low temperatures (1150 K), the latter mechanism allows production of luminescent $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles in the cubic phase, with straightforward particle size control from 10 to 100 nm by adjusting the precursor concentration in the 0.01–1 mol/L range. At higher flame temperatures (2750 K), results show that nanoparticles are formed via the gas-to-particle mechanism and have a size of 4–5 nm. In comparison with micron-size droplets, specific surface area measurements of the product powders show that sub-micron droplets form an increased fraction of nanoparticles via the gas-to-particle route. The greater developed surface area of sub-micron droplets enhances vaporisation of metal precursor molecules into the gas phase. Timescale analysis shows that the relative rates of solvent evaporation and bulk solute diffusion are also dependent on the droplet size. Electron microscopy confirms that dense particles are formed from sub-micron droplets subjected to a rapid rate of temperature increase in the flame.

Status: published work at *Proceedings of the Combustion Institute*, 2018

Anode Characterization in Zinc-Manganese Dioxide AA Alkaline Batteries Using Electrochemical-Acoustic Time-of-Flight Analysis

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Using an ultrasonic flaw detector, electrochemical-acoustic time of flight (EAToF) experiments are performed on commercially available alkaline Zn/MnO₂ LR6 (AA) batteries during discharge. The EAToF data are compared to in situ energy-dispersive X-ray diffraction (EDXRD) data and scanning electron microscope (SEM) images taken *post mortem*. Changes in the acoustic waveforms from EAToF measurements are shown to correlate with dehydration of the Zn gel anode and formation of ZnO, as shown by peak evolution in the EDXRD data and morphology analysis using SEM. We show that the physical transitions during discharge change the transmission of an ultrasonic pulse, and that ultrasonic time-of-flight analysis can be used to determine differences between brands of alkaline AA cells.

Status: published work at J. Electrochem. Soc. 2016, **163**, A1050-A1056

Anode Materials for Li-ion Batteries

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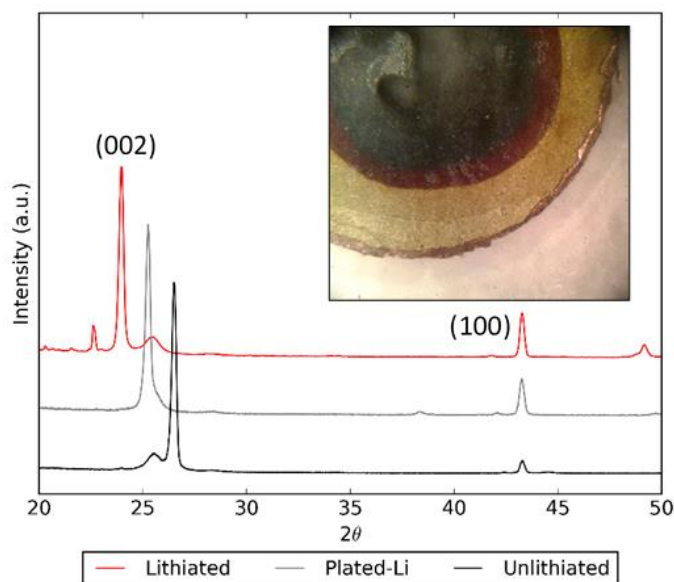


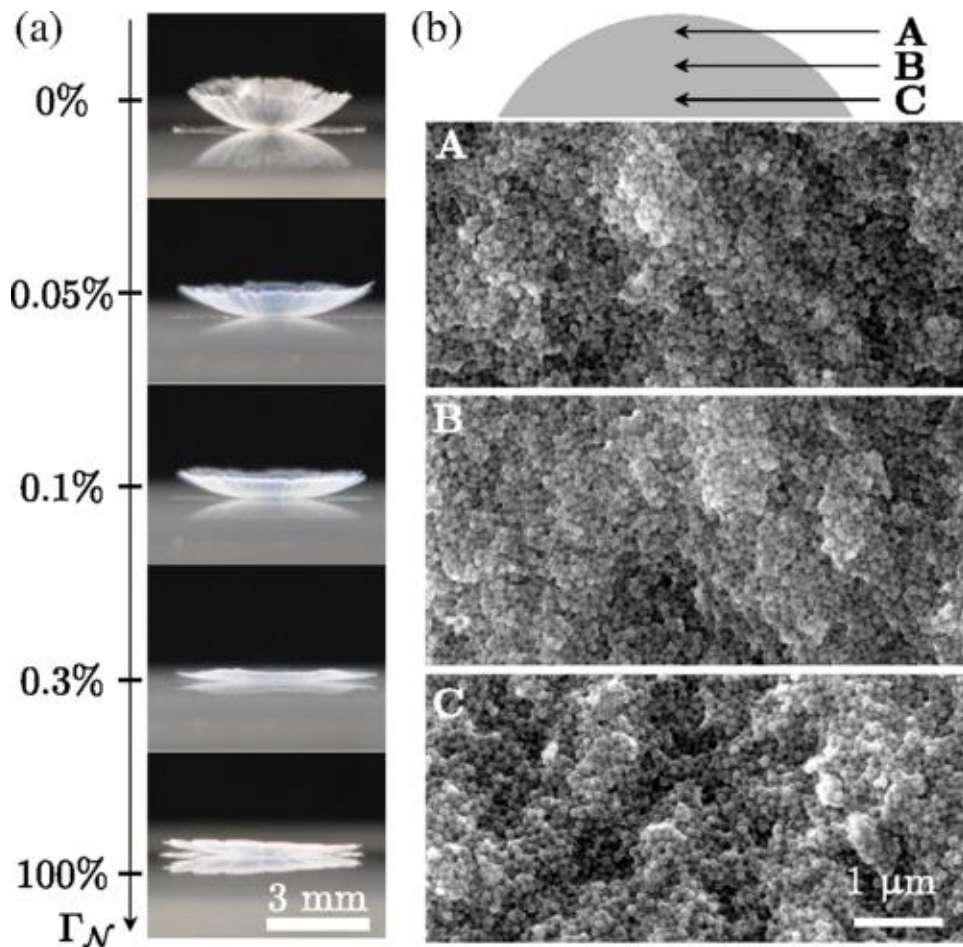
Figure: XRD patterns of LIB anodes under varied states of lithiation, showing the main (002) peak representing the graphite dilation around 23° to 26°, and the (100) basal peak at 43°. The (002) peak shifts as a function of lithiation, with the shift not being as pronounced with the plated graphite. The inset shows a graphite anode with lithium slowly diffusing into it: the gold band in fully lithiated graphite, the red band is in transition, while the black part has yet to be lithiated.

My research utilizes the Bruker D8 Discovery in the IAC to characterize the structure of graphite materials used as anode materials for Li-ion batteries (LIBs). More specifically, we are interested in finding out whether lithium that is plated onto the graphite surface during low-temperature electrochemical cycling remains there as a passivation layer, or engages in solid-state diffusion into the graphite after being deposited. This has large implications for LIBs operating in extreme environments, or used for fast charging: plating of lithium onto the graphite during electrochemical cycling is regarded as very damaging to the battery, and as such, knowing proper operational parameters is critical for battery performance and long term health. Showing the rate at which lithium effectively diffuses into graphite following deposition would allow for a more complete understanding of battery operational conditions, which could enhance their use in extreme environments, as well as prolong their lifetime in traditional applications. The XRD is a valuable tool for this, as it allows us to precisely obtain the graphitic structure, thus allowing us to elucidate the degree of lithiation, and consequently, the solid-state diffusion parameters.

Status: ongoing research project

Effect of the Polydispersity of a Colloidal Drop on Drying Induced Stress as Measured by the Buckling of a Floating Sheet

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Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA



We study the stress developed during the drying of a colloidal drop of silica nanoparticles. In particular, we use the wrinkling instability of a thin floating sheet to measure the net stress applied by the deposit on the substrate and we focus on the effect of the particle polydispersity. In the case of a bidisperse suspension, we show that a small number of large particles substantially decreases the expected stress, which we interpret as the formation of lower hydrodynamic resistance paths in the porous material. As colloidal suspensions are usually polydisperse, we show for different average particle sizes that the stress is effectively dominated by the larger particles of the distribution and not by the average particle size.

Status: published work at Phys. Rev. Lett. 2016, **116**, 238001

Poor Man's Atomic Layer Deposition of LiF for Additive-Free Growth of Lithium Columns

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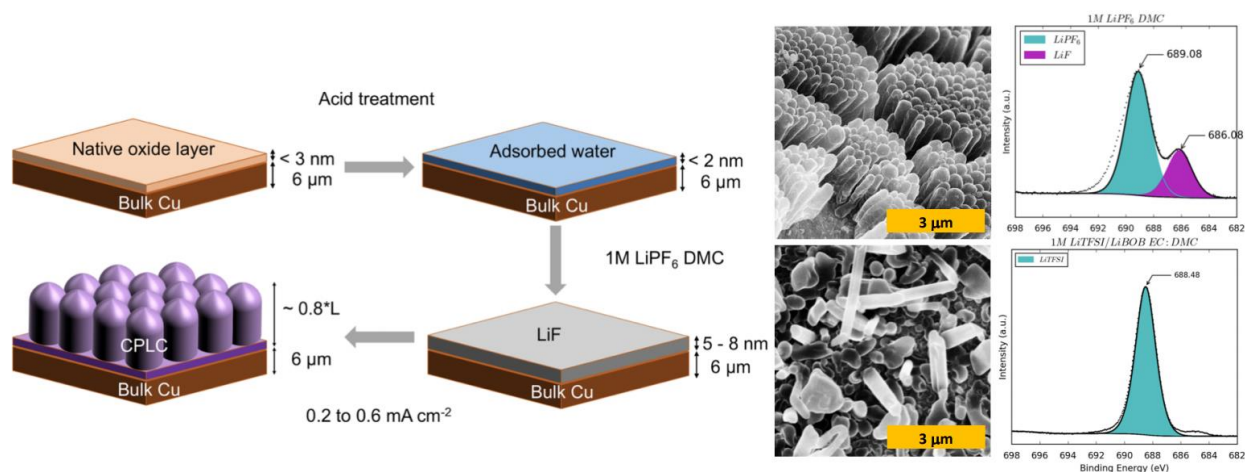


Figure: The Thermo K-Alpha XPS in the IAC was used to characterize the chemical composition of various lithium nanostructures from electrodeposition and elucidate a mechanism for columnar lithium growth (left). Electrolytes prone to decomposition in trace amounts of water exhibited presence of a secondary decomposition peak assigned to LiF in the XPS F 1s scan, while a more stable electrolyte did not exhibit a significant secondary peak (right)

My research focuses on the fundamental nucleation and growth processes of electrodeposited lithium on substrates. Lithium is a unique metal that has optimal properties for use as an electrode in next-generation rechargeable batteries. Because of its high reactivity and tendency to form a chemical passivation layer in the presence of conventional battery electrolytes, this interphase layer between the lithium metal and electrolyte has a critical effect on the subsequent morphology (which in turn affects the electrochemical performance). Specifically, there have been indications in recent literature pointing towards the modulating effect of LiF in this interphase layer, resulting in smooth uniform morphology.

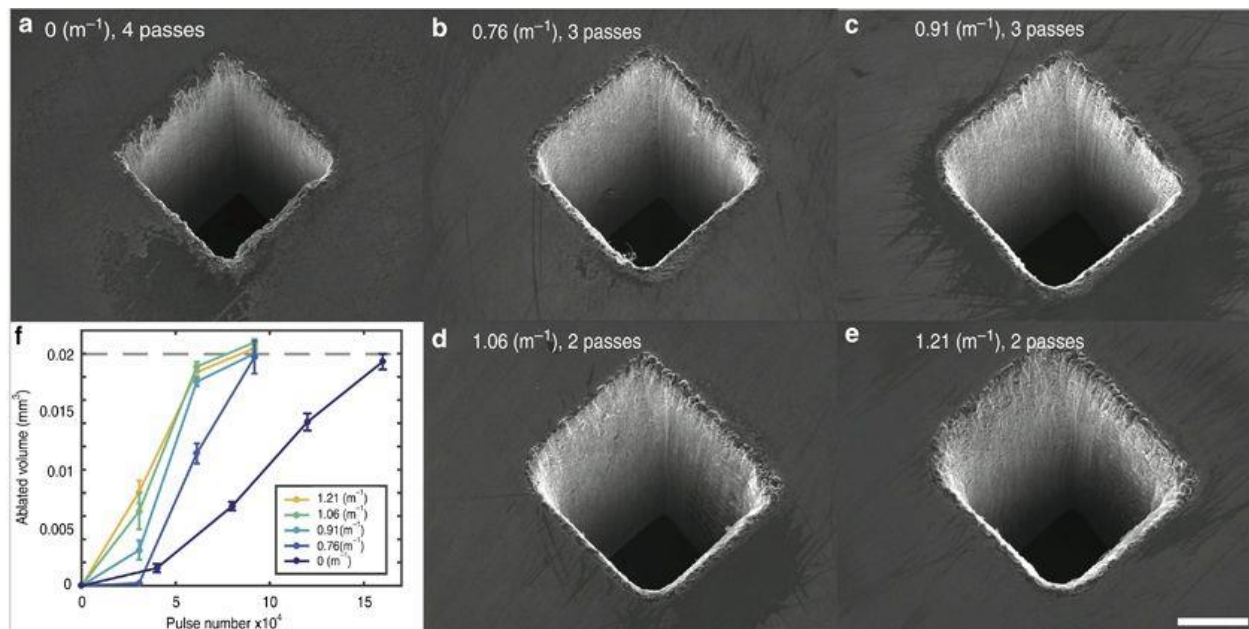
Chemical compositional analysis using the Thermo K-Alpha XPS in the IAC has helped elucidate the reason for columnar lithium growth in certain low current electrodeposition conditions. It has been shown that pretreatment of the copper substrate in acidic solutions and deionized water left behind an adsorbed water layer on the copper substrate, which then reacted with conventional carbonate electrolytes to form a surface LiF layer. This was then correlated one-to-one with uniformly compact columnar growth. Further depth profiling using the ion etch gun in the XPS has indicated that this surface LiF layer was between 5-8 nm on average.

Status: published work at Nano. Lett. 2018, **18**, 7066

Ultrafast Z-Scanning for High-Efficiency Laser Micro-Machining

Ting-Hsuan Chen, Romain Fardel, and Craig B. Arnold

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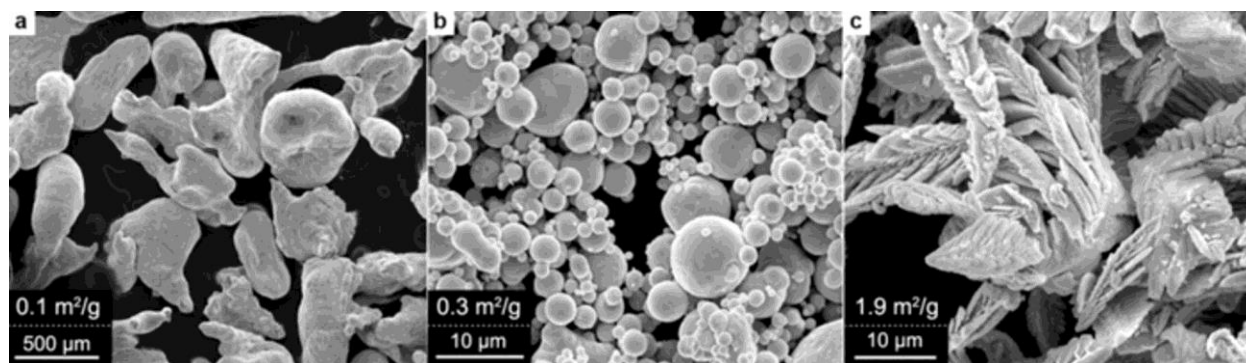
High-throughput laser micro-machining demands precise control of the laser beam position to achieve optimal efficiency, but existing methods can be both time-consuming and cost-prohibitive. In this paper, we demonstrate a new high-throughput micro-machining technique based on rapidly scanning the laser focal point along the optical axis using an acoustically driven variable focal length lens. Our results show that this scanning method enables higher machining rates over a range of defocus distances and that the effect becomes more significant as the laser energy is increased. In a specific example of silicon, we achieve a nearly threefold increase in the machining rate, while maintaining sharp side walls and a small spot size. This method has great potential for improving the micro-machining efficiency of conventional systems and also opens the door to applying laser machining to workpieces with uneven topography that have been traditionally difficult to process.

Status: published work at Light Sci. Appl. 2018, 7, 17181

Utilization of Hyper-Dendritic Zinc during High Rate Discharge in Alkaline Electrolytes

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¹Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA, ²Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA



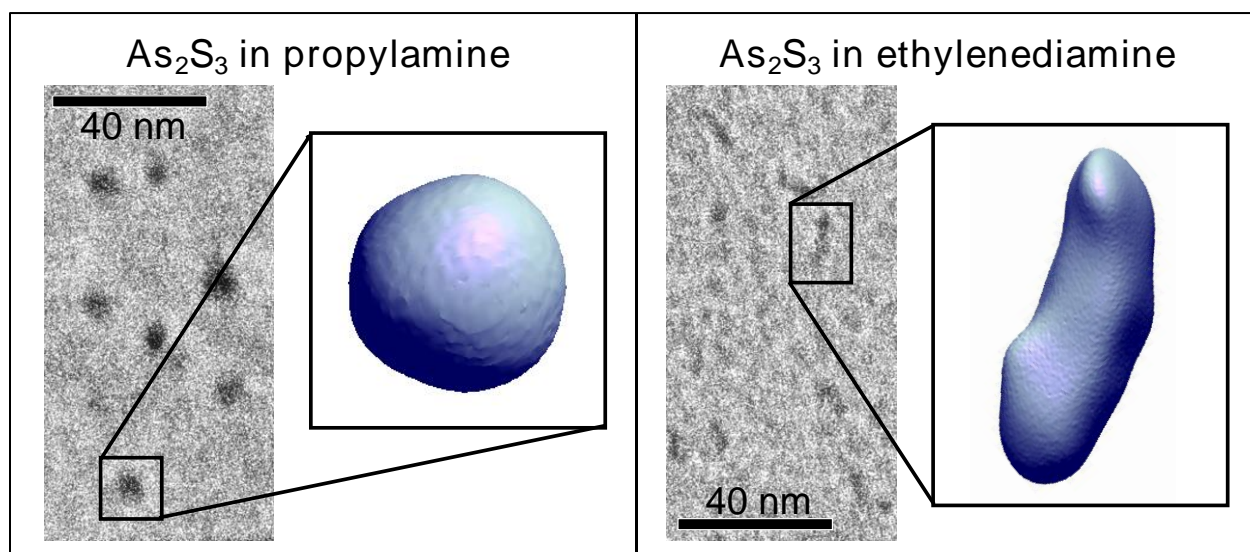
Zinc is a low cost and abundant material, and its strong reducing potential combined with stability in aqueous solutions give it high energy density and safety. It is, therefore, known to be an excellent choice of anode for a wide range of battery designs. However, this material presents some challenges for use in a secondary battery, including morphology changes and dendrite growth during charge (Zn deposition), and low utilization during discharge (Zn dissolution). Low utilization is related to a combination of corrosion and passivation effects. In this paper, we demonstrate a hyper-dendritic (HD) zinc morphology that has a high surface area and allows for rapid discharge in a completely freestanding system with no binders or conductive additives, while still maintaining significantly higher utilization than typical zinc morphologies. At rates of 2.5 A/g, the HD zinc has a utilization level approximately 50% higher than typical zinc granules or dust. Furthermore, we demonstrate that, through tuning of the electrolyte with specific additives, we are able to further increase the utilization of the material at high rate discharge by up to 30%.

Status: published work at J. Electrochem. Soc. 2016, **163**, A1340-A1347

Cryo-EM Characterization of Chalcogenide Glass Solution Structure

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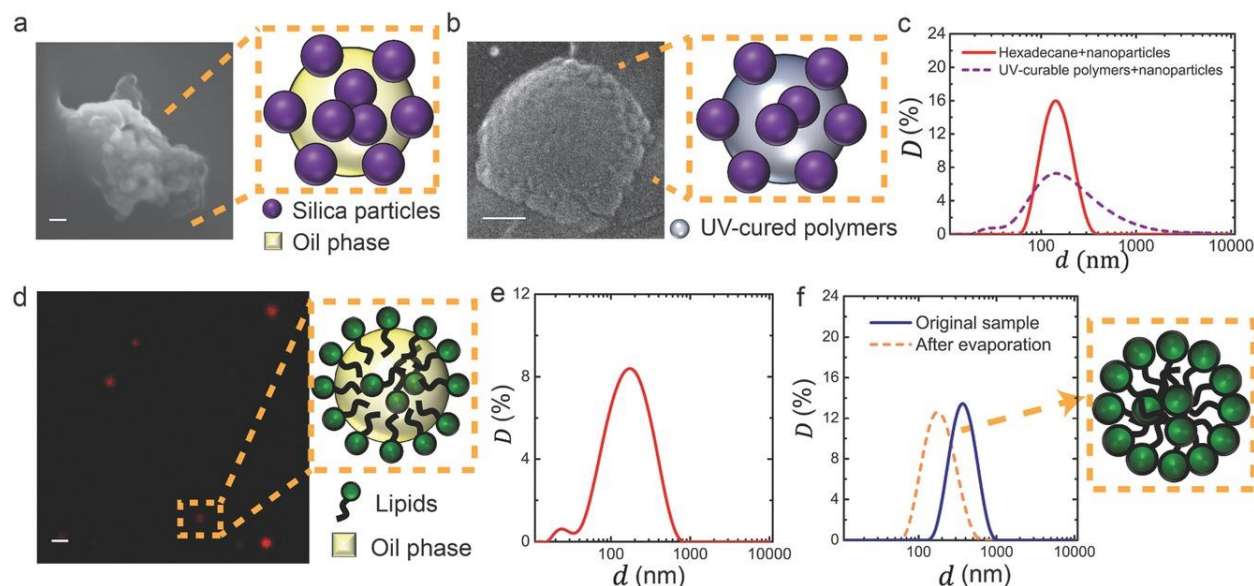
Chalcogenide glasses (ChGs) are a class of amorphous, inorganic materials whose unique optical properties—which include high nonlinearities, efficient mid-infrared transmission, and photoinduced phenomenon like photocrystallization—give rise to numerous applications in optoelectronics. These properties depend on structural features of the ChGs, many of which arise when they are solution processed. However, due to the difficulty of studying a solution in its native liquid state, characterizing ChG structure has long been a challenge. We employ cryo-electron microscopy—a technique from structural biology used to determine the structure of hydrated biological macromolecules—to meet this need. By imaging solutions of arsenic (III) sulfide (As₂S₃) in propylamine and in ethylenediamine, we show for the first time by direct experimentation that the ChG takes on solvent-dependent nanoscale solution structures. This result give insight into how solution processing parameters can be used to affect the morphology of As₂S₃ and other ChGs, and thus enhance their properties of interest.

Status: ongoing research project

A Scalable Platform for Functional Nanomaterials via Bubble-Bursting

¹Jie Feng, ¹Janine K. Nunes, ¹Sangwoo Shin, ¹Jing Yan, ¹Yong Lin Kong, ²Robert K. Prud'homme, ³Luben N. Arnaudov, ³Simeon D. Stoyanov, ¹Howard A. Stone

¹Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA, ²Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA, ³Unilever Research and Development, Vlaardingen, The Netherlands



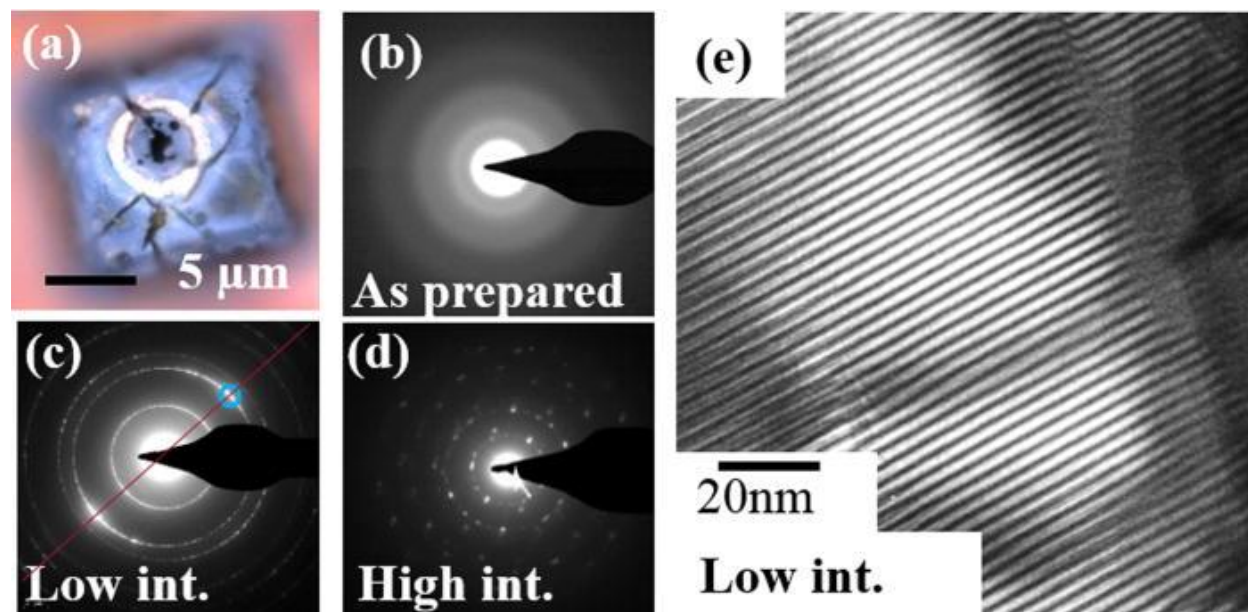
There is strong interest in the utilization of nanoemulsions and nanoparticles for drug delivery, material science, biology, functional foods, and nutraceuticals. Because of the small size, large surface area to volume ratio, and high reactivity, nanomaterials overcome some of the limitations found in conventional emulsions and particles. When certain functional materials are required to be incorporated into nanoemulsions to increase their utility, the fabrication process is typically more complicated since physicochemical interactions need to be considered. A low-cost and energy-efficient system with versatility remains the focus of research. To our best knowledge, such a facile platform to produce nanoemulsions encapsulating various functional materials is not available. Furthermore, many laboratory fabrication processes are not readily scaled up.

Status: published work at Adv. Mater. 2016, **28**, 4047–4052.

Anisotropic Crystallization in Solution Processed Chalcogenide Thin Film by Linearly Polarized Laser

Tingy Gu¹, Hyuncheol Jeong², Kengran Yang^{3,4}, Fan Wu⁵, Nan Yao⁵, Rodney D. Priestley^{2,5}, Claire E. White^{3,4}, and Craig B. Arnold⁵

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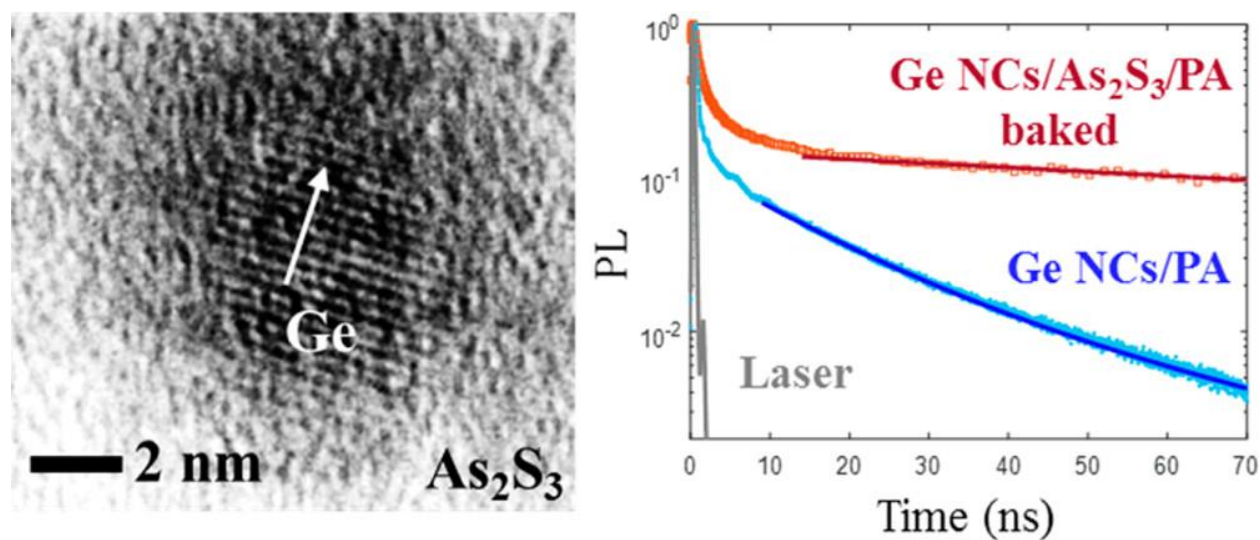
The low activation energy associated with amorphous chalcogenide structures offers broad tunability of material properties with laser-based or thermal processing. In this paper, we study near-bandgap laser induced anisotropic crystallization in solution processed arsenic sulfide. The modified electronic bandtail states associated with laser irradiation lead to a distinctive photoluminescence spectrum, compared to thermally annealed amorphous glass. Laser crystallized materials exhibit a periodic subwavelength ripple structure in transmission electron microscopy experiments and show polarization dependent photoluminescence. Analysis of the local atomic structure of these materials using laboratory-based X-ray pair distribution function analysis indicates that laser irradiation causes a slight rearrangement at the atomic length scale, with a small percentage of S-S homopolar bonds converting to As-S heteropolar bonds. These results highlight fundamental differences between laser and thermal processing in this important class of materials.

Status: published work at Appl. Phys. Lett. 2017, **110**, 041904

Photoluminescence of Functionalized Germanium Nanocrystals Embedded in Arsenic Sulfide Glass

Tingyi Gu¹, Jia Gao², Evgeny E. Ostroumov³, Hyuncheol Jeong², Fan Wu⁴, Romain Fardel^{4,5}, Nan Yao⁴, Rodney D. Priestley^{2,4}, Gregory D. Scholes^{3,4}, Yueh-Lin Loo^{2,5}, and Craig B. Arnold^{2,6}

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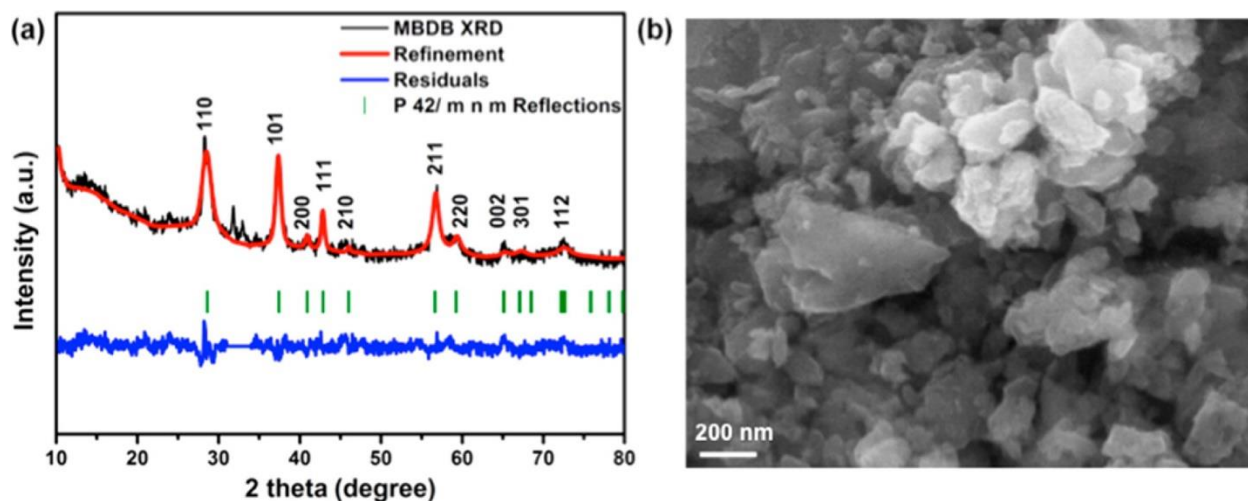


Embedding metallic and semiconductor nanoparticles in a chalcogenide glass matrix effectively modifies the photonic properties. Such nanostructured materials could play an important role in optoelectronic devices, catalysis, and imaging applications. In this work, we fabricate and characterize germanium nanocrystals (Ge NCs) embedded in arsenic sulfide thin films by pulsed laser ablation in aliphatic amine solutions. Unstable surface termination of aliphatic groups and stable termination by amine on Ge NCs are indicated by Raman and Fourier-transform infrared spectroscopy measurements. A broad-band photoluminescence in the visible range is observed for the amine functionalized Ge NCs. A noticeable enhancement of fluorescence is observed for Ge NCs in arsenic sulfide, after annealing to remove the residual solvent of the glass matrix.

Status: published ACS Appl. Mater. Interfaces 2017, **9**, 22

Effect of Multiple Cation Electrolyte Mixtures on Rechargeable ZnMnO₂ Alkaline Battery

¹Benjamin J. Hertzberg, ²An Huang, ¹Andrew Hsieh, ³Mylad Chamoun, ¹Greg Davies, ²Joon Kyo Seo, ⁵Zhong Zhong, ⁶Mark Croft, ⁵Can Erdonmez, ⁴Ying Shirley Meng, and ¹Dan Steingart
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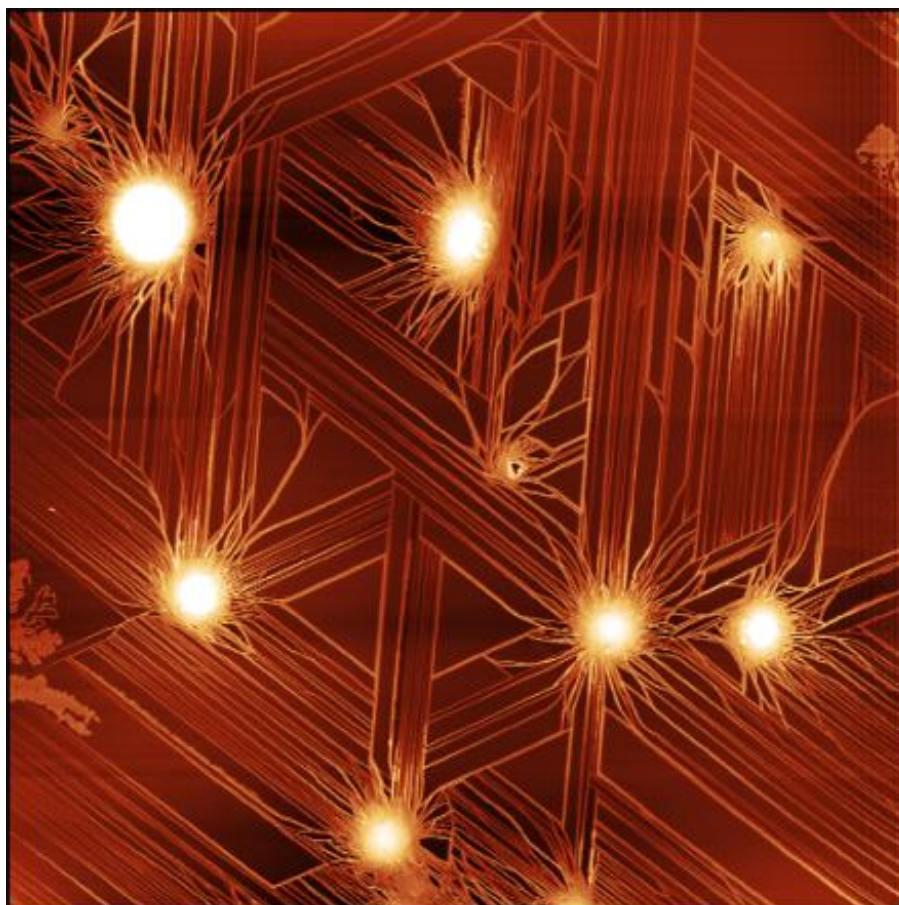
A Bi₂O₃ in β -MnO₂ composite cathode material has been synthesized using a simple hydrothermal method and cycled in a mixed KOH–LiOH electrolyte with a range of concentrations. We show that, at a KOH:LiOH molar ratio of 1:3, both proton insertion and lithium insertion occur, allowing access to a higher fraction of the theoretical capacity of the MnO₂ while preventing the formation of ZnMn₂O₄. This enables a capacity of 360 mAh/g for over 60 cycles, with cycling limited more by anode properties than traditional cathodic failure mechanisms. The structural changes occurring during cycling are characterized using electron microscopy and in situ synchrotron energy-dispersive X-ray diffraction (EDXRD) techniques. This mixed electrolyte shows exceptional cyclability and capacity and can be used as a drop-in replacement for current alkaline batteries, potentially drastically improving their cycle life and creating a wide range of new applications for this energy storage technology.

Status: published work at Chem. Mater. 2016, **28**, 4536-4545

Polymer Crystallization Under Heterogeneous Confinement

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In this work, we deposit thin polymeric films using matrix-assisted pulsed laser evaporation (MAPLE). In the MAPLE method, a frozen polymer solution is ablated by a pulsed laser. This generates an ablation plume which subsequently deposits polymeric material onto various substrates. We are studying the confined crystallization of polymers deposited using this method.

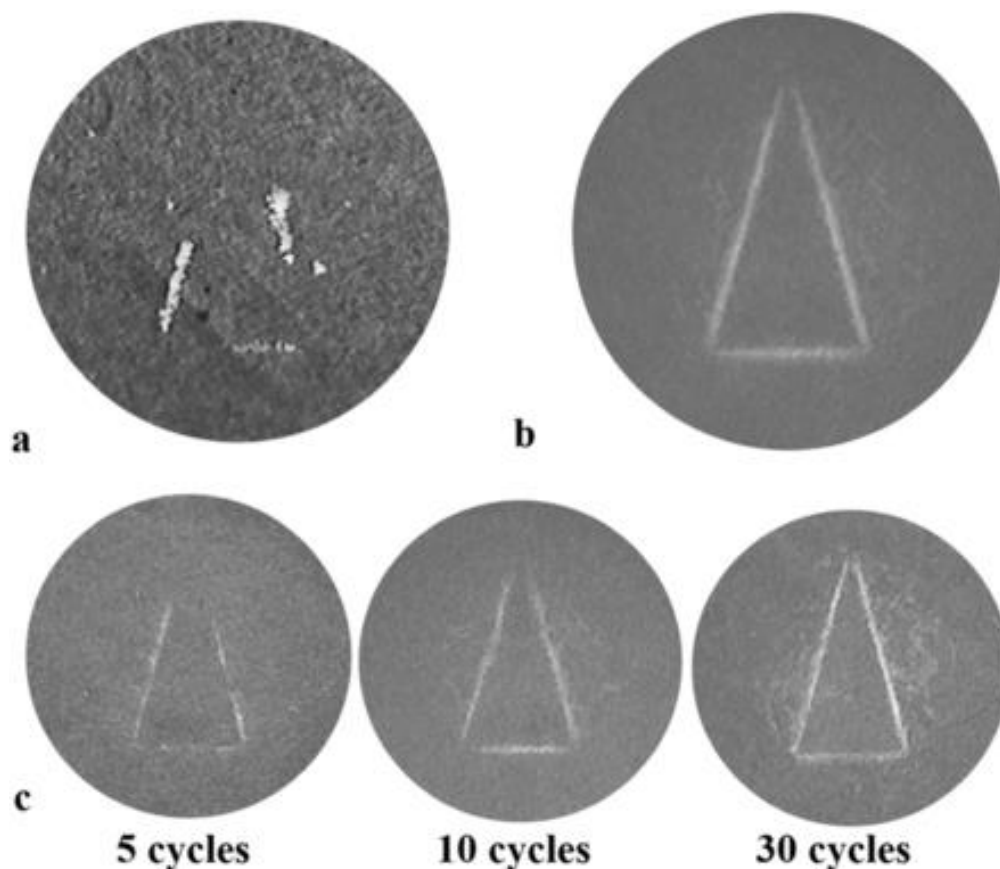
The atomic force microscope (AFM) is a powerful tool which we use to characterize the morphology of the crystalline films we deposit. By using phase-contrast AFM imaging, we may distinguish between different crystal orientations and identify amorphous, uncrystallized regions. Additionally, by using time-resolved AFM we may study the crystallization kinetics and better understand the mechanisms of nucleation and growth.

Status: ongoing research project

Size Dependence of Transport Non-Uniformities on Localized Plating in Lithium-Ion Batteries

Xinyi Liu, Alta Fang, Mikko P. Haataja and Craig B. Arnold

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA



Plating in lithium-ion batteries not only reduces their lifetime, but also raises safety concerns. Preventing metallic lithium from forming is difficult, as the heterogeneity of materials typically used in batteries can create transport non-uniformities, which can lead to unanticipated local plating. Therefore, being able to predict the occurrence of plating due to a non-uniformity of a certain shape and size becomes essential. In this study, we probe the importance of the size scale and geometry on localized plating through numerical simulations and experiments. Using modified separators to create transport non-uniformities, we show that certain geometric features lead to more vulnerability to plating, and localization strongly depends on size. A single large feature in a separator induces more plating than a collection of smaller features with same total area. Our findings help elucidate the fundamentals behind heterogeneous plating, which can provide practical insights into battery safety and product control.

Status: published work at J. Electrochem. Soc. 2018, **165**, A1147

Hydrogels by Mechanical Gelation

Antonio Perazzo, Janine K. Nunes, Howard A. Stone

Department of Mechanical and Aerospace Engineering University, Princeton, NJ, USA

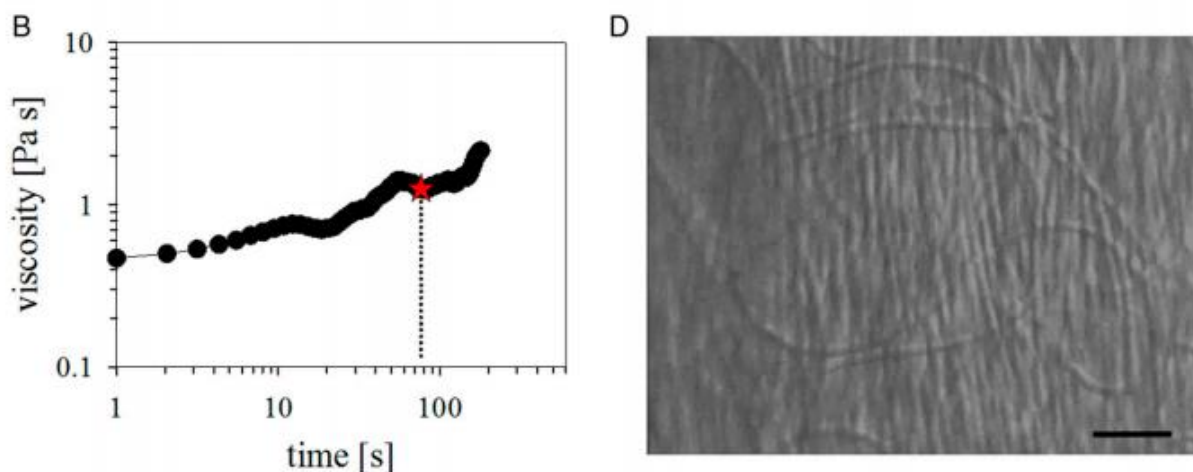


Figure: In situ visualization of a sheared fiber suspension with fiber volume fraction $\phi = 0.4$ at a constant shear rate of 10 s^{-1} between smooth glass parallel plates. Parallel plate diameter is 43 mm. (B) Time-dependent viscosity of the fiber suspension (shear thickening observed). (D) In situ image of the sheared fiber suspension at 77 s (time point indicated on A). Scale bar: 200 μm .

Hydrogels are ubiquitous biomedical materials typically produced by chemical cross-linking or physical interactions. Here, we report a novel mechanical methodology for making hydrogels that does not rely on the use of chemistry. We used the MCR 702 Twin-Drive Rheo-Microscope by Anton Paar, available in the IAC facility, to perform optical characterization of the microstructure of the material under shear flow while simultaneously measuring mechanical properties of the sample (see Figure B, D). The sample is a suspension in water of monodisperse polymeric microfibers (synthesized by Dr. Janine K. Nunes) that irreversibly entangle under the action of flow thus yielding a unique method for obtaining a biocompatible hydrogel owing to the flexibility of the fibers. The microstructural arrangements associated with the gelation process are tuned by fiber entanglements (see Figure D) and signaled by a sudden increase in fluid viscosity (see Figure B).

Status: published work at Proceedings of the National Academy of Sciences, 2017, **114**, E8557

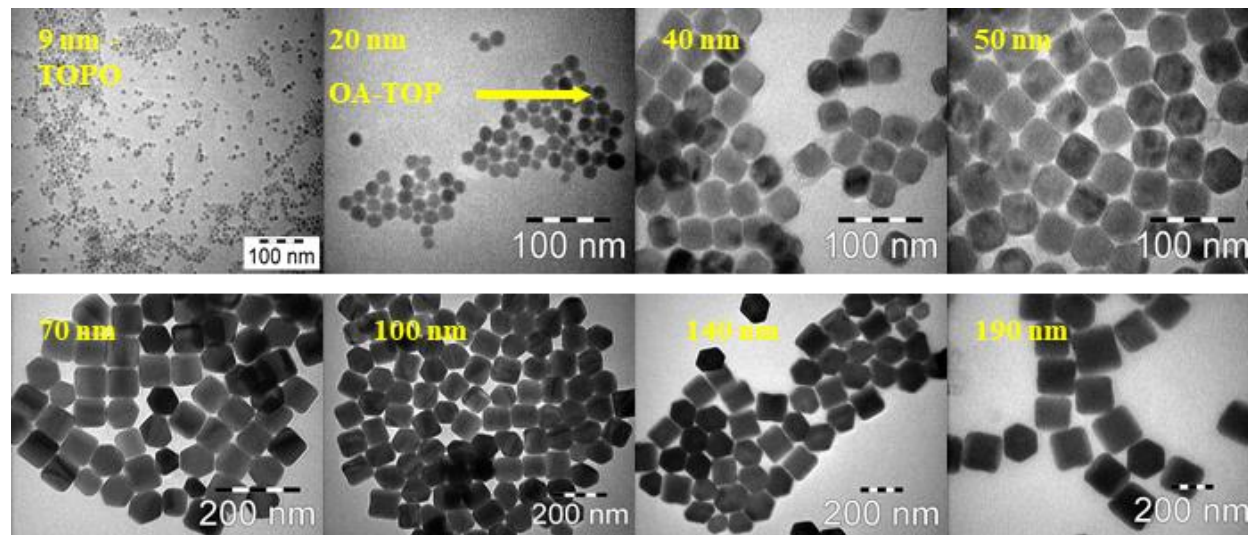
Size Tunable Synthesis of NaYF₄:Yb,Er Upconversion Nanophosphors and Bio-Applications

Jingning Shan^{1,3} Nan Yao² and Yiguang Ju¹

¹Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, USA; ²

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Synthesis of monodisperse and hexagonal phase (β) NaYF₄:Yb,Er upconversion nanophosphors (UCNPs) with a consistent hexagonal prism shape in the size range from 18 – 200 nm was achieved. Using oleic acid and trioctylphosphine as the combination ligands, the particle sizes can be controlled monotonically by adjusting precursor ratios. The kinetic mechanism for the particle nucleation and growth was presented; size-dependent photophysical properties were verified. A lot of work has been conducted to transfer the particle surface from hydrophobic to hydrophilic, which was further modified with various functional groups or biomolecules for the applications of bio-imaging, photodynamic therapy (PDT), and inkjet printing etc.

Status: published work at

[1] Nanotechnology 2009, **20**, 275603

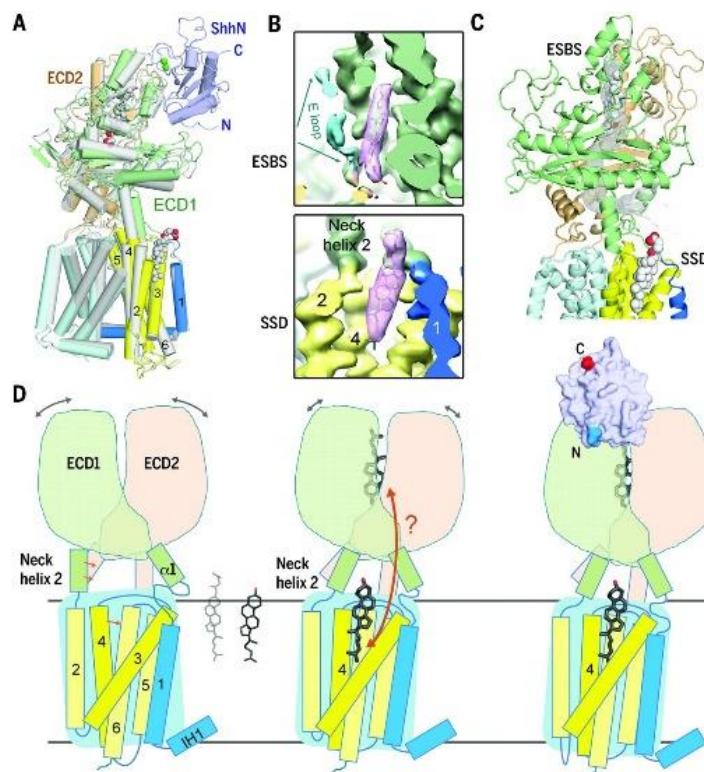
[2] Adv. Func. Mater. 2010, **20**, 3530

Department of Molecular Biology

Structural Basis for the Recognition of Sonic Hedgehog by Human Patched

Xin Gong^{1,3}, Hongwu Qian^{1,3}, Pingping Cao¹, Xin Zhao¹, Qiang Zhou¹, Jianlin Lei², Nieng Yan^{1,3}

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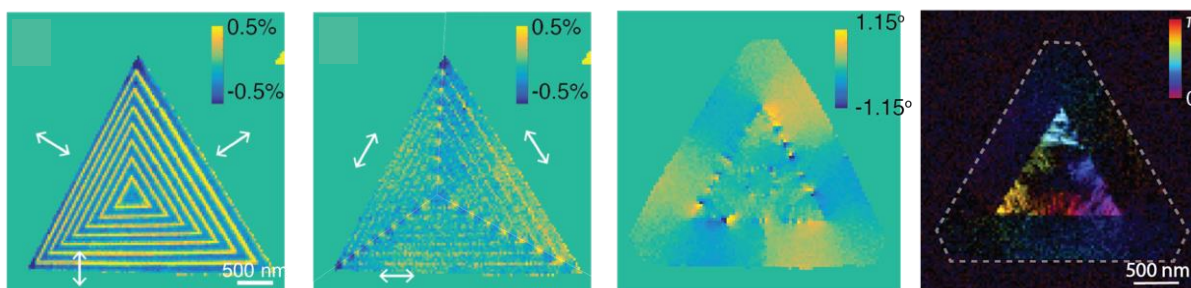
The Hedgehog (Hh) pathway involved in development and regeneration is activated by the extracellular binding of Hh to the membrane receptor Patched (Ptch). We report the cryo-EM structures of human Ptch1 alone and in complex with the N-terminal domain of human Sonic hedgehog (ShhN) at resolutions of 3.9 Å and 3.6 Å, respectively. Ptch1 comprises two interacting extracellular domains ECD1 and ECD2 and twelve transmembrane segments (TMs), with TMs 2-6 constituting the sterol-sensing domain (SSD). Two steroid-shaped densities are resolved in both structures, one enclosed by ECD1/2, and the other on the membrane-facing cavity of SSD. Structure-guided mutational analysis shows that interaction between ShhN and Ptch1 is steroid-dependent. The structure of a steroid binding-deficient Ptch1 mutant displays pronounced conformational rearrangements.

Status: published work at Science 2018, **361**, 6402

Strain, Dislocations, and Ripples in 2D Lateral Heterojunctions

Yimo Han^{1,2}, Kayla Nguyen², Michael Cao², Paul Cueva², Mark W. Tate³, Prafull Purohit³, Saein Xie⁴, Ming-Yang Li⁵, Lain-Jong Li⁵, Jiwoong Park⁴, Sol M. Gruner^{3,6,7,8}, David A. Muller^{2,7}

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Next-generation, atomically thin devices require in-plane, one-dimensional heterojunctions to electrically connect different two-dimensional (2D) materials [1]. However, the lattice mismatch between most 2D materials leads to unavoidable strain, dislocations, or ripples, which can strongly affect their mechanical, optical, and electronic properties. We developed an approach to map 2D heterojunction lattice and strain profiles with sub-picometer precision and the ability to identify dislocations and out-of-plane ripples [2]. We collected diffraction patterns from a focused electron beam for each real-space scan position with a high-speed, high dynamic range, momentum-resolved detector—the electron microscope pixel array detector (EMPAD) [3]. The resulting four-dimensional (4D) phase space data sets contain the full spatially resolved lattice information on the sample. By using this technique, broad and narrow lateral heterojunctions ($\text{WS}_2\text{-WSe}_2$) were examined. In broad lateral heterojunctions, we observed that the lattice strain is mostly released by misfit dislocations and out-of-plane ripples. In contrast, the narrow lateral heterojunctions form coherent superlattices with strong uniaxial strain, while containing minor misfits and ripples that partially release small amount of the strain. These achievements uncover the fundamental strain relaxation mechanism in epitaxial 2D lateral heterojunctions, where the misfit dislocations and internal rotation strain fields perform similarly as those in their bulk counterparts, while the ripples presented here are novel and unique in 2D materials.

Status: published work at

[1] Nature Materials 2018, **17**, 129

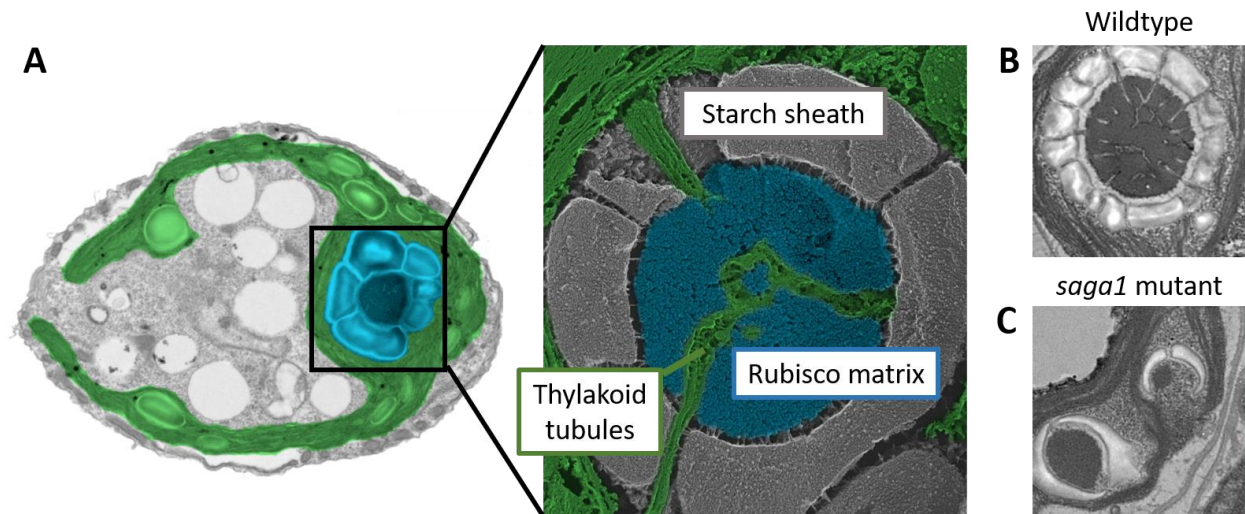
[2] Nano Letters, 2018, **18**, 3746

[3] Microscopy and Microanalysis, 2016, **22**, 237

Pyrenoid Structure

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During photosynthesis, the enzyme Rubisco catalyzes the fixation of inorganic CO₂ into a form that is usable by living organisms. To speed up Rubisco's activity, most eukaryotic algae supply Rubisco with concentrated CO₂ in a liquid-like organelle known as the pyrenoid. The pyrenoid (Fig. 1A/B) is composed of three main regions: 1) a liquid-like matrix densely packed with Rubisco 2) thylakoid tubules traversing the matrix that are thought to deliver CO₂ and other necessary biomolecules and 3) a starch sheath surrounding the matrix that may serve as a barrier to CO₂ diffusion away from the pyrenoid. We are interested in understanding the mechanisms that guide the formation and function of the pyrenoid, as it is responsible for approximately one-third of global carbon fixation.

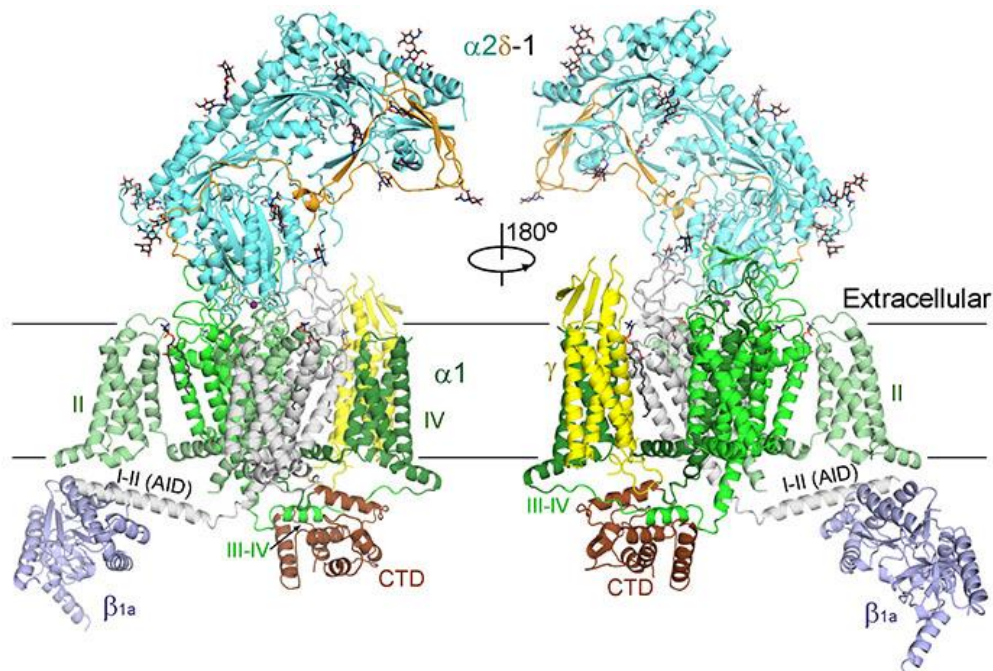
FIB-SEM has been a useful tool to examine detailed structures throughout a cell. We embed our samples in resin, and the FIB allows us to obliterate slices off the top of the resin block. After each obliteration, we are able to image the surface using SEM. Altogether, this allows us to acquire a three-dimensional image of the cell. In particular, I am interested in examining a mutant called *saga1* which has multiple pyrenoids per cell that are surrounded by thin, elongated starch sheaths (Fig. 1C). Many *saga1* pyrenoids appear to be missing thylakoid tubules in TEM cross-sectional images, and by using FIB-SEM I will be able to look through a mutant cell to see if a thylakoid tubule network is still in place somewhere in the cell.

Status: ongoing research project

Structure of the Voltage-Gated Calcium Channel $\text{Ca}_v1.1$ at 3.6 Å Resolution

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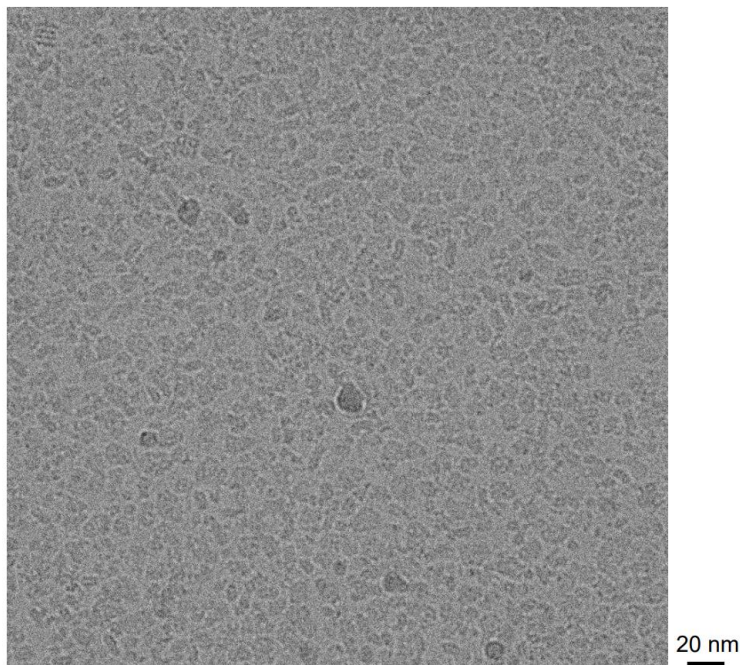
The voltage-gated calcium (Ca_v) channels convert membrane electrical signals to intracellular Ca^{2+} -mediated events. Ca_v channels play a critical role in diverse physiological processes such as muscle contraction, hormone secretion, neurotransmission, gene transcription, fertilization and cell death. Malfunction or dysregulation of Ca_v channels is associated with a broad spectrum of neurological, cardiovascular, and muscular disorders. Among the ten subtypes of Ca_v channels in mammals, $\text{Ca}_v1.1$ is specified for the excitation–contraction (E-C) coupling of skeletal muscles. It is a large protein complex consists the pore-forming subunit $\alpha1$ and auxiliary $\alpha2\delta$, β and γ subunits. Here we present the cryo-electron microscopy structure of the rabbit $\text{Ca}_v1.1$ complex at 3.6 Å resolution. The atomic model of the $\text{Ca}_v1.1$ complex establishes a foundation for mechanistic understanding of E-C coupling and provides a 3D template for molecular interpretations of the functions and disease mechanisms of Ca_v and related Na_v channels.

Status: published work at Nature 2016, **537**, 191

Single-Particle CryoEM Analysis of *V. cholerae* QS Receptors

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Quorum sensing (QS) is a chemical communication process that bacteria use to orchestrate collective behaviors. QS relies on different extracellular signaling molecules called autoinducers. Structural and functional study of QS transmembrane receptors provides a valuable opportunity to discover fundamental principles underlying signal transduction through cell membrane upon ligands binding. Such studies could have the added benefit of revealing the key steps to target for the development of new anti-microbial therapies that interfere with QS.

After purification, protein samples are fixed in a thin layer of amorphous ice on Quantifoil grids by using FEI Vitrobot. We then use the FEI Titan Krios Cryo Electron Microscope (CryoEM) equipped with the Gatan G3 detector to check these grids and collect terabyte-level data. Primarily, the Titan Krios CryoEM allows us to directly observe and study the high-resolution structure of QS receptors at different conditions closely related to cellular environment. To be noted, most QS transmembrane receptors are around 100 kDa and highly flexible due to their natural property. By using CryoEM, it is possible to capture and solve the structures of these QS receptors with different conformations at the same time. With Titan Krios CryoEM, we are able to unveil the mystery of signal transduction during QS at atomic level.

Status: ongoing research project

Princeton Neuroscience Institute

Classification of All Neurons in the Mouse Ganglion Cell Layer

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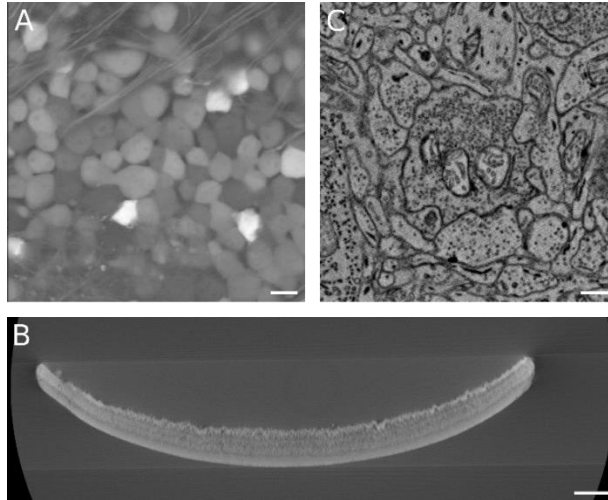


Figure: **A** Example of a ganglion cell scan field from calcium imaging experiments. Differing brightness of ganglion cell bodies indicates different intracellular calcium concentrations. Scale: 10 μm . **B** Retina sample embedded in resin visualized by Xradia Versa micro computer tomography. Please note the block of resin as slightly brighter block carrying the sample. Scale: 200 μm . **C** Example of ultrastructure in the inner plexiform layer of the retina sample from panel B Scale: 500 nm.

In the most recent years, two methods have been applied towards a complete classification of all neurons in the mouse ganglion cell layer: (1) using micrographs of scanning electron microscopes for mapping all of the cells in a patch of mouse retina (Bae et al., 2018) and (2) using calcium imaging to classify retinal ganglion cells based on their responses to visual stimuli and therefore their functional tuning (Baden et al., 2016). In our project we combine both calcium imaging and dense electron microscopy to achieve the first complete classification of all of the murine retinal ganglion cell types to enhance our understanding of the retina.

Initially, the retina sample undergoes calcium imaging for functional characterization of the neurons. Following that, fixation, staining and embedding of the sample for electron microscopy takes place leaving the retina samples in a block of resin. The resin incorporates the retina sample and serves as the vehicle for ultra-thin sectioning.

The Zeiss Xradia tool helps us both for overall orientation of the sample in the resin block and for tissue quality assessment in a non-destructive way. Orientation of the sample is important for optimal placement of the sample in the ultramicrotome so that no tissue is lost during the sectioning. Additionally, tissue quality assessment is essential to keep the use of crucial and rare research materials at a minimum to collect as much data as possible.

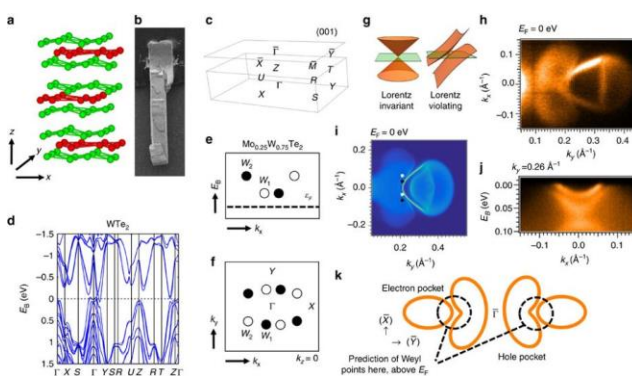
Status: ongoing research project

Department of Physics

Discovery of a New Type of Topological Weyl Fermion Semimetal State in $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$

Ilya Belopolski¹, Daniel S. Sanchez¹, Yukiaki Ishida², Xingchen Pan³, Peng Yu⁴, Su-Yang Xu¹, Guoqing Chang^{5,6}, Tay-Rong Chang⁷, Hao Zheng¹, Nasser Alidoust¹, Guang Bian¹, Madhab Neupane⁸, Shin-Ming Huang^{5,6}, Chi-Cheng Lee^{5,6}, You Song⁹, Haijun Bu³, Guanghou Wang³, Shisheng Li^{5,6}, Goki Eda^{5,6,10}, Horng-Tay Jeng^{7,11}, Takeshi Kondo², Hsin Lin^{5,6}, Zheng Liu^{4,12,13}, Fengqi Song³, Shik Shin², and M. Zahid Hasan^{1,14}

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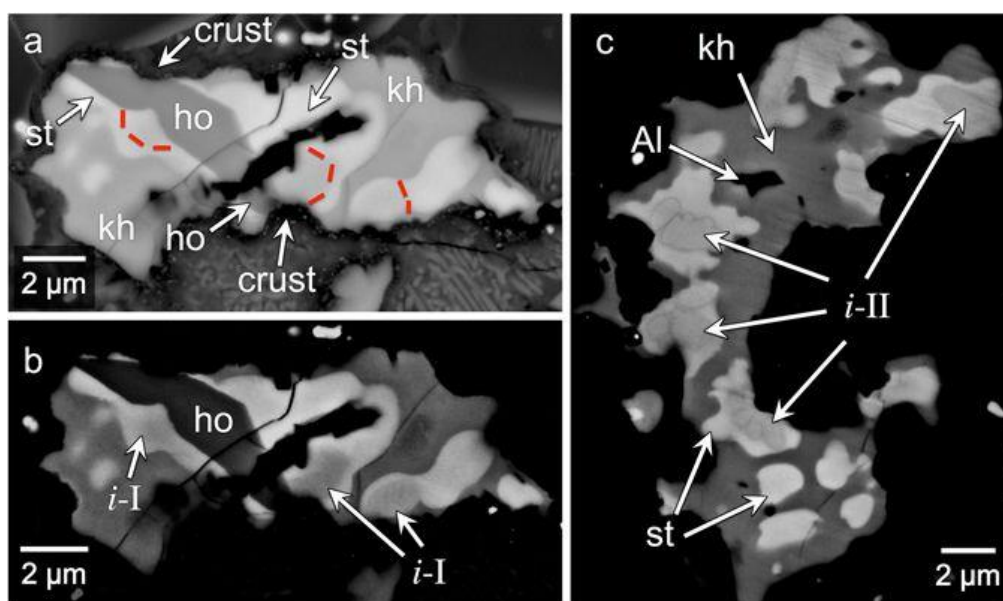
The recent discovery of a Weyl semimetal in TaAs offers the first Weyl fermion observed in nature and dramatically broadens the classification of topological phases. However, in TaAs it has proven challenging to study the rich transport phenomena arising from emergent Weyl fermions. The series $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ are inversion-breaking, layered, tunable semimetals already under study as a promising platform for new electronics and recently proposed to host Type II, or strongly Lorentz-violating, Weyl fermions. Here we report the discovery of a Weyl semimetal in $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ at $x=25\%$. We use pump-probe angle-resolved photoemission spectroscopy (pump-probe ARPES) to directly observe a topological Fermi arc above the Fermi level, demonstrating a Weyl semimetal. The excellent agreement with calculation suggests that $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ is a Type II Weyl semimetal. We also find that certain Weyl points are at the Fermi level, making $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ a promising platform for transport and optics experiments on Weyl semimetals.

Status: published work at Nat. Commun. 2016, **7**, 13643

Evidence of Cross-Cutting and Redox Reaction in Khatyrka Meteorite Reveals Metallic-Al Minerals Formed in Outer Space

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We report on a fragment of the quasicrystal-bearing CV3 carbonaceous chondrite Khatyrka recovered from fine-grained, clay-rich sediments in the Koryak Mountains, Chukotka (Russia). We show higher melting-point silicate glass cross-cutting lower melting-point Al-Cu-Fe alloys, as well as unambiguous evidence of a reduction-oxidation reaction history between Al-Cu-Fe alloys and silicate melt. The redox reactions involve reduction of FeO and SiO₂ to Fe and Fe-Si metal, and oxidation of metallic Al to Al₂O₃, occurring where silicate melt was in contact with Al-Cu-Fe alloys. In the reaction zone, there are metallic Fe and Fe-Si beads, aluminous spinel rinds on the Al-Cu-Fe alloys, and Al₂O₃ enrichment in the silicate melt surrounding the alloys. From this and other evidence, we demonstrate that Khatyrka must have experienced at least two distinct events: first, an event as early as 4.564 Ga in which the first Al-Cu-Fe alloys formed; and, second, a more recent impact-induced shock in space that led to transformations of and reactions between the alloys and the meteorite matrix. The new evidence firmly establishes that the Al-Cu-Fe alloys (including quasicrystals) formed in outer space in a complex, multi-stage process.

Status: published work at Sci. Rep. 2017, 7, 1637

Topological Semimetal Microscale Devices

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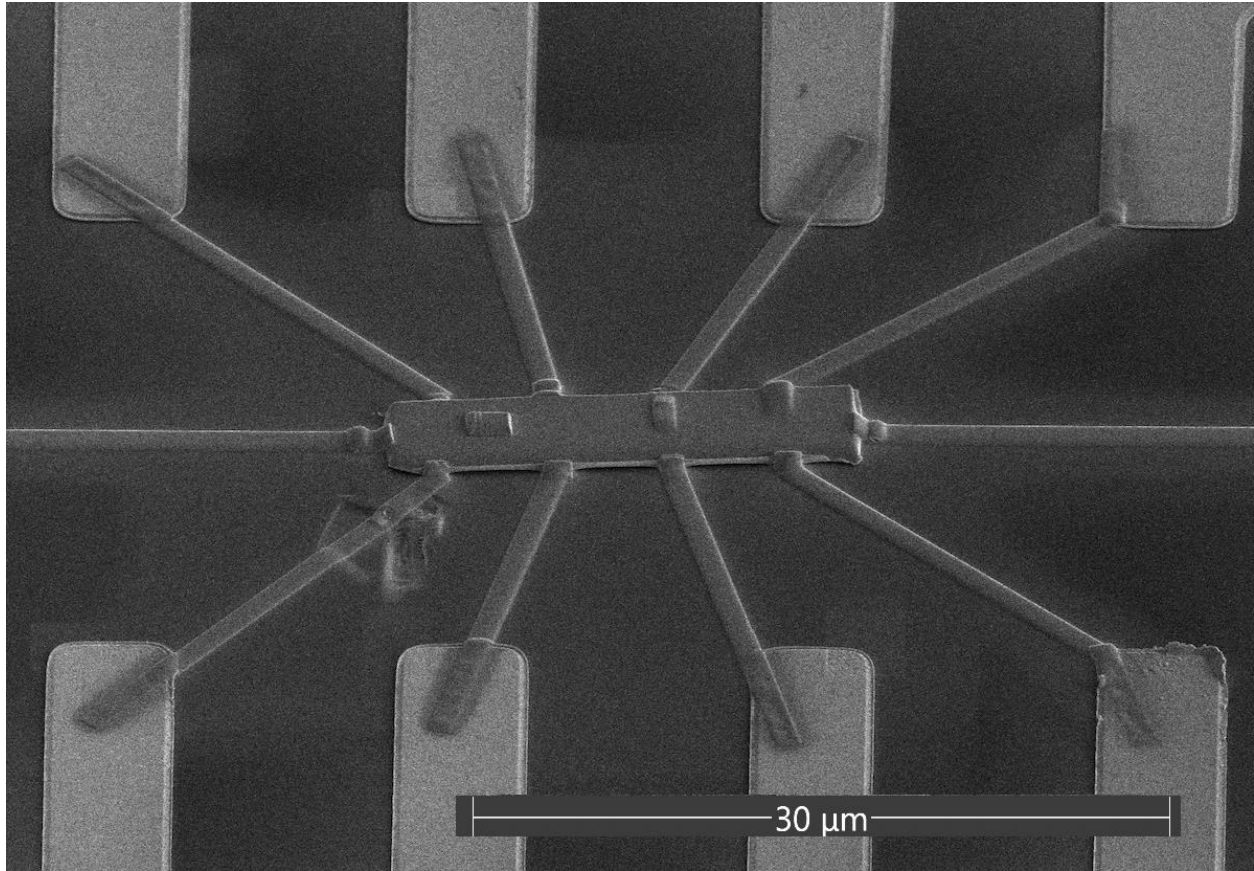


Figure: This 500 nm-thick sample of the Weyl semimetal NbAs was mounted to a SiO₂/Si substrate and connected to gold electrodes with in-situ platinum deposition using FIB.

Topological semimetals are crystals with massless chiral fermion bulk states and surface states that are disconnected arcs. These states give rise to interesting electronic conduction mechanisms that may be seen when sample thicknesses are on the scale of the electronic mean free paths. Since these materials cannot be mechanically exfoliated, we used focused-ion beam (FIB) microscopy to plane small pieces of bulk crystals down to sub- μm thicknesses. We measured the magneto-electric transport properties of samples of different thicknesses at 2 K. By carefully milling at a glancing angle with low ion acceleration voltages we were able to preserve the quantum oscillations in the samples, which indicate that the milling produced few ion-induced defects. We are currently probing the conduction properties of these thin, low-defect samples with more low-temperature measurements.

Status: ongoing research project

2D Materials and Heterostructures

Luke Shaw, Xiaomeng Liu, Yonglong Xie, and Ali Yazdani

Class of 2019, Nanoscale Microscopy Laboratory, Department of Physics, Princeton University, Princeton, NJ, USA



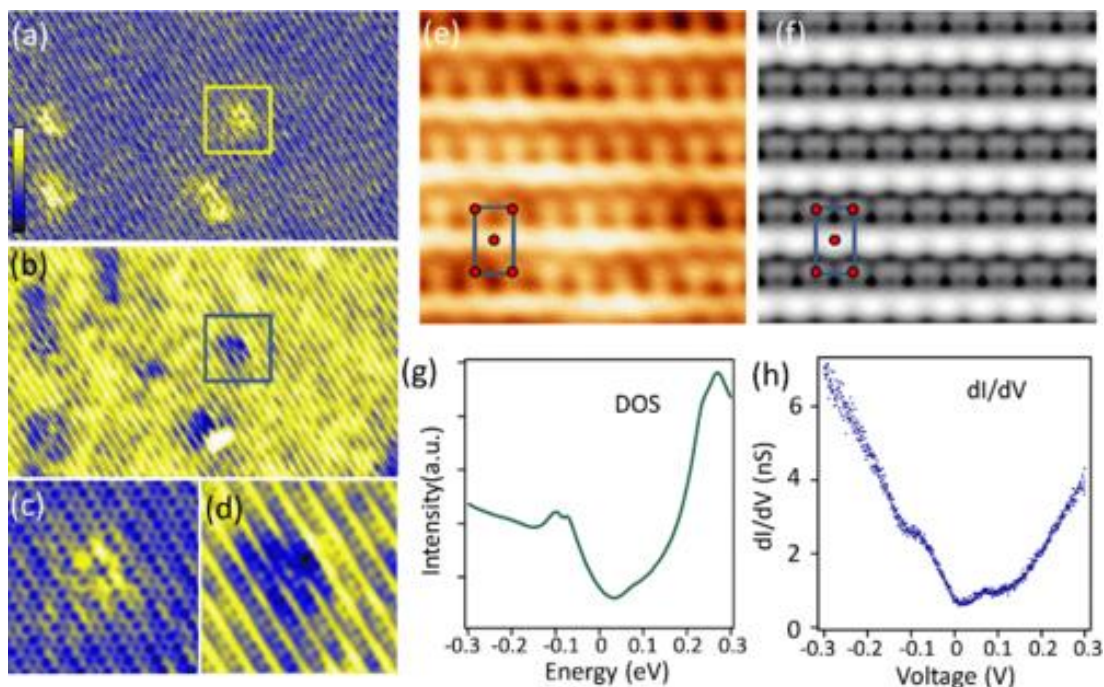
The hexagonal Boron-Nitride (h-BN) flake imaged above was mechanically exfoliated onto a Si chip using scotch tape. After inspecting the chip using an optical microscope, this flake was determined to be of the right size, thickness and surface smoothness to be a good candidate for the fabrication of a Van der Waals heterostructure, in combination with monolayer graphene. The flake was imaged with the AFM to check its cleanliness to sub-nanometre accuracy. If clean, the flake can be used as one layer in a h-BN/graphene heterostructure. By using different so-called '2D materials' (such as h-BN, graphene, or transition metal dichalcogenides (TMDs)) for the different layers of the heterostructure, the composite material's properties can be tuned as desired, with novel high-temperature superconductor materials one exciting possibility.

Status: undergraduate senior thesis

Atomic-Scale Visualization of Quasiparticle Interference on a Type-II Weyl Semimetal Surface

Hao Zheng¹, Guang Bian¹, Guoqing Chang^{2,3}, Hong Lu⁴, Su-Yang Xu¹, Guangqiang Wang⁴, Tay-Rong Chang⁵, Songtian Zhang¹, Ilya Belopolski¹, Nasser Alidoust¹, Daniel S. Sanchez¹, Fengqi Song⁶, Horng-Tay Jeng^{5,7}, Nan Yao⁸, Arun Bansil⁹, Shuang Jia^{4,10}, Hsin Lin^{2,3}, and M. Zahid Hasan¹

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We combine quasiparticle interference simulation (theory) and atomic resolution scanning tunneling spectromicroscopy (experiment) to visualize the interference patterns on a type-II Weyl semimetal $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ for the first time. Our simulation based on first-principles band topology theoretically reveals the surface electron scattering behavior. We identify the topological Fermi arc states and reveal the scattering properties of the surface states in $\text{Mo}_{0.66}\text{W}_{0.34}\text{Te}_2$. In addition, our result reveals an experimental signature of the topology via the interconnectivity of bulk and surface states, which is essential for understanding the unusual nature of this material.

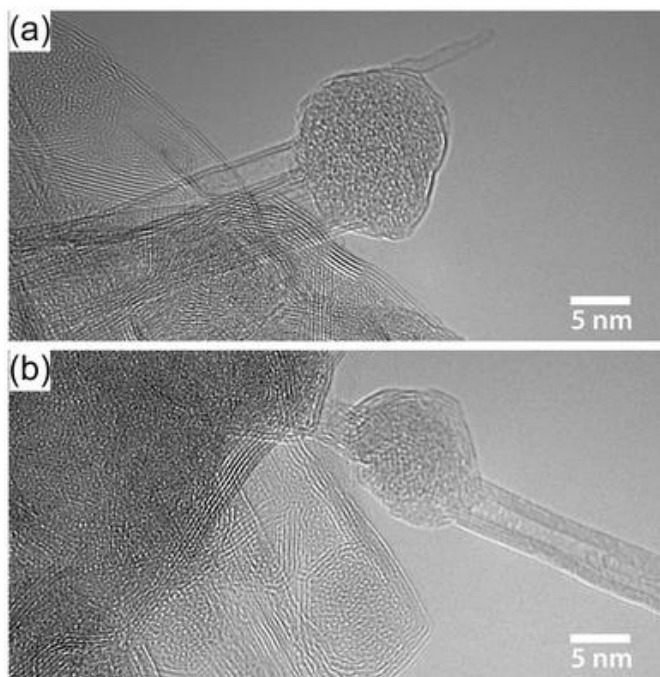
Status: published work at Phys. Rev. Lett. 2016, **117**, 266804

Princeton Plasma Physics Laboratory

Root-Growth of Boron Nitride Nanotubes: Experiments and Ab Initio Simulations

Biswajit Santra¹, Hsin-Yu Ko¹, Yao-Wen Yeh², Fausto Martelli¹, Igor Kaganovich², Yevgeny Raitses², and Roberto Car¹

¹Department of Chemistry, Princeton University, Princeton, USA, ²Princeton Plasma Physics Laboratory, Princeton, USA



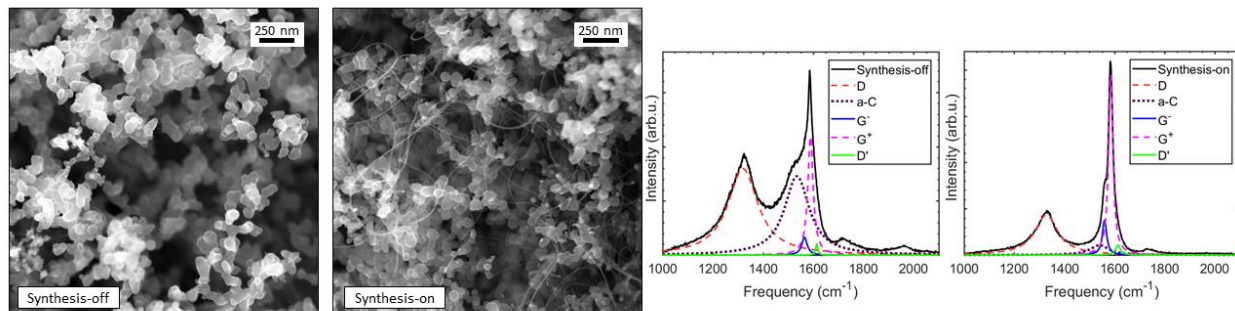
We have synthesized boron nitride nanotubes (BNNTs) in an arc in the presence of boron and nitrogen species. We find that BNNTs are often attached to large nanoparticles, suggesting that root-growth is a likely mechanism for their formation. Moreover, the tube-end nanoparticles are composed of boron, without transition metals, indicating that transition metals are not necessary for the arc synthesis of BNNTs. To gain further insight into this process we have studied key mechanisms for root growth of BNNTs on the surface of a liquid boron droplet by *ab initio* molecular dynamics simulations. We find that nitrogen atoms reside predominantly on the droplet surface where they organize to form boron nitride islands below 2400 K. To minimize contact with the liquid particle underneath, the islands assume non-planar configurations that are likely precursors for the thermal nucleation of cap structures. Once formed, the caps are stable and can easily incorporate nitrogen and boron atoms at their base, resulting in further growth. Our simulations support the root-growth mechanism of BNNTs and provide comprehensive evidence of the active role played by liquid boron.

Status: published work at *Nanoscale*, 2018, **10**, 22223-22230

“Synthesis-on” and “Synthesis-off” Modes of Carbon Arc Operation During Carbon Nanotube Synthesis

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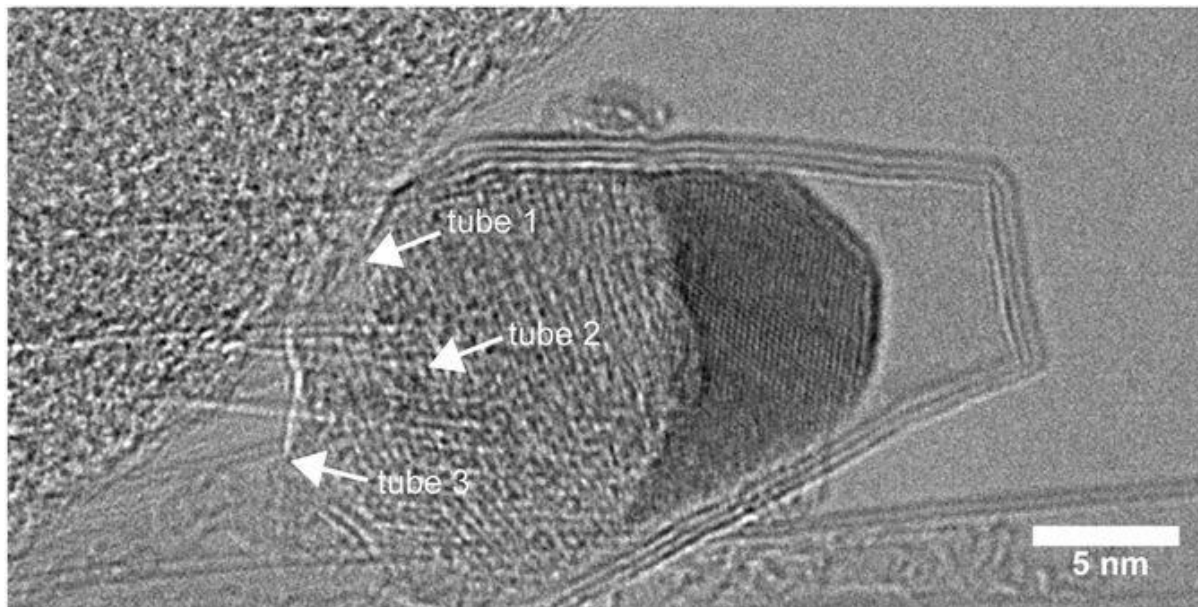
Arc discharge synthesis of exclusively single-walled carbon nanotubes (SWCNTs) remains elusive, in large part due to an incomplete understanding of the synthetic process itself. We showed that SWCNTs synthesis by carbon arc is a discontinuous process, consisting of two distinct modes: “synthesis-on” and “synthesis-off.” Samples were synthesized using a typical arc configuration: a hollow anode filled with a mixture of powdered metal catalysts and graphite. The process was monitored using *in situ* electrical, imaging, and spectroscopic diagnostics. Composition characterization was performed *ex situ* by electron imaging and Raman spectroscopy. Using scanning and transmission electron microscopy, we identified the products to be mixtures of SWCNTs, single-walled carbon nanohorns (SWCNHs), amorphous carbon, and metallic nanoparticles. Raman analysis confirmed these observations, revealing that both modes produced SWCNTs, SWCNHs, and amorphous carbon. The relative contributions of the aforementioned nanomaterials to the measured spectra of samples collected during each mode were determined by curve fitting. Using these fits, we confirmed that a higher ratio of SWCNTs to other carbon nanomaterials are produced during synthesis-on. The fact that the selective synthesis-on mode occurs during only a small fraction of the arc total run-time may help explain the poor selectivity observed for arc synthesis.

Status: published work at Carbon, 2017, **125**, 336-343

Stable Synthesis of Few-Layered Boron Nitride Nanotubes by Anodic Arc Discharge

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Boron nitride nanotubes (BNNTs) were successfully synthesized by a dc arc discharge using a boron-rich anode as synthesis feedstock in a nitrogen gas environment at near atmospheric pressure. The synthesis was achieved independent of the cathode material suggesting that under such conditions the arc operates in so-called anodic mode with the anode material being consumed by evaporation due to the arc heating. To sustain the arc current by thermionic electron emission, the cathode has to be at sufficiently high temperature, which for a typical arc current density of $\sim 100 \text{ A/cm}^2$, is above the boron melting point (2350 K). With both electrodes made from the same boron-rich alloy, we found that the arc operation unstable due to frequent sticking between two molten electrodes and formation of molten droplets. Stable and reliable arc operation and arc synthesis were achieved with the boron-rich anode and the cathode made from a refractory metal which has a melting temperature above the melting point of boron. *Ex-situ* characterization of synthesized BNNTs with electron microscopy and Raman spectroscopy revealed that independent of the cathode material, the tubes are primarily single and double walled. The results also show evidence of root-growth of BNNTs produced in the arc discharge.

Status: published work at Sci. Rep. 2017, 7, 3075