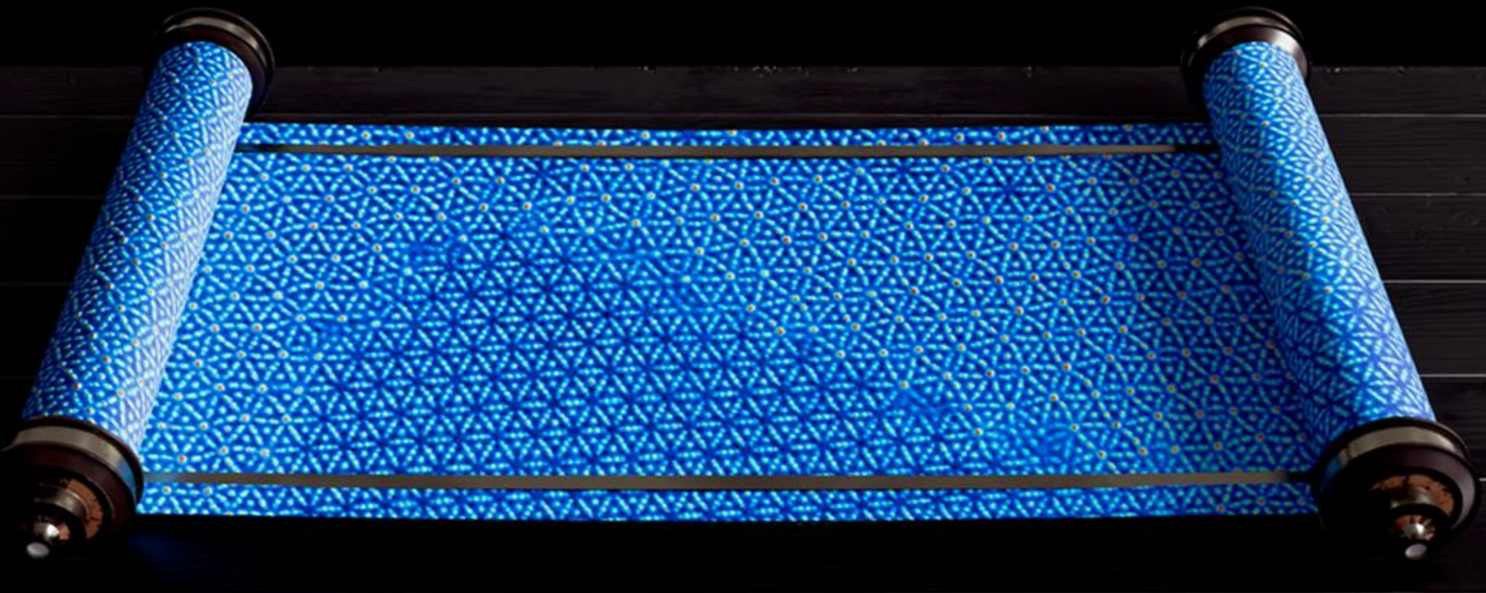
RESEARCH REPORT

Imaging and Analysis Center
PMI
PRINCETON UNIVERSITY

2024



iac.princeton.edu

A MESSAGE FROM THE DIRECTORS

Dear Friends of the Imaging and Analysis Center,

The Imaging and Analysis Center (IAC) in the Princeton Materials Institute (PMI) 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 ~30 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 4,500 student enrollments. Additionally, over 700 industrial scientists from more than 140 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 350 students and researchers from more than 90 research groups. The IAC supports ~240 current research contracts worth a total of ~$450M. 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, Rhodes Scholarship, Barry M. Goldwater National Scholarship, Fulbright Scholarship, National Science Foundation Graduate Research 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, Imaging and Analysis Center

Richard A. Register, Director, Princeton Materials Institute

Imaging and Analysis Center

Recent IAC users include over 300 students and researchers from 18 departments and centers on campus. Undergraduates, graduate students, and postdocs 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

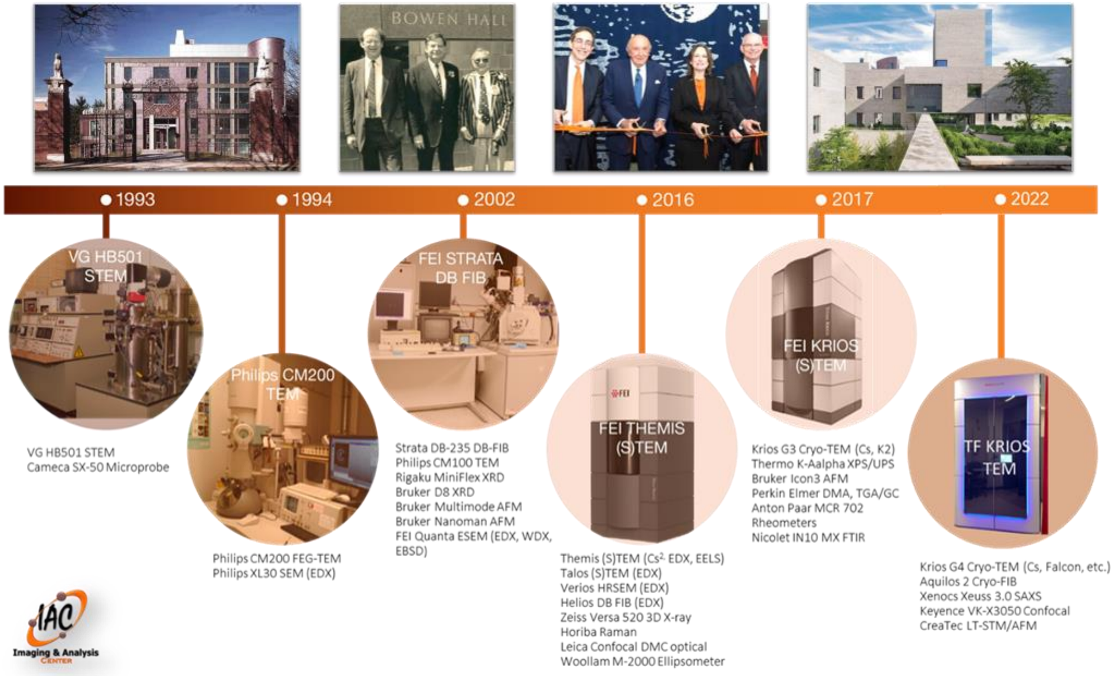
corrosion resistance supports, turbine blades, automobile chassis, etc.

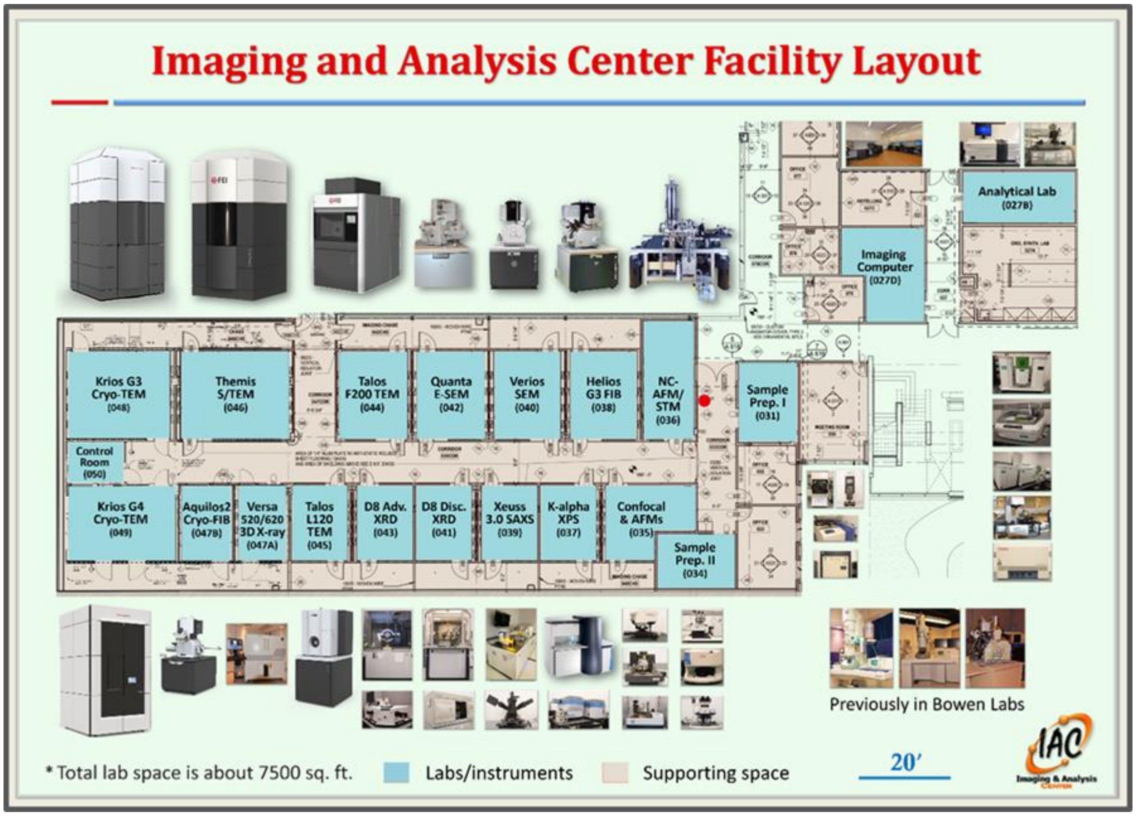
Pharmaceutical Materials

drug coating, toothpaste, molecular crystals, etc.

Imaging and Analysis Center (IAC)

IAC Background: It started in 1993 with one person and one microscope, and today, it has grown to nine staff and has become a world-leading materials characterization center for the physical and life sciences.





IAC team members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John Schreiber

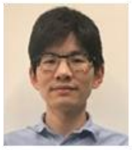

Paul Shao


Denis Potapenko


Dan McNesby


Kevin Lamb


Gary Cheng


PC Chen


Will Chiusano

IAC faculty users from Princeton in 2024

Astrophysical Sciences
Dave McComas

Civil & Environmental Eng.
Catherine Peters
Claire White
Ian Bourg
Jason Ren
Jyotirmoy Mandal
Peter Jaffe
Reza Moini
Ryan Kingsbury

Ecology and Evolutionary Biology
Mary Stoddard
Tiago R. Simoes

Materials Institute
Aditya Sood
Loren Pfeiffer
Marcella Lusardi
Nan Yao
Saien Xie

Mechanical and Aerospace Eng.
Aimy Wissa
Craig Arnold
Daniel Cohen
Egemen Kolemen
Howard Stone
Kelsey Hatzell
Yiguang Ju

Plasma Physics
Robert Goldston
Yevgeny Raitses

Chemical & Biological Eng.
Bruce Koel
Emily Davidson
Jonathan Conway
Jose Avalos
Lynn Loo
Marcella Lusardi
Michele L. Sarazen
PT Brun
Richard Register
Rodney Priestley
Sujit Datta

Electrical & Computer Eng.
Andrew Houck
Antoine Kahn
Barry Rand
Claire Gmachl
Iain McCulloch
David Wentzlaff
Mansour Shayegan
James Sturm
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Minjie Chen
Jeff Thompson
Nathalie De Leon
Steve Lyon
Tian-Ming Fu
Yasaman Ghasempour

Neuroscience
Sebastian Seung

Physics
Ali Yazdani
Barry Rand
Jason Petta
N. Phuan Ong
Sanfeng Wu
Zahid Hasan

Chemistry
Andrew Bocarsly
Bob Cava
Erin Stache
Haw Yang
Leslie M. Schoop
Marissa Weichman
Michael Hecht
Mohammad Seyedsayamdost

Geosciences
Adam Maloof
Christopher Griffin
Curtis Deutsch
Elizabeth Niespolo
Satish Myneni
Thomas Duffy

Molecular Biology
Alexander Ploss
Bonnie Bassler
Fred Hughson
John Jimah
Jonathan Bouvette
Martin Jonikas
Nieng Yan
Ricardo Mallarino
Sabine Petry
Zemer Gitai

IAC users from industry and other universities in recent years

Industrial and government seminar speakers

Some key highlights related to the IAC

3rd Princeton-Nature Conference on Frontiers in Electron Microscopy for Physical and Life Sciences Held Successfully at Princeton

The 3rd Princeton-Nature conference, entitled "Frontiers in Electron Microscopy for the Physical and Life Sciences," successfully took place at Princeton from October 16 to 18, 2024. Hosted by the Imaging and Analysis Center in collaboration with the scientific publisher *Nature*, the event featured over 20 invited talks, 45 flash presentations, and engaging panel discussions on cutting-edge methods and technologies. More than 180 delegates from around the globe participated in the conference.

National Science Foundation Recognizes IAC as a World Leader in Advanced Imaging and Material Analysis

The Imaging and Analysis Center (IAC) provides cutting-edge instrumentation and expertise for the characterization of hard and soft materials, including biological specimens. The center is crucial in advancing research and education at Princeton University and beyond. The IAC is closely associated with the Princeton Center for Complex Materials [a Materials Research Science and Engineering Center (MRSEC), a prominent research hub funded by the National Science Foundation (NSF)]. In a recent NSF-MRSEC review, the committee highly praised the IAC, stating that "**it is among the best in the world for advanced imaging and analysis of materials.**"

Princeton Engineering School Celebrates Exceptional Teaching for MSE 505 Class Following Outstanding Student Evaluations

Dean Andrea Goldsmith and Dean Antoine Kahn of SEAS are very impressed by the outstanding student evaluations that Professor Yao received for his Spring 2024 course MSE 505 (41 students enrolled). Princeton University places a high value on teaching. Indeed, the school takes pride in this accomplishment and realizes that excellent teaching of such caliber requires superior dedication, skills, and effort. They join the students in applauding Professor Yao.

IAC was awarded the University's transformative research equipment Initiative for a new state-of-the-art Versa 630 three-dimensional computed tomography (CT) X-ray microscopy (XRM) instrument

IAC's capacity to analyze materials — ranging from 3-D-printed metal parts to precious vertebrate fossils, from strange crystals created during the testing of the first atomic bomb to battery research, life sciences, and more — will expand substantially by replacing the existing Zeiss Versa 520 with a state-of-the-art Versa 630 -dimensional computed tomography (CT) X-ray microscopy (XRM) instrument. The new XRM, one of the most advanced instruments at any institution globally, will analyze materials from the centimeter to submicron scale, enabling more rapid acquisition of higher-quality data. The system will be housed in Princeton's Imaging and Analysis Center, which is expected to be used by more than 35 university research groups and external users.

IAC upgraded its two Krios TEM with a new imaging filter and direct-electron detector

Supported by the University's transformative research equipment funds, these updates to our two cryogenic transmission electron microscopes (cryo-TEM) enable researchers to capture images of biological processes in their crowded cellular milieu. First, a new direct-electron detector was added to offer better sensitivity and triple the imaging speed. A new energy filter can reduce the thicker samples' noise, leading to higher-quality data. The upgraded cryo-TEMs are used across Molecular Biology, Chemistry, and Chemical and Biological Engineering departments.

A new in-situ fluorescence microscope was added to our state-of-the-art Cryo FIB/SEM

IAC has acquired a new iFLM Correlative System, an integrated fluorescence light microscope, and a value-added component for our Aquilos 2 Cryo-FIB. This enhancement enables cell biologists to streamline their sample preparation process for cellular cryo-electron tomography (cryo-ET). The iFLM Correlative System allows fluorescently labeled areas localized in the frozen sample from within the Cryo-FIB chamber, enabling users to select specific cellular regions for FIB milling and facilitating monitoring and validation by helping to ensure the correct target sites are being prepared.

IAC Installed a New Nexsa G2 X-ray Photoelectron Spectroscopy System to Advance Materials Science Research and Education

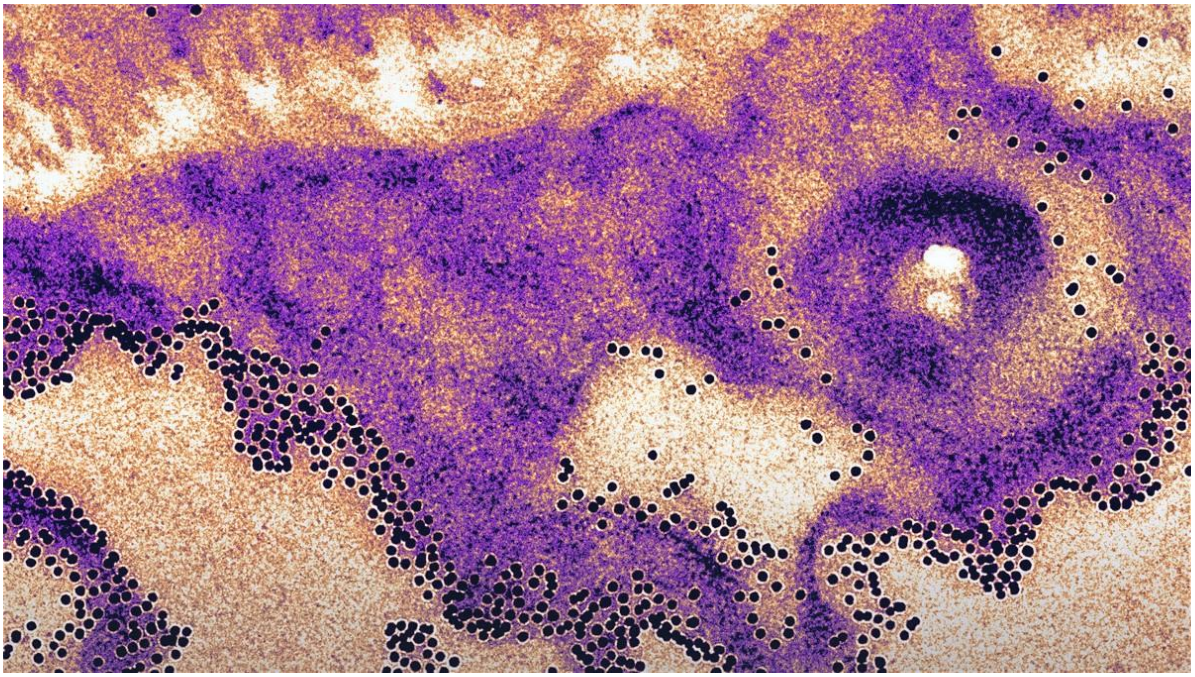
With the support of the PMI faculty, a new Nexsa G2 X-ray Photoelectron Spectroscopy (XPS) system was added to the IAC to support our research and education in materials science. XPS is a highly surface-sensitive, quantitative chemical analysis technique that can solve many materials problems.

The Princeton University website cover story highlights that IAC and other microscopy efforts are making a giant impact on the minuscule

The Imaging and Analysis Center (IAC) at the Princeton Materials Institute provides advanced instrumentation and expertise for characterizing hard and soft materials, including biological specimens. This center is essential for advancing research, education, and innovation at Princeton University and beyond. The IAC's impressive technological capabilities are supported by federal research grants, donor contributions, and the University endowment, enabling the acquisition of top-tier equipment for cutting-edge to support the University's mission to advance learning through scholarship, research, and teaching of unsurpassed quality. The IAC is a resource hub offering state-of-the-art instrumentation and expertise to all Princeton and outside researchers.

IAC researchers contributed to the discovery of an exotic quantum interference effect in a topological insulator device

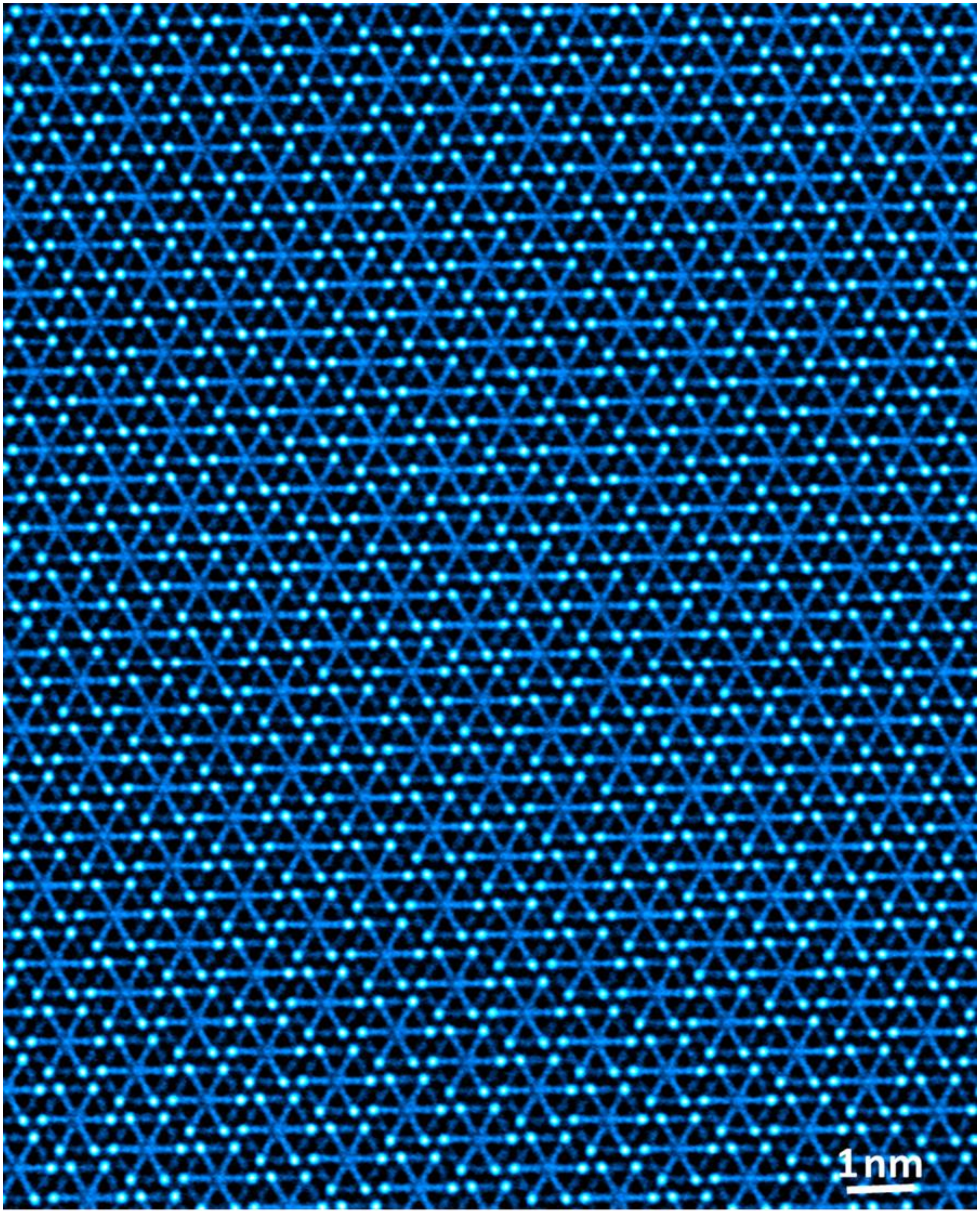
This work, published in a recent issue of Nature Physics, highlights over 15 years of work at Princeton. Scientists developed a bismuth bromide (α-Bi_4Br_4) topological insulator just a few nanometers thick to explore quantum coherence. They observed long-range quantum coherence effects from Aharonov-Bohm interference, opening new possibilities for topological quantum physics and engineering. This could also advance spin-based electronics for improved energy efficiency and new avenues in quantum information science.



3rd Princeton-Nature Conference on Frontiers in Electron Microscopy for Physical and Life Sciences Held Successfully at Princeton. (Image courtesy of Nature Materials)

Acknowledgment:

The Imaging and Analysis Center acknowledges partial support from the National Science Foundation through the Princeton University Materials Research Science and Engineering Center (PCCM), DMR-2011750.



This high-resolution electron microscopy image was obtained using the Titan Cubed Themis 300 double Cs-corrected Scanning/Transmission Electron Microscope (S/TEM). It shows a complex atomic structure, $Al_{52}Cu_{31}Fe_{10}Si_7$, of a micrometeorite discovered at the top of Mt. Gariglione in Southern Italy. (Image courtesy of G. Cheng, P. Steinhardt, and N. Yao)

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Andlinger Center for Energy and the Environment

Nonintuitive Role of Solid Electrolyte Porosity on Failure

Lin Lin,[1] Abhinand Ayyaswamy,[2] Yanjie Zheng,[3] Austin Fan,[4] Bairav S. Vishnugopi,[2] Partha P. Mukherjee,[2] and Kelsey B. Hatzell[1,3]

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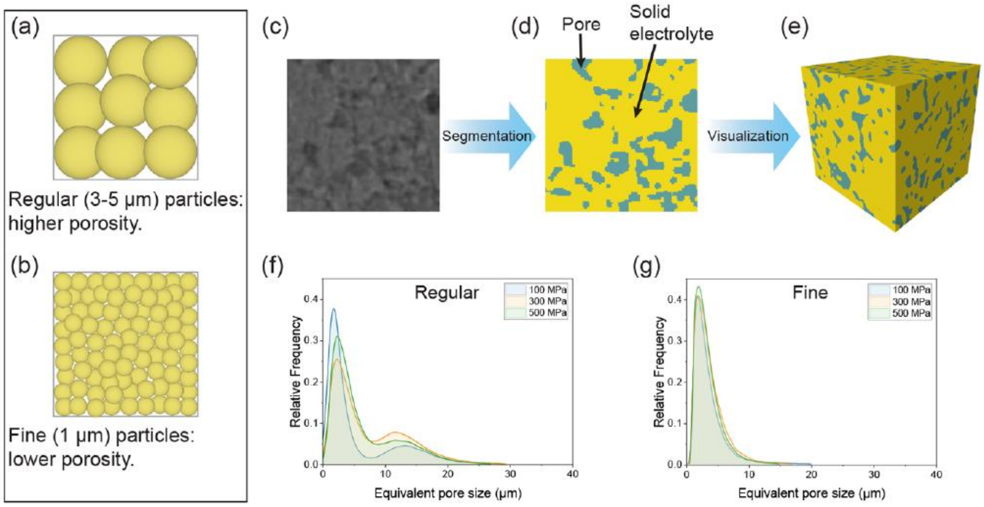

Solid electrolyte failure can occur through a range of different mechanisms. Electrochemical delamination at electrode and electrolyte interfaces is a prominent failure mechanism during high capacity and low N/P operating conditions, and filament formation is prevalent during a high rate and long cycle-life deposition. Interface coherency and the solid electrolyte microstructure both impact the ultimate degradation mode. The solid electrolyte microstructure, described in part by the density, periodicity, and interconnected arrangement of pores, plays a role in failure. Herein, we combine modeling, synchrotron imaging, and electrochemical experiments to systematically understand how densification and processing of solid electrolytes influence filament formation. The work reveals that the density of pores is not correlated with failure. Instead, the periodicity, size, and arrangement of pores is a driver for failure in amorphous solid electrolytes absent of grain boundaries.

Status: published work in ACS Energy Letters 2024, **9**, 2387

Polymorphism control of fast-sintered NASICON-type $LiZr_2(PO_4)_3$

Lin Lin[1] and Kelsey B. Hatzell[1,2]

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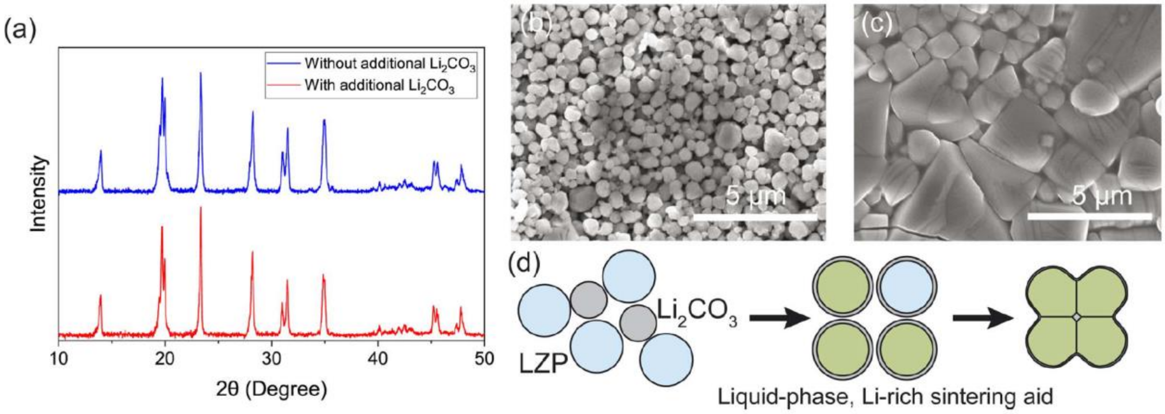

Long processing times and high temperature sintering can lead to high energy intensities and costs for all solid state battery manufacturing. Fast-sintering methods that are compatible with air can potentially overcome these challenges. Dynamic pulses of electrified heat also provide a pathway for manipulating materials and material transformation pathways to provide more control over structural heterogeneity. Herein, we examine how ultra-fast sintering approaches impact polymorphism in NASICON-type solid electrolytes (e.g. $LiZr_2(PO_4)_3$). The role of microstructure (e.g. porosity), the polymorphism in starting powders, and the presence of liquid sintering aids are all examined to understand how polymorphic phases can be tailored with fast-sintering approaches. Fast sintering techniques which decrease the loss of volatile lithium may enable high density solid electrolytes with tailored material phases.

Status: published work in Journal of Materials Chemistry A 2024, **12**, 29932

Impact of Asymmetric Microstructure on Ion Transport in $Ti_3C_2T_x$ Membranes

Kimberly Ventura-Martinez[1,2], Yaguang Zhu[1], Austin Booth[1,3], and Kelsey B. Hatzell[1,4]
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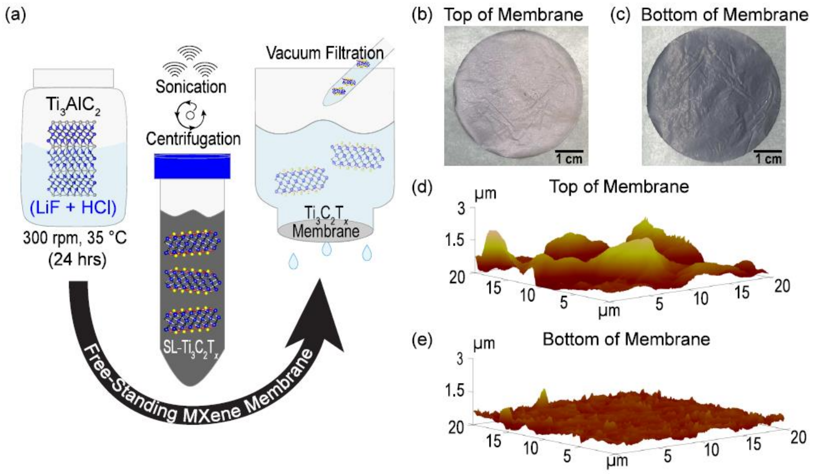

Consolidation or densification of low-dimensional MXene materials into membranes can result in the formation of asymmetric membrane structures. Nanostructural (short-range) and microstructural (long-range) heterogeneity can influence mass transport and separation mechanisms. Short-range structural dynamics include the presence of water confined between the 2D layers, while long-range structural properties include the formation of defects, micropores, and mesopores. Herein, it is demonstrated that structural heterogeneity in $Ti_3C_2T_x$ membranes fabricated via vacuum-assisted filtration significantly affects ion transport. Higher ion permeabilities are achieved when the dense “bottom” side of the membrane, rather than the porous “top” side, faces the feed solution. Characterization of the membrane reveals distinct differences in flake alignment, surface roughness, and porosity across the membrane. The directional dependence on permeability suggests that one region of the membrane experiences stronger internal concentration polarization, potentially suppressing permeability through the porous side of the membrane.

Status: published work in Nano Letters 2024, **24**, 13551.

Confinement Effects on Moisture-Swing Direct Air Capture

Yaguang Zhu[1], Austin Booth[1,3], and Kelsey B. Hatzell[1,2,3]

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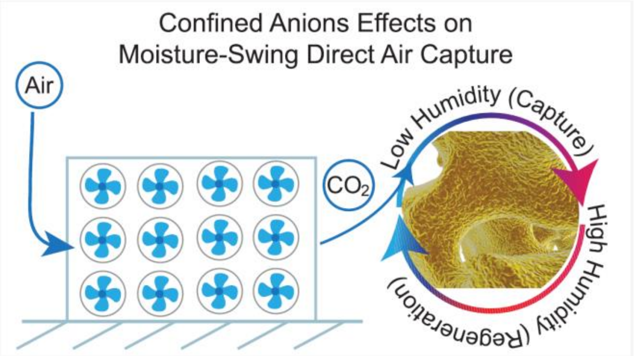

Direct air capture technologies are energy intensive and often utilize pressure and temperature swings for sorbent regeneration. An alternative approach, called moisture-swing direct air capture, relies on the hydrolysis of a confined anion to produce hydroxide anions. These hydroxide anions are active sites for CO_2 capture. Here, we examine how confinement affects moisture-swing CO_2 capture and regeneration mechanisms. The local short-range order in micropores determines the capacity for hydroxide formation in the moisture-controlled reversible hydrolysis/neutralization reaction during capture and regeneration. Carbon capture scales with the basicity of the confined anion. Sulfide exhibits excessive interactions with water and thus can release only small amounts of CO_2 during the regeneration step. Control over local water−anion chemical microenvironments is critical for reversible operation of moisture-swing sorbent materials. Accessibility of water is largely governed by the distribution of resin macropores. Engineering materials for control over micro, meso, and macropores is critical for achieving favorable interactions between active sites and water in confinement.

Status: published work in Environ. Sci. Technol. Lett. 2024, **11**, 89.

Department of Chemical and Biological Engineering

Kinetic implications of (hierarchical) zeolite fouling during liquid-phase aromatics upgrading

Hayat I. Adawi, Michele L. Sarazen
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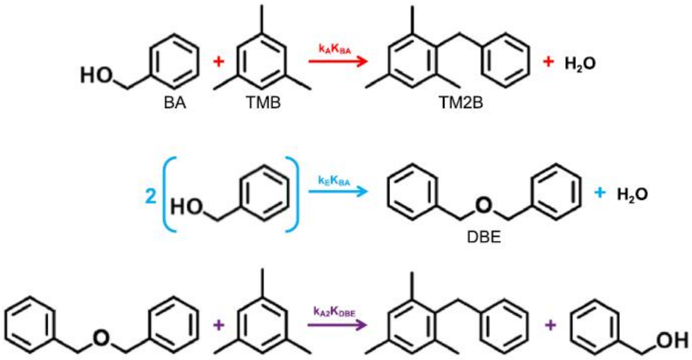

The kinetics of fouling in large pore zeolites (BEA, MOR), including those with hierarchical pore systems, were probed during the Brønsted acid catalyzed reaction of benzyl alcohol (BA) with 1,3,5-trimethylbenzene (TMB) by varying reactant driving force (i.e., $[TMB]_0/[BA]_0$; 11–119). In BEA, initial deactivation rate constants ($k_{D,0}$) decreased exponentially with $[TMB]_0/[BA]_0$, highlighting the significance of oxygenates as deactivation precursors. Further, seeding pores with oxygenates completely suppressed measured rates in parent MOR and BEA, while seeding with TMB had no effect. Comparisons of mass accumulations of different organics (low molecular weight reaction species and coke) as functions of $\ln([TMB]_0/[BA]_0)$ revealed that coke (derived from oxygenate seeded polyalkylation of TMB) disproportionately controlled deactivation rates by damping apparent (diffusion-controlled) and intrinsic (diffusion-corrected) rate constants through proton losses and/or altered molecule confinement within shrinking pores. These kinetic consequences were delayed upon introduction of mesopores, demonstrating how zeolite porosity impacts coke proliferation and behavior in liquid-phase reactions.

Status: published work in Journal of Catalysis 2024, **433**, 115456

Influence of Ordered Mesoporous Oxides in Plasma-Assisted Ammonia Synthesis

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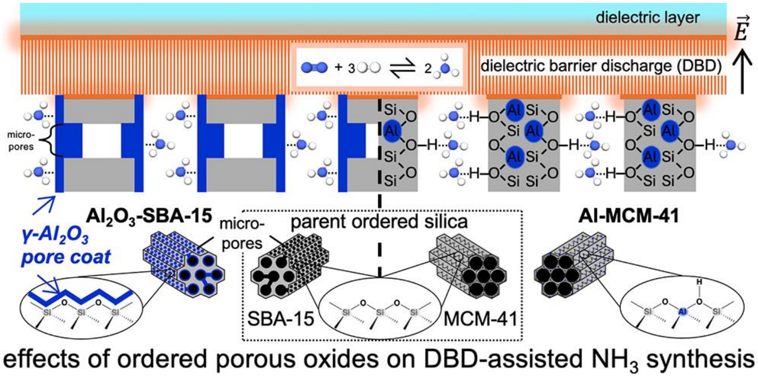

Widespread implementation of dielectric barrier discharge (DBD)-assisted NH_3 synthesis, a nascent technology operating under sustainable, ambient conditions, is hindered by low energy yields due to poor fundamental understanding. Porous oxides used to support metal nanoparticle catalysts have shown significant energy yield contributions for DBD-assisted NH3 synthesis even without metal. Using an AC-powered, coaxial, single-stage reactor at 16 kV with equimolar (N_2/H_2) feed, we measured NH_3 synthesis rates in the presence of different nonordered oxides, ordered SiO_2 structures (SBA-15 and MCM-41), and ordered Al-incorporated analogues (Al_2O_3-SBA-15 and Al-MCM-41). We quantified NH_3 energy yield dependence on pore structures and material identities known to facilitate higher DBD-assisted NH_3 synthesis rates. SBA-15 displayed a higher steady-state energy yield than MCM-41, indicating that framework type is a crucial factor, with both ordered porous systems outperforming fumed SiO_2. 10 wt % Al maximized in situ NH_3 uptake, exhibiting a higher steady-state energy yield and similar power to SBA-15. However, Al-MCM-41 had a similar steady-state energy yield and lower power than MCM-41, likely due to the extended γ-Al_2O_3 surface that has a dielectric constant higher than that of SiO_2. Thus, Al incorporation via γ-Al_2O_3 coating more successfully improves the NH_3 energy yield; together with the high-performing ordered framework, these analogues are potential metal catalyst supports with promising energy yields for DBD-assisted synthesis of NH_3 and other chemicals.

Status: published work in Energy and Fuels 2024, **38**, 23150

3D Printing Bacteria to Study Motility and Growth in Complex 3D Porous Media

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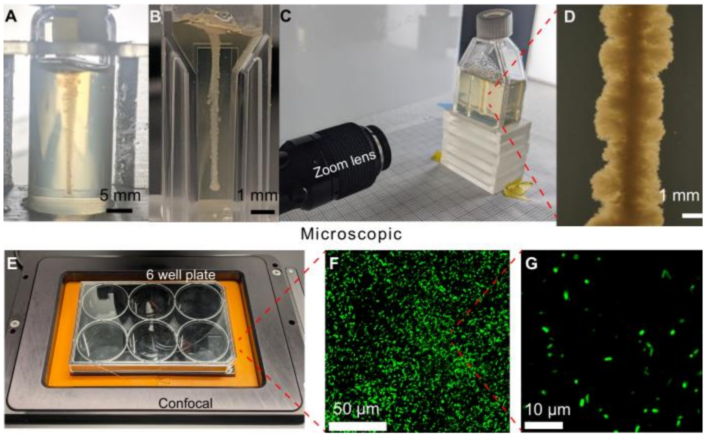

Bacteria are ubiquitous in complex three-dimensional (3D) porous environments, such as biological tissues and gels, and subsurface soils and sediments. However, the majority of previous work has focused on studies of cells in bulk liquids or at flat surfaces, which do not fully recapitulate the complexity of many natural bacterial habitats. Here, this gap in knowledge is addressed by describing the development of a method to 3D-print dense colonies of bacteria into jammed granular hydrogel matrices. These matrices have tunable pore sizes and mechanical properties; they physically confine the cells, thus supporting them in 3D. They are optically transparent, allowing for direct visualization of bacterial spreading through their surroundings using imaging. As a proof of this principle, here, the capability of this protocol is demonstrated by 3D printing and imaging non-motile and motile Vibro cholerae, as well as non-motile Escherichia coli, in jammed granular hydrogel matrices with varying interstitial pore sizes.

Status: published work in J. Vis. Exp. 2024, **203**, e66166.

Harnessing elastic instabilities for enhanced mixing and reaction kinetics in porous media

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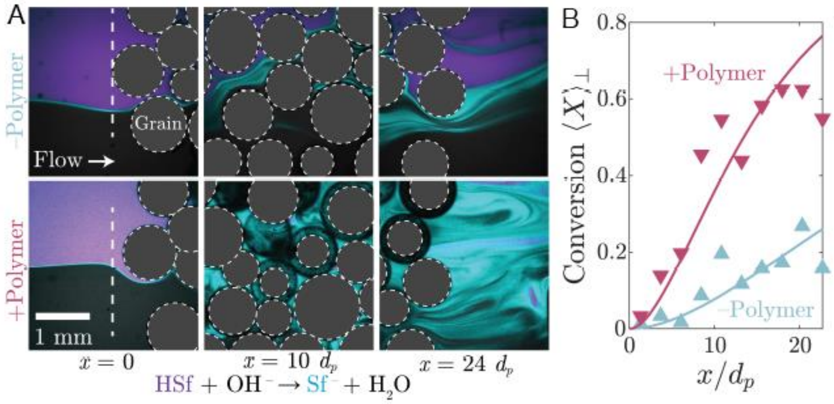

Turbulent flows have been used for millennia to mix solutes; a familiar example is stirring cream into coffee. However, many energy, environmental, and industrial processes rely on the mixing of solutes in porous media where confinement suppresses inertial turbulence. As a result, mixing is drastically hindered, requiring fluid to permeate long distances for appreciable mixing and introducing additional steps to drive mixing that can be expensive and environmentally harmful. Here, we demonstrate that this limitation can be overcome just by adding dilute amounts of flexible polymers to the fluid. Flow-driven stretching of the polymers generates an elastic instability, driving turbulent-like chaotic flow fluctuations, despite the pore-scale confinement that prohibits typical inertial turbulence. Using in situ imaging, we show that these fluctuations stretch and fold the fluid within the pores along thin layers (“lamellae”) characterized by sharp solute concentration gradients, driving mixing by diffusion in the pores. This process results in a 3x reduction in the required mixing length, a 6x increase in solute transverse dispersivity, and can be harnessed to increase the rate at which chemical compounds react by 5x—enhancements that we rationalize using turbulence-inspired modeling of the underlying transport processes. Our work establishes a simple, robust, versatile, and predictive way to mix solutes in porous media, with potential applications ranging from large-scale chemical production to environmental remediation.

Status: published work in Proc. Nat. Acad. Sci. 2024, **121**, e2320962121

Silicon Composite Anode Degradation during Freeze−Thaw Temperature-Swings

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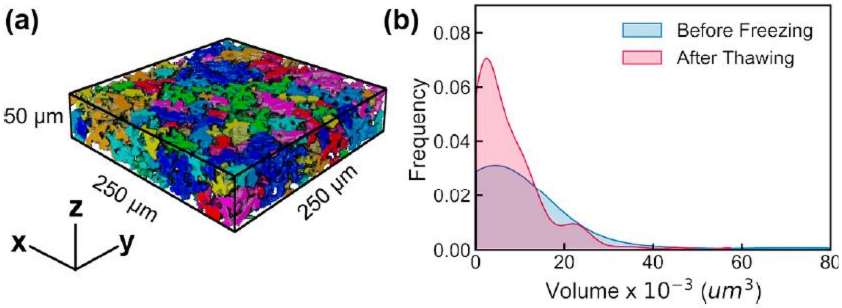

Batteries used in space applications can be exposed to large temperature-swings. During these large temperature swings, the battery electrolyte can undergo a phase transformation from a liquid to a solid and back to a liquid. The nature of the solvent and the type of salt influence the crystallization processes. Herein, we aim to understand how pressure build-up in confined regions of an electrode (e.g., pores) influences degradation processes in silicon-oxide graphite anodes undergoing freeze−thaw dynamics. Our results show that high porosity electrodes lead to a greater density of nucleation sites for electrolyte crystallization. Local pressure build-up at pores results in active material loss and decreased cycle lifetime in batteries exposed to extreme temperature swings.

Status: published work in ACS Applied Materials & Interfaces 2024, **16**, 30031

Reprocessable and Mechanically Tailored Soft Architectures Through 3D Printing of Elastomeric Block Copolymers

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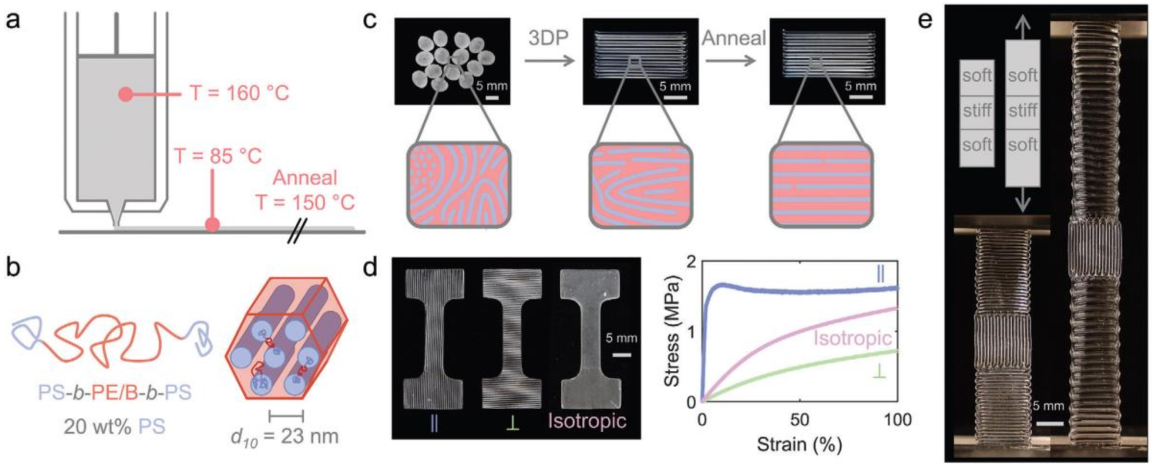

Thermoplastic elastomers (TPEs) are nanostructured, melt-processable, elastomeric block copolymers. When TPEs that form cylindrical or lamellar nanostructures are macroscopically oriented, their material properties can exhibit several orders of magnitude of anisotropy. Here it is demonstrated that the flows applied during the 3D printing of a cylinder-forming TPE enable hierarchical control over material nanostructure and function. It is demonstrated that 3D printing allows for control over the extent of nanostructural and mechanical anisotropy and that thermal annealing of 3D printed structures leads to highly anisotropic properties (up to 85 × anisotropic tensile modulus). This approach is leveraged to print functional soft 3D architectures with tunable local and macroscopic mechanical responses. Further, these printed TPEs intrinsically achieve melt-reprocessability over multiple cycles, reprogrammability, and robust self-healing via a brief period of thermal annealing, enabling facile fabrication of highly tunable, robust, and recyclable soft architectures.

Status: published work in Advanced Functional Materials 2024, **34**, 2411812

Harnessing an elastic flow instability to improve the kinetic performance of chromatographic columns

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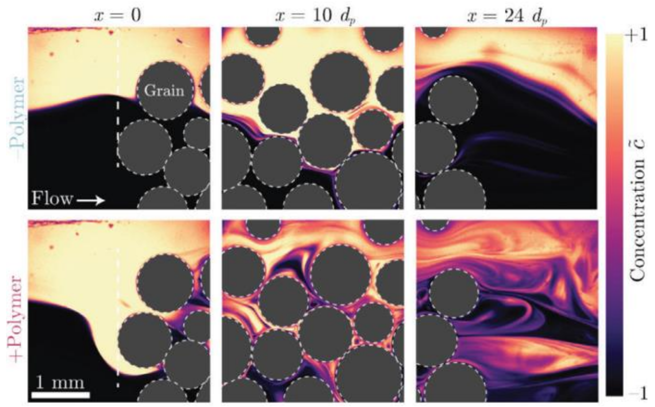

Despite decades of research and development, the optimal efficiency of slurry-packed HPLC columns is still hindered by inherent long-range flow heterogeneity from the wall to the central bulk region of these columns. Here, we show an example of how this issue can be addressed through the straightforward addition of a semidilute amount (500 ppm) of a large, flexible, synthetic polymer (18 MDa partially hydrolyzed polyacrylamide, HPAM) to the mobile phase (1% NaCl aqueous solution, hereafter referred to as ‘‘brine’’) during operation of a 4.6 mm × 300 mm column packed with 10 µm BEHTM 125 Å particles. Addition of the polymer imparts elasticity to the mobile phase, causing the flow in the interparticle pore space to become unstable above a threshold flow rate. We verify the development of this elastic flow instability using pressure drop measurements of the friction factor versus Reynolds number. These experiments thereby suggest that elastic flow instabilities can be harnessed to mitigate the negative impact of trans-column flow heterogeneities on the efficiency of slurry-packed HPLC columns. While this approach has its own inherent limitations and constraints, our results lay the groundwork for future targeted development of polymers that can impart elasticity when dissolved in commonly used liquid chromatography mobile phases and can thereby generate elastic flow instabilities to help improve the resolution of HPLC columns.

Status: published work in Journal of Chromatography A 2024, **1735**, 465326

Interplay between environmental yielding and dynamic forcing modulates bacterial growth

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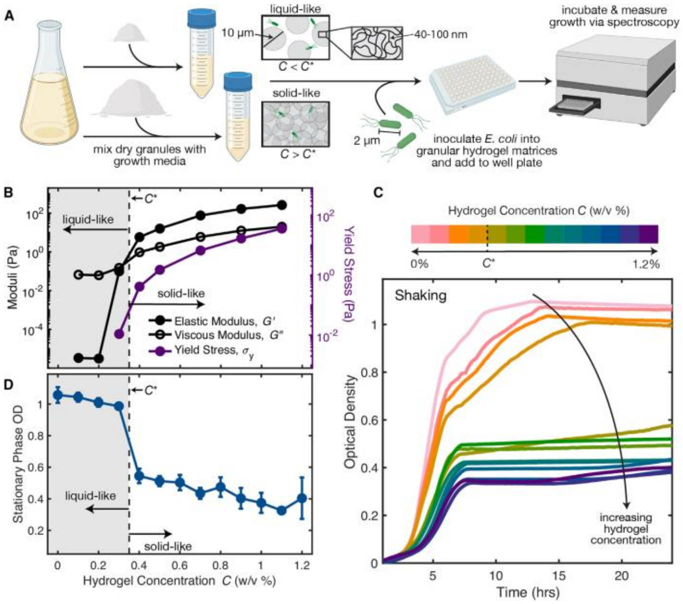

Many bacterial habitats – ranging from gels and tissues in the body to cell-secreted exopolysaccharides in biofilms – are rheologically complex, undergo dynamic external forcing, and have unevenly distributed nutrients. How do these features jointly influence how the resident cells grow and proliferate? Here, we address this question by studying the growth of Escherichia coli dispersed in granular hydrogel matrices with defined and highly tunable structural and rheological properties, under different amounts of external forcing imposed by mechanical shaking, and in both aerobic and anaerobic conditions. Our experiments establish a general principle: that the balance between the yield stress of the environment that the cells inhabit, σ_y, and the external stress imposed on the environment, σ, modulates bacterial growth by altering transport of essential nutrients to the cells. In particular, when $\sigma_y < \sigma$, the environment is easily fluidized and mixed over large scales, providing nutrients to the cells and sustaining complete cellular growth. By contrast, when $\sigma_y > \sigma$, the elasticity of the environment suppresses large-scale fluid mixing, limiting nutrient availability and arresting cellular growth. Our work thus reveals a new mechanism by which the rheology of the environment may modulate microbial physiology.

Status: published work in Biophysical Journal 2024, **123**, 957

A General Approach to Activate Second-Scale Room Temperature Photoluminescence in Organic Small Molecules

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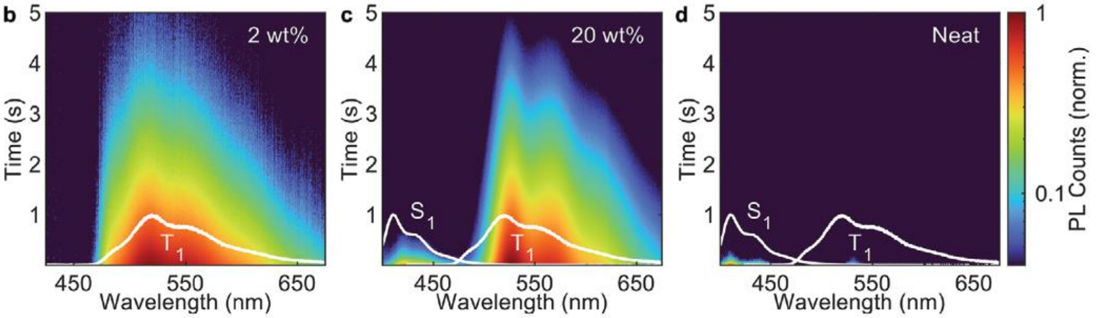

Organic small molecules that exhibit second-scale phosphorescence at room-temperature are of interest for potential applications in sensing, anticounterfeiting, and bioimaging. However, such materials systems are uncommon—requiring millisecond to second-scale triplet lifetimes, efficient intersystem crossing, and slow rates of nonradiative recombination. Here, a simple and scalable approach is demonstrated to activate long-lived phosphorescence in a wide variety of molecules by suspending them in rigid polymer hosts and annealing them above the polymer's glass transition temperature. This process produces submicron aggregates of the chromophore, which suppresses intramolecular motion that leads to nonradiative recombination and minimizes triplet–triplet annihilation that quenches phosphorescence in larger aggregates. In some cases, evidence of excimer-mediated intersystem crossing that enhances triplet generation in aggregated chromophores is found. In short, this approach circumvents the current design rules for long-lived phosphors, which will streamline their discovery and development.

Status: published work in Advanced Materials 2024, **36**, 2402478

Investigation of W-SiC compositionally graded films as a divertor material

Zihan Lin[1], Carlos Monton[2], Stefan Bringuier[2], Gregory Sinclair[2], Guangming Cheng[3], Eduardo Marin[2], Zachary Bergstrom[2], Dmitry Rudakov[4], Zana Popovic[5], Ulises Losada[6], Igor Bykov[2], Evan T. Ostrowski[1], Shota Abe[7], Nan Yao[3], Bruce E. Koel[1], Tyler Abrams[2]

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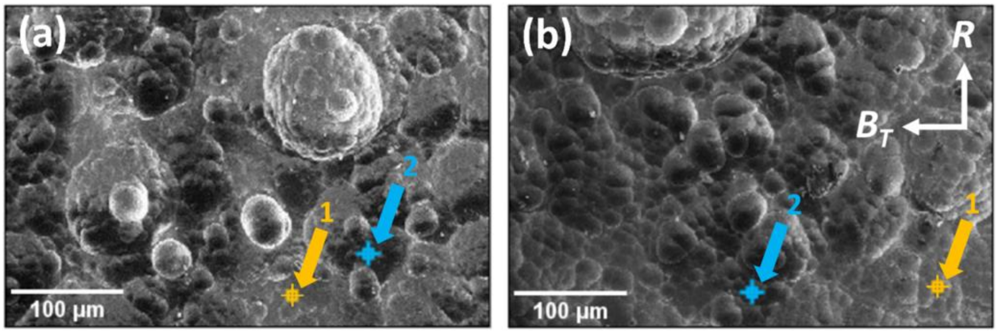

W-SiC composite material is a promising plasma-facing material candidate alternative to pure W due to the low neutron activation, low impurity radiation, and low tritium diffusivity of SiC while leveraging the high erosion resistance of the W armor. Additionally, W and SiC have high thermomechanical compatibility given their similar thermal expansion rates. The present study addresses the synthesis and performance of compositionally graded W-SiC films fabricated by pulsed-DC magnetron sputtering. Compositional gradients were characterized using transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS), and crystallographic information was obtained using electron diffraction and X-ray diffraction (XRD). Samples were exposed to Lmode deuterium plasma discharges in the DIII-D tokamak using the Divertor Material Evaluation System (DiMES). Post-mortem characterizations were performed using scanning electron microscopy (SEM) and XRD. Electron diffraction and XRD showed that the compositionally graded W-SiC films were composed of polycrystalline W and amorphous SiC with amorphous W+SiC interlayers. No macroscopic delamination or microstructural changes were observed under mild exposure conditions. This study serves as a preliminary examination of W-SiC compositionally graded composites as a potential candidate divertor material in future tokamak devices.

Status: published work in Journal of Nuclear Materials 2024, **592**, 154942

UiO(Zr)-based MOF catalysts for light-driven aqueous pollutant degradation

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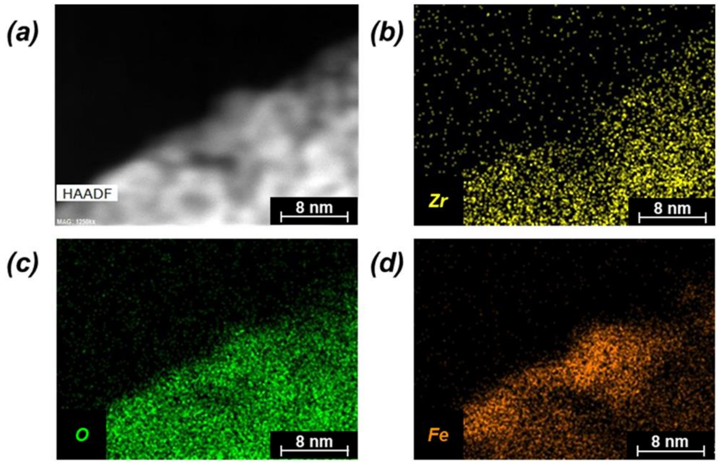

Zirconium-carboxylate metal–organic frameworks (MOFs) of isoreticular crystal morphologies and contrasting pore sizes are examined to understand the relative influence of linker size (UiO-67 vs. UiO-68) and secondary metal incorporation in photocatalytic aqueous pollutant degradation. Here, iron (Fe) is chosen given its prevalence in wastewater treatment literature and applications, resulting from its low toxicity and ability to activate benign oxidants. UiO-67 with Fe incorporated (Fe-UiO-67) via incipient wetness impregnation demonstrates reduced band gap energy relative to the UiO-67 parent and higher apparent photocatalytic degradation under UV light toward methylene blue dye using hydrogen peroxide (H_2O_2), with catalyst mass-normalized pseudo-first order rate constants of 6.8 ± 0.5 g^{-1} ks^{-1} and 2.0 ± 0.3 g^{-1} ks^{-1}, respectively. Some Fe leaching is evident, as indicated by recharge experiments in the filtrate. Synthesized UiO-68, which possesses increased pore size, also has reduced band gap energy resulting in higher UV-light activation than UiO-67 (pseudo-first order rate constant of 3.5 ± 0.4 g^{-1} ks^{-1}). Further, UiO-68 demonstrates high stability and exhibits a higher productive H_2O_2 utilization fraction than either of the UiO-67 catalysts. Together, this work clarifies the relative influence of linker modulation and active metal incorporation in UiO-MOFs for pollutant degradation and aqueous applications broadly.

Status: published work in Reaction Chemistry and Engineering 2024, **9**, 2333

Reaction-driven restructuring of defective $PtSe_2$ into ultrastable catalyst for the oxygen reduction reaction

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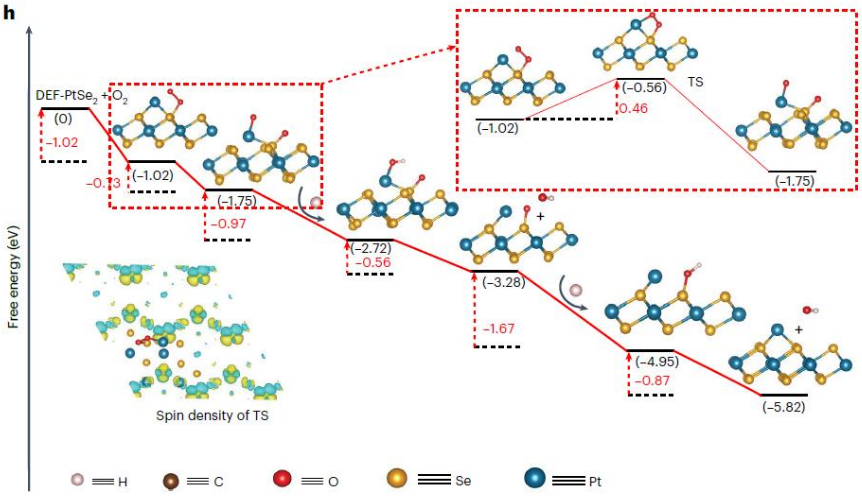

PtM (M = S, Se, Te) dichalcogenides are promising two-dimensional materials for electronics, optoelectronics and gas sensors due to their high air stability, tunable bandgap and high carrier mobility. However, their potential as electrocatalysts for the oxygen reduction reaction (ORR) is often underestimated due to their semiconducting properties and limited surface area from van der Waals stacking. Here we show an approach for synthesizing a highly efficient and stable ORR catalyst by restructuring defective platinum diselenide (DEF-$PtSe_2$) through electrochemical cycling in an O_2-saturated electrolyte. After 42,000 cycles, DEF-$PtSe_2$ exhibited 1.3 times higher specific activity and 2.6 times higher mass activity compared with a commercial Pt/C electrocatalyst. Even after 126,000 cycles, it maintained superior ORR performance with minimal decay. Quantum mechanical calculations reveal that the improved performance is due to the synergistic contributions from Pt nanoparticles and the apical active sites on the DEF-$PtSe_2$ surface. This work highlights the potential of DEF-$PtSe_2$ as a durable electrocatalyst for ORR, offering insights into PtM dichalcogenide electrochemistry and the design of advanced catalysts.

Status: published work in Nature Materials 2024, **23**, 1704

Fluid drainage in erodible porous media

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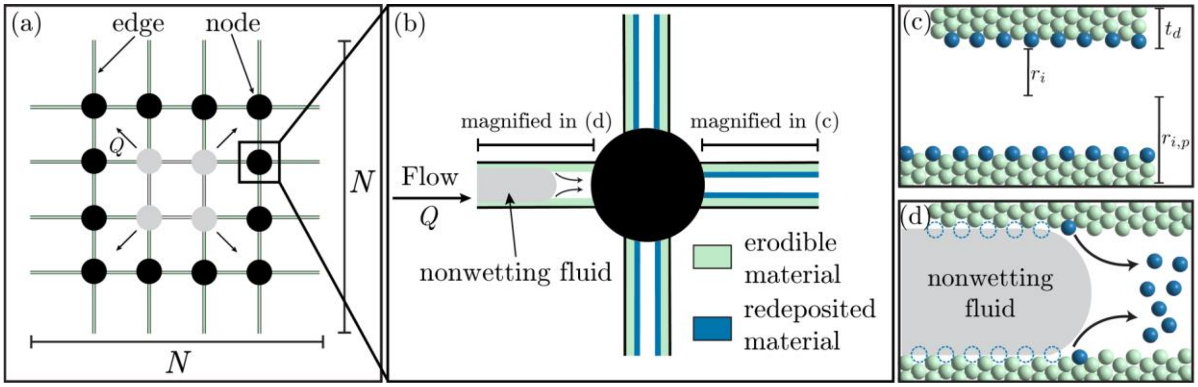

Drainage, in which a nonwetting fluid displaces a wetting fluid from a porous medium, is well studied for media with unchanging solid surfaces. However, many media can be eroded by drainage, with eroded material redeposited in pores downstream, altering further flow. Here we use theory and simulation to examine how these coupled processes both alter the overall fluid displacement pathway and help reshape the solid medium. We find two drainage behaviors with markedly different characteristics and quantitatively delineate the conditions under which they arise. Our results thereby help expand the current understanding of these rich physics, with implications for applications of drainage in industry and the environment.

Status: published work in Physical Review Research 2023, **5**, 043015

Physical Aging of Poly(methyl methacrylate) Brushes and Spin-Coated Films

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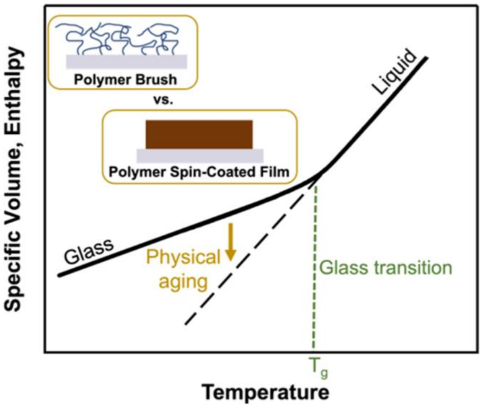

While there is significant attention aimed at understanding how one-dimensional confinement and chain confirmations can impact the glass transition temperature (T_g) of polymer films, there remains a limited focus on similar effects on sub-T_g processes, notably, structural relaxation. Using spectroscopic ellipsometry, we investigated the combined influence of confinement and molecular packing on T_g and physical aging, i.e., the property changes that accompany structural relaxation, at select film thicknesses and aging temperatures (T_a). We used poly(methyl methacrylate) (PMMA) films in the brush and spin-coated morphologies as model systems. We found that whether a PMMA film exhibited a decrease or increase in physical aging rate with confinement was dependent on the morphology. Notably, PMMA brushes exhibited higher physical aging rates compared to similarly thick spin-coated films at all values of T_a. These intriguing findings reveal the strong effects of confinement and molecular packing on the structural relaxation of polymer films. Results from this study have the potential to aid in the design of thin-film materials with controllable long-term glassy-state properties.

Status: published work in J. Phys. Chem. B 2024, **128**, 11999

Catalytic Consequences of Hierarchical Pore Architectures within MFI and FAU Zeolites for Polyethylene Conversion

Jun Zhi Tan[1], Maaso Ortega[1], Sophia A. Miller[1], Cole W. Hullfish[1], Hojoon Kim[1], Sungmin Kim[2], Wenda Hu[3], Jian Zhi Hu[2,3], J. A. Lercher[2,4], Bruce E. Koel[1], and Michele L. Sarazen[1]
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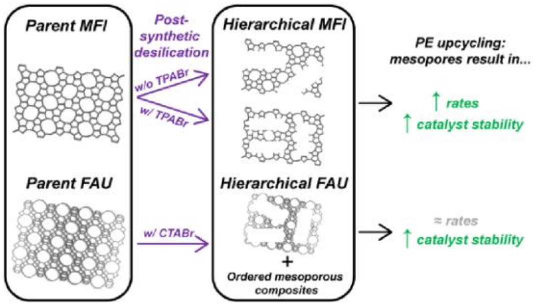

The benefits of hierarchical zeolites for the conversion of bulky molecules like polymeric waste have been reported in the literature; however, the impact of mesopore sizes and connectivities on rates, product selectivities, and catalyst deactivation in the context of plastic upcycling has not been systematically probed. Here, we synthesized a suite of hierarchical MFI and FAU zeolites via desilication under varying conditions for metal-free polyethylene conversion reactions under batch and flow conditions (473−523 K). Polyethylene conversion rates were higher on hierarchical than parent microporous MFI regardless of mesopore connectivities suggesting that the incorporation of mesopores facilitates diffusion of intermediate products to access medium-pore protons for successive scission events. Furthermore, higher branched: linear gaseous product ratios were produced on hierarchical than parent MFI. Solid conversion rates on hierarchical FAU synthesized via desilication with cetyltrimethylammonium bromide (CTABr), however, were not higher than parent FAU. In situ 1H MAS NMR performed on polyethylene with MFI zeolite show that PE isomerizes at temperatures near 450 K. Catalyst recyclability studies showed that all catalysts undergo deactivation during plastic upcycling reactions. Overall, hierarchical materials have better catalyst stability than parent materials. These findings demonstrate how rates, selectivities, and catalyst deactivation from plastic upcycling reactions can be controlled via fine-tuning the identity and connectivity of mesopores.

Status: published work in ACS Catalysis 2024, **14**, 7536.

Control of Solution Phase Behavior through Block−Random Copolymer Sequence

Lauren W. Taylor, Rodney D. Priestley, and Richard A. Register
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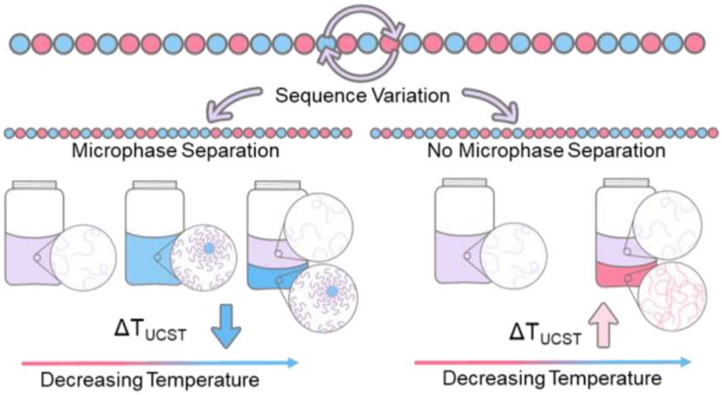

The phase behavior of polymers in solution is of both fundamental and practical interest. Previous work using coarse-grained molecular simulations suggests that the critical temperature (T_c) of macromolecules in solution can be controlled by the monomer sequence. Here, we experimentally investigated the solution phase behavior of a series of styrene−isoprene copolymers in both styrene- and isoprene-selective solvents. Across the series, the copolymers had a similar overall composition and molecular weight but subtle changes in the monomer sequence obtained by systematically placing a short homopolymer block of either polystyrene or polyisoprene at the end or the center of an otherwise random styrene−isoprene copolymer chain. Compared with a fully random copolymer, sequences that microphase-separate to form starlike or crew-cut micelles produce a lower T_c. Conversely, sequences that do not form micelles exhibit a higher T_c. Through a delicate balance of solvent/polymer compatibility, we demonstrate the spontaneous and thermoreversible formation of unusually large (aggregation number, ∼1000), stable crew-cut micelles. Despite the unusual structure, the thermodynamics of formation of these crew-cut micelles is similar to that of starlike block copolymer micelles.

Status: published work in Macromolecules 2024, **57**, 916.

Molecular Interactions Underlying Dissolution Trends in Cannabidiol-Polymer Amorphous Solid Dispersions

Baris E. Ugur, Nicholas J. Caggiano, Stephanie Monson, Alexander G. Bechtold, Yejoon Seo, Robert K. Prud'homme, Rodney D. Priestley, and Michael A. Webb.
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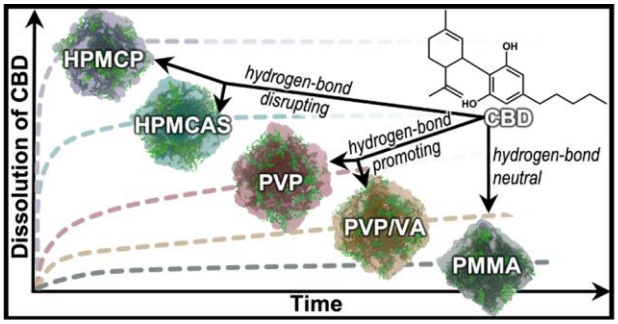

Cannabidiol (CBD) is viewed as a promising therapeutic agent against a variety of health ailments; however, its efficacy is limited by poor aqueous solubility. Amorphous solid dispersions (ASDs) can enhance the solubility of therapeutics by distributing them throughout a polymer matrix. In consideration of ASD formulations with CBD, we investigate the interactions of CBD with various polymers: poly(vinylpyrrolidone) (PVP), poly(vinylpyrrolidone)/vinyl acetate (PVP/VA) copolymer, hydroxypropyl methylcellulose phthalate (HPMCP), hydroxypropyl methylcellulose acetate succinate (HPMCAS), and poly(methyl methacrylate) (PMMA). Both the experiment and molecular dynamics simulation reveal diverse mixing behavior among the set of polymers. Detailed structural and nanoscale interaction analyses suggest that positive deviations from ideal mixing behavior arise from the formation of stable polymer−CBD hydrogen bonds, whereas negative deviations are associated with disruptions to the polymer−polymer hydrogen bond network. Polymer−water interaction analyses indicate the significance of polymer hydrophobicity that can lead to poor dissolution of CBD. These results have implications for drug dissolution rates based on how CBD and water interact with each polymer. Furthermore, these insights may be used to guide ASD formulations for CBD or other small-molecule therapeutic agents.

Status: published work in Macromolecules 2024, **57**, 8287.

Effects of Ligand Chemistry on Ion Transport in 2D Hybrid Organic–Inorganic Perovskites

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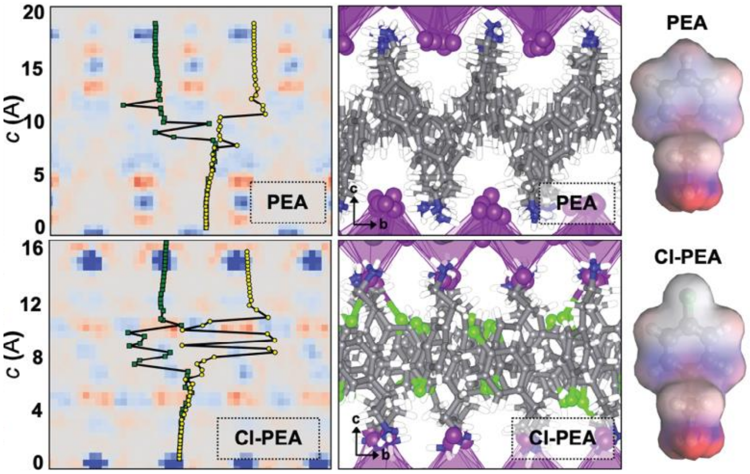

2D hybrid organic–inorganic perovskites are potentially promising materials as passivation layers that can enhance the efficiency and stability of perovskite photovoltaics. The ability to suppress ion transport is proposed as a stabilization mechanism, yet an effective characterization of relevant modes of halide diffusion in 2D perovskites is nascent. In light of this knowledge gap, molecular dynamics simulations with enhanced sampling and experimental validation to systematically characterize how ligand chemistry in seven $(R\text{-}NH_3)_2PbI_4$ systems impacts halide diffusion, particularly in the out-of-plane direction is combined. It is found that increasing stiffness and length of ligands generally inhibits ion transport, while increasing ligand polarization generally enhances it. Structural and energetic analyses of the migration pathways provide quantitative explanations for these trends, which reflect aspects of the disorder of the organic layer. Overall, this mechanistic analysis greatly enhances the current understanding of halide migration in 2D hybrid organic–inorganic perovskites and yields insights that can inform the design of future passivation materials.

Status: published work in Advanced Energy Materials 2024, **14**, 2401087

Polyelectrolyte-Doped Block Copolymer-Stabilized Nanocarriers for Continuous Tunable Surface Charge

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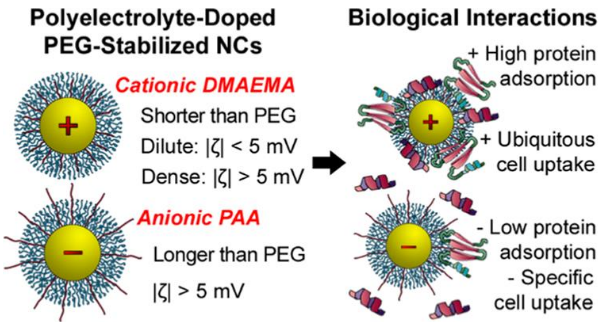

The surface charge of nanoparticles or nanocarriers (NCs) plays a critical role in the vehicle function, distribution, and fate in drug delivery applications. Flash NanoPrecipitation (FNP) is a platform for producing block copolymer-stabilized NCs. We show that NC charge (measured as the ζ-potential) can be continuously tuned from +40 to −40 mV by using blends of neutral poly(styrene)-block-poly(ethylene glycol) (PS-b-PEG) with polyelectrolyte block copolymers, anionic poly(styrene)-block-poly(acrylic acid) (PS-b-PAA) or cationic poly(styrene)-block-poly(N,N-dimethylaminoethyl methacrylate) (PS-b-DMAEMA), while simultaneously controlling NC diameters between 40 and 180 nm. The dense polymer brush on the surface of these FNP NCs provides a better platform to test NC surface charge effects on cellular interactions than NC systems in which charge is applied onto hydrophobic surfaces. NC charge gradually increases as more PS-b-PEG is replaced with a polyelectrolyte stabilizer, where sparsely substituted NCs (1−20 wt %) have nearly neutral (|ζ| < 5 mV) followed by a region where ζ-potential increases with increasing polyelectrolyte substitution. The protein binding to negatively charged NCs is low and equivalent to the adsorption on PEG-coated NCs, which are normally considered as the gold standard in “stealth” low protein adsorbing surfaces. In contrast, as little as 1 mol % cationic polymer produces strong protein adsorption, and cellular uptake, even though the ζ-potentials are still near zero, |ζ| < 5 mV. These results are discussed in terms of the protein corona differences on the NCs and the receptor differences between these cell lines.

Status: published work in ACS Applied Nano Materials 2024, **7**, 11071

Intestinal distribution of anionic, cationic, and neutral polymer-stabilized nanocarriers measured with a lanthanide (europium) tracer assay

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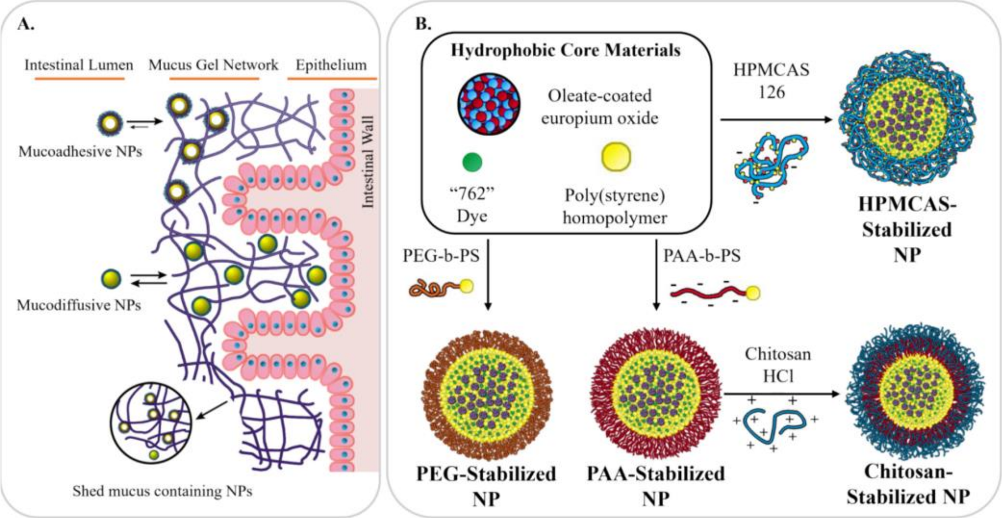

Nanocarriers, more commonly called nanoparticles (NPs), have found increasing use as delivery vehicles which increase the oral bioavailability of poorly water-soluble and peptide therapeutics. Therapeutic bioavailability is commonly assessed by measuring plasma concentrations that reflect the absorption kinetics. This bioavailability is a convolution of the gastrointestinal distribution of the NP vehicle and other factors. The spatiotemporal distribution of the NP vehicle in the gastrointestinal tract is not well studied and is a buried parameter in PK studies used to measure the effectiveness of an NP formulation. This work is a study of the intestinal distribution and fate of orally dosed NPs in male CD-1 mice over 24 h. NPs have identical hydrophobic cores – composed of poly(styrene) homopolymer, a naphthalocyanine dye, and oleate-coated europium oxide colloids – with one of four different surface stabilizers: PS-b-PEG, HPMCAS, PS-b-PAA, and chitosan HCl on PS-b-PAA stabilized NPs. NP hydrodynamic diameters are all below 200 nm, with some variation attributable to the molecular properties of the stabilizing polymer. The encapsulated hydrophobic europium oxide colloids do not release soluble europium ions, enabling the use of highly sensitive inductively coupled plasma mass spectrometry (ICP-MS) to detect NP concentrations in digested biological tissues.

Status: published work in Journal of Controlled Release 2024, **376**, 200.

Co-encapsulation of organic polymers and inorganic superparamagnetic iron oxide colloidal crystals requires matched diffusion time scales.

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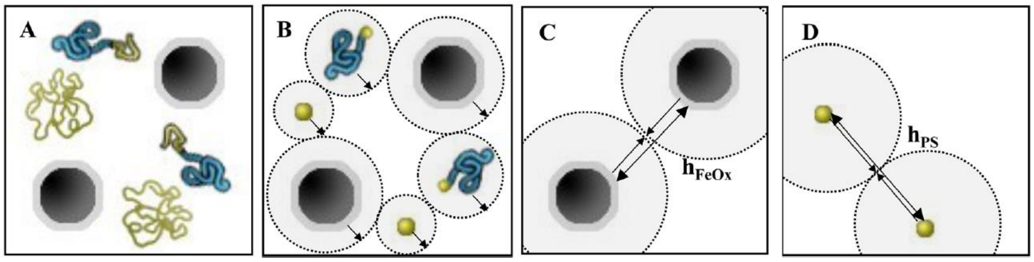

Nanoparticles (NPs) that contain both organic molecules and inorganic metal or metal oxide colloids in the same NP core are ''composite nanoparticles'' which are of interest in many applications. The rapid precipitation technique Flash NanoPrecipitation (FNP) enables continuous and scalable production of composite nanoparticles with hydrodynamic diameters between 40–200 nm that contain hydrophobic superparamagnetic iron oxide primary colloids. Composite NPs co-encapsulate these primary colloids (diameters of 6 nm, 15 nm, or 29 nm), a fluorescent dye (600 Daltons), and poly(styrene) homopolymer (1800, 50 000, or 200 000 Daltons) with NPs stabilized by a poly(styrene)-block-poly(ethylene glycol) (1600 Da-b-5000 Da) block copolymer. Nanoparticle assembly in FNP occurs by diffusion limited aggregation of the hydrophobic core components followed by adsorption of the hydrophobic block of the stabilizing polymer. We use a magnetic capture process to separate magnetic composite nanoparticles from organic-only nanoparticles and quantify the amount of iron oxide colloids and hydrophobic fluorescent dye in the magnetic and nonmagnetic fractions of each formulation. Analysis of the microstructure in over 1100 individual nanoparticles by TEM imaging and composition measurements identifies the conditions that produce nonstoichiometric composite NP populations without co-encapsulated magnetic iron oxide colloids. Stoichiometric magnetically responsive composite NPs are produced when the ratio of characteristic diffusion-aggregation time scales between the inorganic primary colloid and the organic core component is less than 30 and all NPs in a dispersion contain organic and inorganic species in approximately the same ratio. These rules for assembly of colloids and organic components into homogeneous composite nanoparticles are broadly applicable.

Status: published work in Soft Matter 2024, **20**, 8312.

Implications of Defect Density and Polymer Interactions for CO_2 Capture on Amine-Functionalized MIL-101(Cr)

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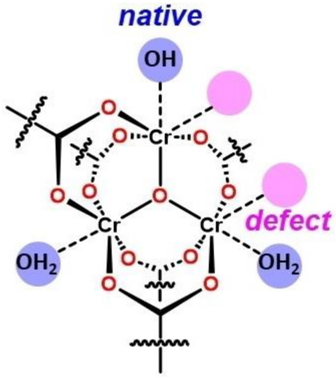

Rising anthropogenic carbon emissions have dire environmental consequences, necessitating remediative approaches, which includes use of solid sorbents. Here, aminopolymers (poly(ethylene imine) (PEI) and poly(propylene imine) (PPI)) are supported within solid mesoporous MIL-101(Cr) to examine effects of support defect density on aminopolymer-MOF interactions for CO_2 uptake and stability during uptake-regeneration cycles. Using simulated flue gas (10% CO2 in He), MIL-101(Cr)-ρ_{high} (higher defect density) shows 33% higher uptake capacity per gram adsorbent than MIL-101(Cr)-ρ_{low} (lower defect density) at 308 K, consistent with increased availability of undercoordinated Cr adsorption sites at missing linker defects. Increasing aminopolymer weight loadings (10–50 wt.%) within MIL-101(Cr)-ρ_{low} and MIL-101(Cr)-ρ_{high} increases amine efficiencies and CO_2 uptake capacities relative to bare MOFs, though both incur CO_2 diffusion limitations through confined, viscous polymer phases at higher (40–50 wt.%) loadings. Benchmarked against SBA-15, lower polymer packing densities (PPI>PEI), weaker and less abundant van der Waals interactions between aminopolymers and pore walls, and open framework topology increase amine efficiencies. Interactions between amines and Cr defect sites incur amine efficiency losses but grant higher thermal and oxidative stability during uptake-regeneration cycling. Finally, >25% higher CO_2 uptake capacities are achieved for aminopolymer/MIL-101(Cr)-ρ_{high} under humid conditions, demonstrating promise for realistic applications.

Status: published work in ChemSusChem 2024, **17**, e202400249.

Department of Civil and Environmental Engineering

Co-valorization of Food Waste and CO_2 to Produce Volatile Fatty Acids Using Liter-Scale Tubular Microbial Electrosynthesis Cells

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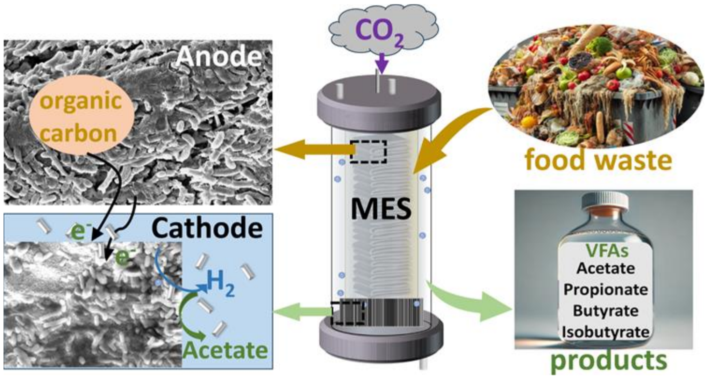

This study presents the simultaneous conversion of food waste and CO_2 into volatile fatty acids (VFAs) using a 6 L tubular microbial electrosynthesis cell (MES). The MES reactor uses a bioanode to convert food waste into current and CO_2, while on the cathode, H_2 is produced and subsequently consumed by cathode microbes for the conversion of CO_2 to VFAs. The study reveals that system performance is impacted by organic loading, applied voltage, and flow rate, and optimal operational conditions achieve a VFA titer of 1763 mg/L with the Coulombic efficiency (CE) exceeding 90% at the anode, highlighting efficient electron recovery from food waste. Resistance analysis indicates that the cathode contributed most to system resistance, while microbial community analysis shows a synergy between fermentative and electroactive bacteria in the anode and dominant acetogens in the cathode, facilitating efficient electron recovery and VFA synthesis, respectively. The research underscores the tubular MES's potential for sustainable food waste treatment and CO_2 valorization into valuable VFAs, contributing to waste management and greenhouse gas mitigation strategies.

Status: published work in ACS ES&T Engineering 2024, **4**, 2243-2251

H_2 mediated mixed culture microbial electrosynthesis for high titer acetate production from CO_2

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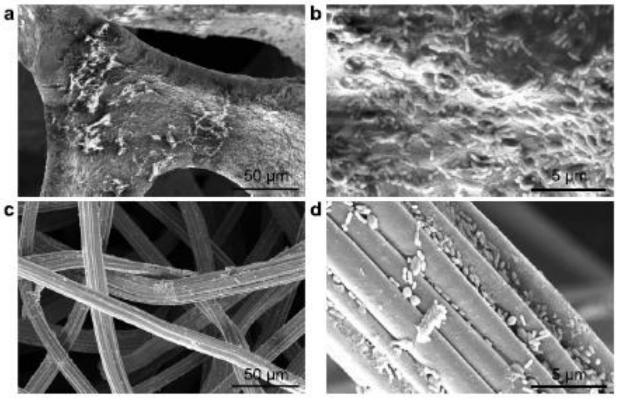

Microbial electrosynthesis (MES) converts CO_2 into value-added products such as volatile fatty acids (VFAs) with minimal energy use, but low production titer has limited scale-up and commercialization. Mediated electron transfer via H_2 on the MES cathode has shown a higher conversion rate than the direct biofilm-based approach, as it is tunable via cathode potential control and accelerates electrosynthesis from CO_2. Here we report high acetate titers can be achieved via improved in situ H_2 supply by nickel foam decorated carbon felt cathode in mixed community MES systems. Acetate concentration of 12.5 g L^{-1} was observed in 14 days with nickel-carbon cathode at a poised potential of – 0.89 V (vs. standard hydrogen electrode, SHE), which was much higher than cathodes using stainless steel (5.2 g L^{-1}) or carbon felt alone (1.7 g L^{-1}) with the same projected surface area. A higher acetate concentration of 16.0 g L^{-1} in the cathode was achieved over long-term operation for 32 days, but crossover was observed in batch operation, as additional acetate (5.8 g L^{-1}) was also found in the abiotic anode chamber. We observed the low Faradaic efficiencies in acetate production, attributed to partial H_2 utilization for electrosynthesis. The selective acetate production with high titer demonstrated in this study shows the H_2-mediated electron transfer with common cathode materials carries good promise in MES development.

Status: published work in Environmental Science and Ecotechnology 2024, **19**, 100324

Mechanistic Insights on Solution-Based Green Synthesis of Phase-Pure Ca-Based Layered Double Hydroxides from $Ca(OH)_2$

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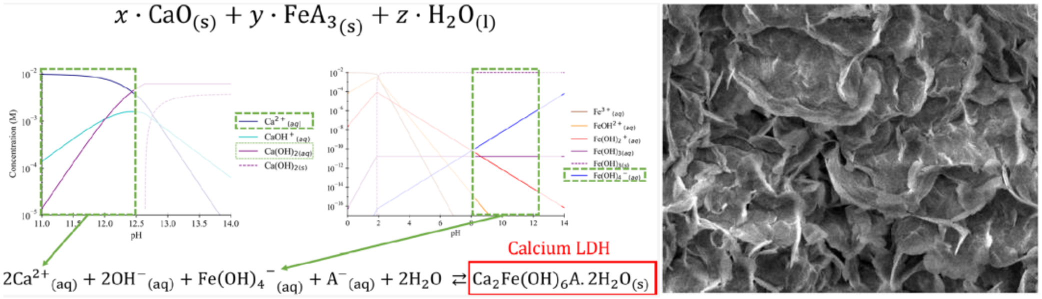

Ca-based layered double hydroxides (LDHs) are ideal candidates for applications that require the selective adsorption of anions and acidic molecules due to their positively charged layers and high density of exposed basic adsorption sites. Traditional LDH synthesis methods require use of non-environmentally friendly precursors and/or additional post-synthetic treatments. More recently, green synthesis of crystalline Ca-LDH has been achieved by means of $Ca(OH)_2$ hydrolysis without the need for strong alkalis; however, attainment of phase-pure Ca-LDHs using this approach remains elusive due to a lack of understanding of the Ca-LDH formation mechanism. In this work, we develop a comprehensive solution speciation model for the synthesis of $Ca_2Fe(OH)_6Cl{\cdot}2H_2O$ via $Ca(OH)_2$ hydrolysis and discuss the effect of initial Ca/Fe(III) solution molar ratio ($SMR_{Ca/Fe}$) on sample purity and crystallinity. Our calculations show a $SMR_{Ca/Fe} \approx 3$ is needed to (i) achieve full conversion of the solid precursors and (ii) avoid the coprecipitation of less soluble impurities. This value stems from the chemical equilibria of species in solution and the need to be above a specific pH level to drive the precipitation of the Ca-LDH. Characterization of the samples using thermogravimetric analysis (TGA) coupled with gas Fourier transform infrared spectroscopy (gas-FTIR), high-resolution X-ray diffraction (HR-XRD), and pair distribution function analysis (PDF) supports the theoretical findings, showing evidence of high purity samples synthesized with $SMR_{Ca/Fe} \approx 3$. Based on these results, we introduce a new simplified method for the green synthesis of crystalline Ca-LDHs, consisting of a one-pot synthesis at ambient temperature without the need for strong alkalis.

Status: published work in Crystal Growth & Design 2024, **24**, 56

Tough and Ductile Architected Nacre-Like Cementitious Composites

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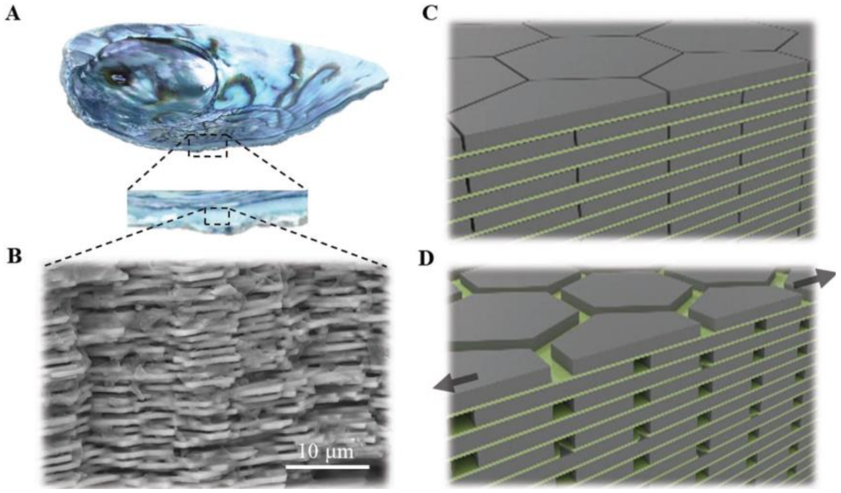

Enhancing fracture toughness and ductility of brittle materials such as concrete remains a challenge. Nature offers numerous mechanisms to enhance fracture toughness using purposeful designs of materials' architecture. Natural nacre exhibits high fracture toughness by promoting inelastic deformation and hierarchical toughening mechanisms. Here, "nacre-like-separated" and "nacre-like-grooved" cementitious composites inspired by brick-and-mortar arrangement of mollusk shells are proposed. These nacre-like composites are engineered by laser processing cement paste into individual tablets and grooved patterns and laminating them with limited amounts of suitable elastomeric (polyvinyl siloxane) interlayers. The study hypothesizes tablet sliding as an additional toughening mechanism in "nacre-like-separated", preventing tablet failure and leading to the postponed onset of bulk composite failure. These mechanisms significantly enhance both fracture toughness and ductility by 17.1 and 19 folds, compared to constituent hardened cement paste, respectively. By engineering laser-induced defects into tabulated cementitious-elastomeric material at meso-scale, a class of tough and ductile cementitious composites is introduced, resulting in significantly high fracture toughness values (73.68 MPa.mm$^{1/2}$), comparable to Ultra-high-performance-concrete without sacrificing the strength.

Status: published work in Advanced Functional Materials 2024, **34**, 2313516

The convergence of lactic acid microbiomes and metabolites in long-term electrofermentation

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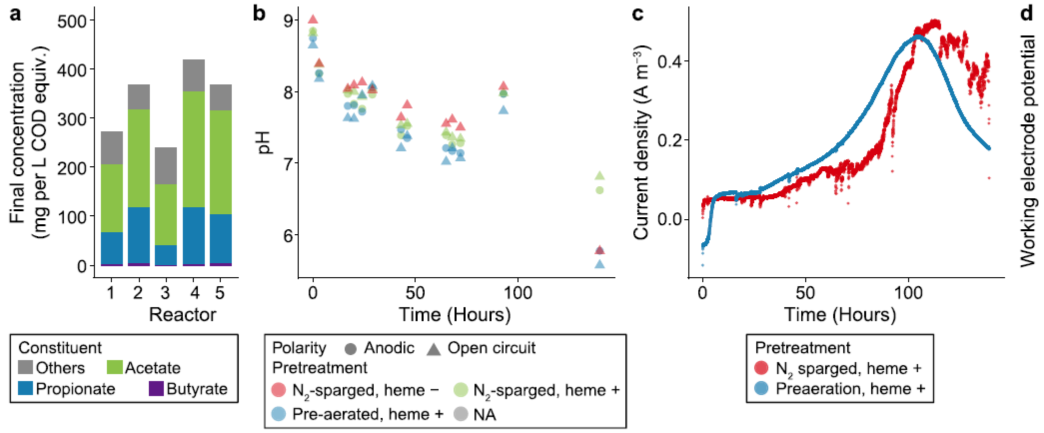

Regulating electron transfer in predominantly fermentative microbiomes has broad implications in environmental, chemical, food, and medical fields. Here we demonstrate electrochemical control in fermenting food waste, digestate, and wastewater to improve lactic acid production. We hypothesize that applying anodic potential will expedite and direct fermentation towards lactic acid. Continued operation that introduced epi/endophytic communities to pure culture *Lactiplantibacillus* plantarum reactors with static electrodes was associated with the loss of anode-induced process intensification despite 80% L. plantarum retention. Employing fluidized electrodes discouraged biofilm formation and extended electrode influence to planktonic gram-positive fermenters using mediated extracellular electron transfer. While short-term experiments differentially enriched *Lactococcus* and *Klebsiella* spp., longer-term operations indicated convergent microbiomes and product spectra. These results highlight a functional resilience of environmental fermentative microbiomes to perturbations in redox potential, underscoring the need to better understand electrode induced polymicrobial interactions and physiological impacts to engineer tunable open-culture or synthetic consortia.

Status: published work in Environmental Science and Ecotechnology 2024, **22**, 100459.

3D-printing of architected calcium silicate binders with enhanced and in-situ carbonation

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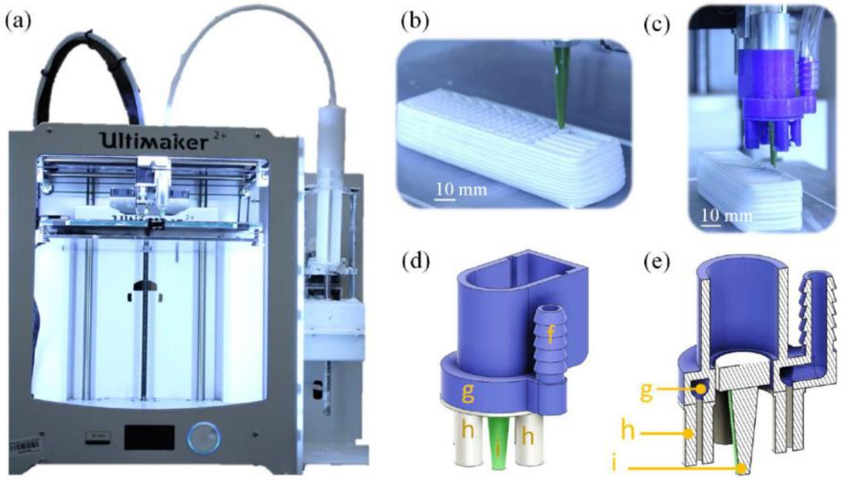

This paper investigates the use of architected cellular and solid designs of materials via additive manufacturing and in-situ CO_2 circulation to augment the carbonation and mechanical properties of a calcium silicate-based cement (CSC) binder. A wollastonite-based binder was formulated for extrusion-based 3D-printing. Solid and cellular lamellar architectures were designed to probe the role of layered interfaces and higher surface area on the degree of carbonation (DOC), respectively. Two carbonation exposure scenarios, with and without in-situ carbonation were employed. The DOC, microstructural phases, and flexural strength were characterized using TGA, modified over-flow image analysis technique, and three-point-bending, respectively. By exploiting 3D-printing and harnessing the higher surface area of cellular architecture, the material obtained a significantly higher DOC (by 8.9-folds) and flexural strength (by 5.7-folds) compared to reference cast. In-situ carbonation of cellular architected materials can additionally improve early-stage deformation, DOC (by 12.9-folds) and flexural strength (by 16.5-folds), compared to cast.

Status: published work in Virtual and Physical Prototyping 2024, **19**, e2350768

Soft matter physics of the ground beneath our feet

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This perspective article is a multi-voice effort to bring together different views and approaches, questions and insights, from researchers that work in area of the soft matter physics of the ground beneath our feet. We identify four major challenges concerned with the dynamics in and of the ground: (I) modeling from the grain scale, (II) near-criticality, (III) bridging scales, and (IV) life. For each challenge, we present a selection of topics by individual authors, providing specific context, recent advances, and open questions.

Status: published work in Soft Matter 2024, **20**, 5859

Machine Learning for Polymer Design to Enhance Pervaporation- Based Organic Recovery

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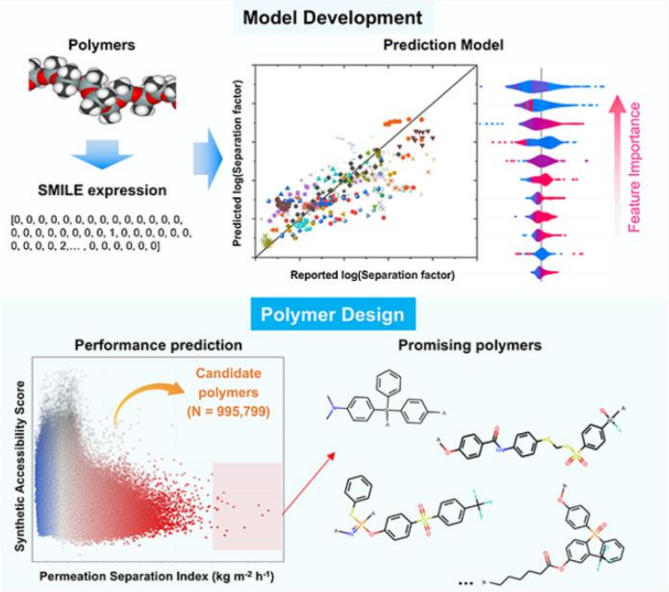

Pervaporation (PV) is an effective membrane separation process for organic dehydration, recovery, and upgrading. However, it is crucial to improve membrane materials beyond the current permeability-selectivity trade-off. In this research, we introduce machine learning (ML) models to identify high-potential polymers, greatly improving the efficiency and reducing cost compared to conventional trial-and-error approach. We utilized the largest PV data set to date and incorporated polymer fingerprints and features. Dimensionality reduction, missing data treatment, seed randomness, and data leakage management were employed to ensure model robustness. The optimized LightGBM models achieved RMSE of 0.447 and 0.360 for separation factor and total flux, respectively (logarithmic scale). Screening approximately 1 million hypothetical polymers with ML models resulted in identifying polymers with a predicted permeation separation index >30 and synthetic accessibility score <3.7 for acetic acid extraction. This study demonstrates the promise of ML to accelerate tailored membrane designs.

Status: published work in Environmental Science and Technology 2024, **58**, 10128.

Ca-Based Layered Double Hydroxides for Environmentally Sustainable Carbon Capture

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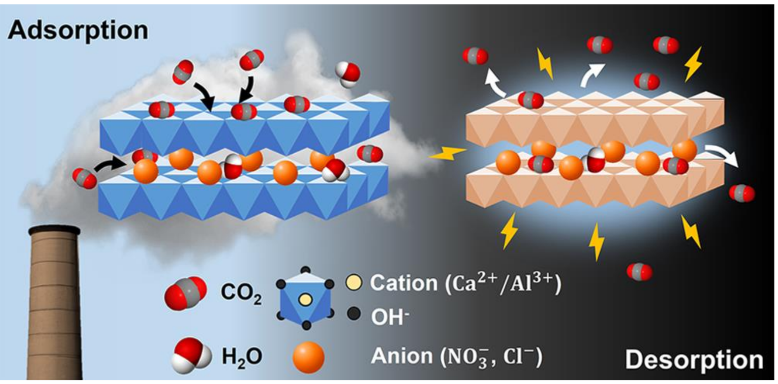

The process of carbon dioxide capture requires a large amount of energy for the separation of carbon dioxide from other gases, which has been a major barrier to the widespread deployment of carbon capture. Innovation of carbon dioxide adsorbents is vital for the a sustainable carbon capture process. In this study, we investigated the electrified synthesis and rejuvenation of calcium-based layered double hydroxides (Ca-based LDHs) as solid adsorbents for CO_2. We discovered that the particle morphology and phase purity of the LDHs, can be controlled by tuning the current density during electrodeposition on a porous carbon substrate. By decoupling the adsorption of water and CO_2, we showed that the adsorbed water largely promoted CO_2 adsorption, most likely through a sequential dissolution and reaction pathway. A carbon capture capacity of 4.3 ± 0.5 mmol/g was measured at 30 °C and relative humidity of 40% using 10 vol % CO_2 in nitrogen as the feed stream. After CO_2 capture occurred, the thermal regeneration step was carried out by directly passing an electric current through the conductive carbon substrate. CO_2 was found to start desorbing from the Ca-based LDHs at a temperature as low as 220 °C as opposed to the temperature above 700 °C required for calcium carbonate. Finally, we evaluated the cumulative energy demand of the LDH-based capture process using a life cycle assessment. We identified the most environmentally concerning step in the process and concluded that the post-combustion CO_2 capture using LDH could be advantageous compared with existing technologies.

Status: published work in Environmental Science and Technology 2024, **57**, 17212.

Concentrated C_{2+} Alcohol Production Enabled by Post-Intermediate Modulation and Augmented CO Adsorption in CO Electrolysis

Guangye Zhou[1], B. Li[2], G. Cheng[3], Ch. J. Breckner[4], D. P. Dean[4], M. Yang[1], Nan Yao[3], Jeffrey T. Miller[4], Johannes B.M. Klok[5], Nicolas Tsesmetzis[5], Guofeng Wang[2], and Zhiyong Jason Ren[1]
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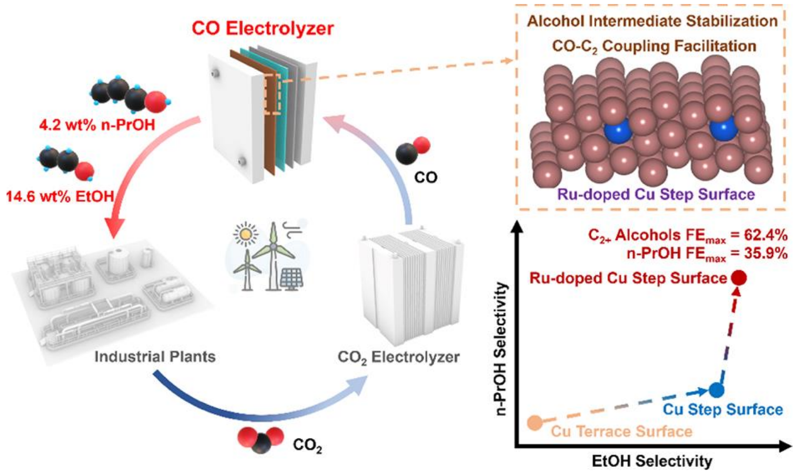

The electrocatalytic synthesis of multicarbon products from CO_2/CO feedstock represents a sustainable method for chemical production with a reduced carbon footprint. Traditional copper catalysts predominantly produce alkenes. Here, we present the construction of Ru-doped Cu nanowires that enhance the selectivity of n-PrOH and C_{2+} alcohols. In situ Raman spectroscopy shows that our approach promotes both *CO binding and availability. Density-functional theory simulations illustrate that introducing Ru species simultaneously stabilizes CO and alcohol-related intermediates. In an alkaline gas-diffusion electrolyzer, we attained a maximum Faradaic efficiency (FE) of 35.9% for n-PrOH and 62.4% for the total C_{2+} alcohols. A record concentration of 18.8 wt % (4.2 wt % n-PrOH and 14.6 wt % EtOH) with nearly 100% purity at 200 mA/cm^2 over 100 h is achieved. This work not only provides new insights and guidance for the development of future catalysts from the perspectives of surface science and mechanisms but also highlights the importance of coupling material engineering with reactor engineering to optimize the production process of high-value alcohol products.

Status: published work in J. Am. Chem. Soc. 2024, **146**, 31788.

Department of Chemistry

Bonding Interactions Can Drive Topological Phase Transitions in a Zintl Antiferromagnetic Insulator

Tanya Berry[1], Jaime M. Moya[1], David Smiadak[2], Scott B. Lee[1], Sigalit Aharon[1], Alexandra Zevalkink[2], Tyrel M. McQueen[3], and Leslie M. Schoop[1]

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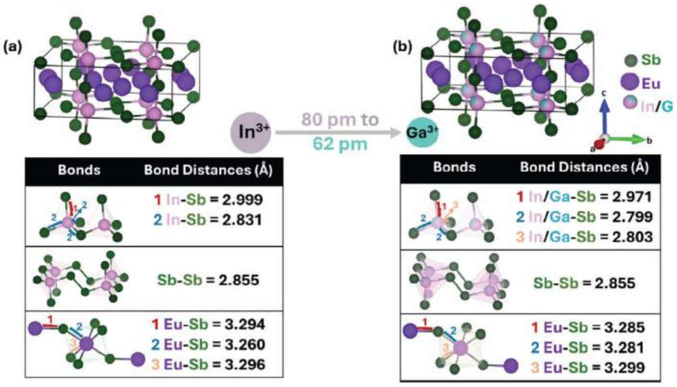

While ~30% of materials are reported to be topological, topological insulators are rare. Magnetic topological insulators (MTI) are even harder to find. Identifying crystallographic features that can host te coexistence of a topological insulating phase with magnetic order is vital for finding intrinsic MTI materials. Thus far, most materials that are investigated for the determination of an MTI are some combination of known topological insulators with a magnetic ion such as $MnBi_2Te_4$. Motivated by the recent success of $EuIn_2As_2$, the role of chemical pressure on topologically trivial insulator is investigated, $Eu_5In_2Sb_6$ via Ga substitution. $Eu_5Ga_2Sb_6$ is predicted to be topological but is synthetically difficult to stabilize. The intermediate compositions between $Eu_5In_2Sb_6$ and $Eu_5Ga_2Sb_6$ are observed through theoretical works to explore a topological phase transition and band inversion mechanism. The band inversion mechanism is attributed to changes in Eu–Sb hybridization as Ga is substituted for In due to chemical pressure. $Eu_5In_{4/3}Ga_{2/3}Sb_6$ is also synthesized, the highest Ga concentration in $Eu_5In_{2-x}Ga_xSb_6$, and report the thermodynamic, magnetic, transport, and Hall properties. Overall, the work paints a picture of a possible MTI via band engineering and explains why Eu-based Zintl compounds are suitable for the co-existence of magnetism and topology.

Status: published work in Adv. Funct. Mater. 2024, 2415610.

Exploring the impact of vibrational cavity coupling strength on ultrafast CN + c-C_6H_{12} reaction dynamics

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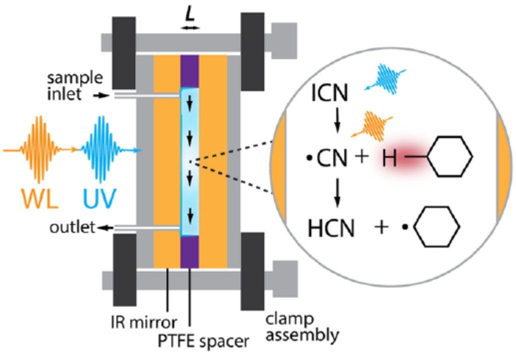

Molecular polaritons, hybrid light-matter states resulting from strong cavity coupling of optical transitions, may provide a new route to guide chemical reactions. However, demonstrations of cavity-modified reactivity in clean benchmark systems are still needed to clarify the mechanisms and scope of polariton chemistry. Here, we use transient absorption to observe the ultrafast dynamics of CN radicals interacting with a cyclohexane (c-C_6H_{12}) and chloroform ($CHCl_3$) solvent mixture under vibrational strong coupling of a C–H stretching mode of c-C_6H_{12}. By modulating the c-C_6H_{12} : $CHCl_3$ ratio, we explore how solvent complexation and hydrogen (H)-abstraction processes proceed under collective cavity coupling strengths ranging from 55 to 85 cm−1. Reaction rates remain unchanged for all extracavity, on-resonance, and off-resonance cavity coupling conditions, regardless of coupling strength. These results suggest that insufficient vibrational cavity coupling strength may not be the determining factor for the negligible cavity effects observed previously in H-abstraction reactions of CN with $CHCl_3$.

Status: published work in Nanophotonics 2024, **13**, 2591

NaW_2S_4 and Rb_xWS_2: Alternative Sources for 2M-WS_2 and 1T′-WS_2 Monolayers

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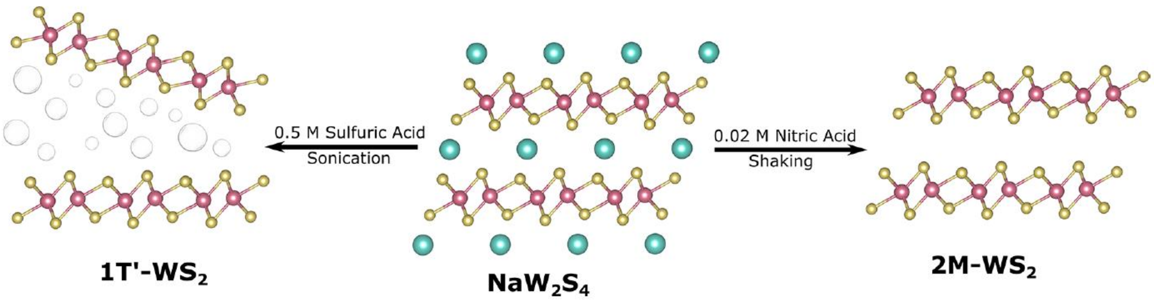

With the recent strive to develop novel quantum materials, including two-dimensional nanosheets, alkali-layered intercalated materials have found a new purpose as starting materials for such compounds. Enriching the library of alkali materials, we present a solid-state synthesis for preparing NaW_2S_4 ($P\bar{1}$, No. 2) and Rb_xWS_2 (C2/m, No. 12). Solving their crystal structure from their powder X-ray diffraction patterns, we show that both materials are layered, the former being a slightly distorted version of the latter. We compare the two structures and find that the main difference is the interlayer spacing in the a-direction. We further show that, like their cousin, K_xWS_2, both compounds can be deintercalated with dilute acid to form superconducting 2M-WS_2, with structural and property characterization showing similar behavior, regardless of the starting material. Lastly, we find that both materials can be exfoliated in the same manner as K_xWS_2 to form superconducting 1T′-WS_2 monolayers. We describe an easy one-step method for preparing two new layered materials and, thus, provide more opportunities to access valuable superconducting materials.

Status: published work in Inorganic Chemistry 2024, **63**, 21954

A pyroxene-based quantum magnet with multiple magnetization plateaus

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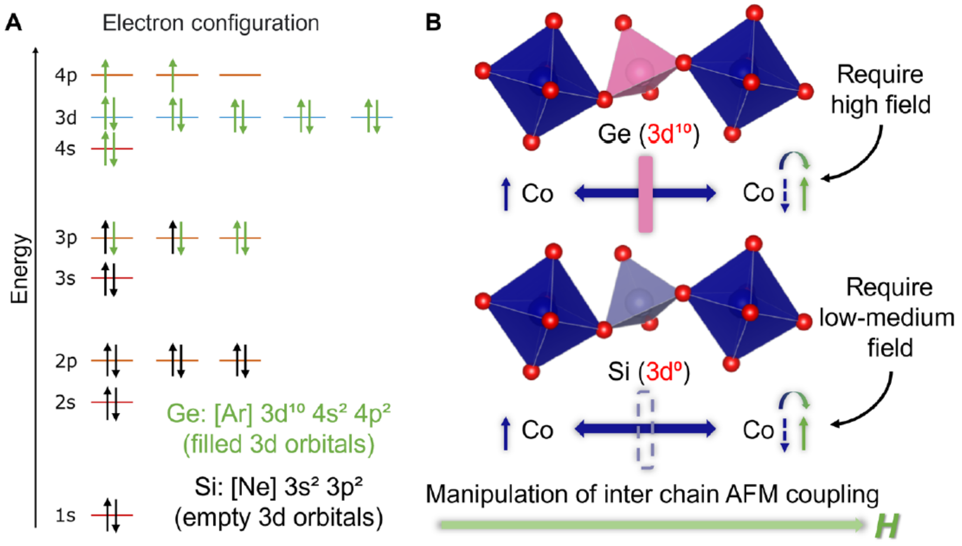

Pyroxenes (AMX_2O_6) consisting of infinite one-dimensional edge-sharing MO_6 chains and bridging XO_4 tetrahedra are fertile ground for finding quantum materials. Thus, here, we have studied calcium cobalt germanate ($CaCo\text{-}Ge_2O_6$) and calcium cobalt silicate ($CaCoSi_2O_6$) crystals in depth. Heat capacity data show that the spins in both compounds are dominantly Ising-like, even after being manipulated by high magnetic fields. On cooling below the Néel temperatures, a sharp field–induced transition in magnetization is observed for $CaCoGe_2O_6$, while multiple magnetization plateaus beneath the full saturation moment are spotted for $CaCoSi_2O_6$. Our analysis shows that these contrasting behaviors potentially arise from the different electron configurations of germanium and silicon, in which the 3d orbitals are filled in the former but empty in the latter, enabling electron hopping. Thus, silicate tetrahedra can aid the interchain superexchange pathway between cobalt(II) ion centers, while germanate ones tend to block it during magnetization.

Status: published work in Science Advances 2024, **10**, eadp4685

Toward 1D Transport in 3D Materials: SOC-Induced Charge-Transport Anisotropy in Sm_3ZrBi_5

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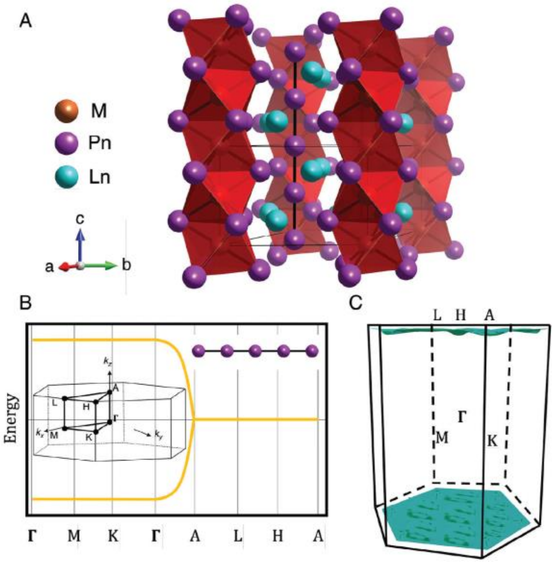

1D charge transport offers great insight into strongly correlated physics, such as Luttinger liquids, electronic instabilities, and superconductivity. Although 1D charge transport is observed in nanomaterials and quantum wires, examples in bulk crystalline solids remain elusive. In this work, it is demonstrated that spin-orbit coupling (SOC) can act as a mechanism to induce quasi-1D charge transport in the Ln_3MPn_5 (Ln = lanthanide; M = transition metal; Pn = Pnictide) family. From three example compounds, La_3ZrSb_5, La_3ZrBi_5, and Sm_3ZrBi_5, density functional theory calculations with SOC included show a quasi-1D Fermi surface in the bismuthide compounds, but an anisotropic 3D Fermi surface in the antimonide structure. By performing anisotropic charge transport measurements on La_3ZrSb_5, La_3ZrBi_5, and Sm_3ZrBi_5, it is demonstrated that SOC starkly affects their anisotropic resistivity ratios at low temperatures, with an ARR of ≈ 4 in the antimonide compared to ≈ 9.5 and ≈ 22 (≈ 32 after magnetic ordering) in La_3ZrBi_5 and Sm_3ZrBi_5, respectively. This report demonstrates the utility of spin-orbit coupling to induce quasi-low-dimensional Fermi surfaces in anisotropic crystal structures, and provides a template for examining other systems.

Status: published work in Advanced Materials 2024, **36**, 2404553

Extending Cyanogel and Prussian Blue Analogue Chemistry to Octacyanometallate-Based Coordination Polymers: Reduced Temperature Routes to Materials Based on Molybdenum and Tungsten

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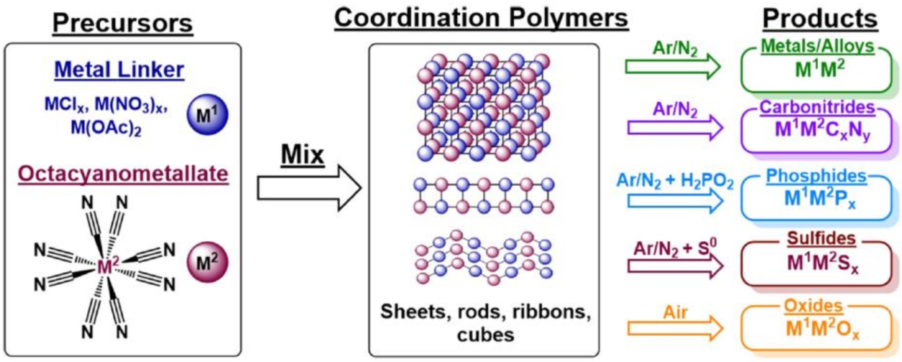
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA



Cyanide coordination polymers (CCPs) and their products made via thermolysis make up a promising class of materials for a variety of energy and analytical applications. While the chemistry of hexacyanometallate-based CCPs is well developed, that of their octacyanometallate $[M(CN)_8]^{4-}$ (M = Mo, W) analogues is underexplored. This work compares the synthesis, morphology, and thermolytic properties of two types of cyanide coordination polymers: the amorphous $[PdCl_4]^{2-}$ based cyanogel, Pd−Mo/W, and the nanocrystalline $CoCl_2$-based Prussian blue analogue, Co−Mo/W. The general decomposition pathways and products for $[M(CN)_8]^{4-}$ containing polymers are comparable to their hexacyanometallate analogues. All four coordination polymers can be converted to mixed oxide and ternary phosphide systems and generally retain morphology upon heating. Notably, the reduction under inert gas generates alloys in the cyanogel systems and complex reduced mixtures in the Prussian blue analogue (PBA) systems.

Status: published work in Chemistry of Materials 2024, **36**, 7857

Polymorphism within the Quasi-One-Dimensional Au_2MP_2 (M = Tl, Pb, Pb/Bi, and Bi) Series

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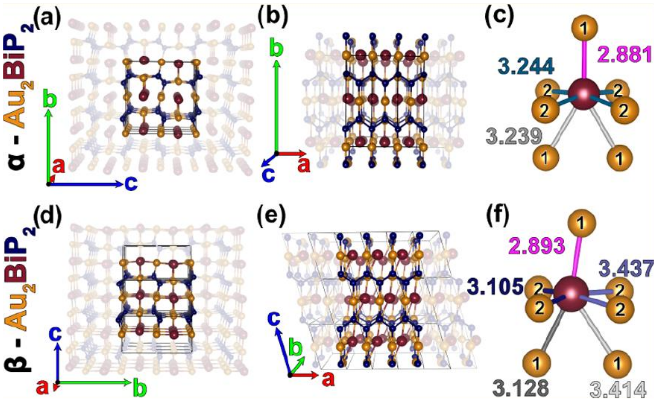

Quasi-1-dimensional (q1D) materials have attracted significant interest for experimentally realizing fundamental physical models. A plethora of q1D systems have been discovered in previous decades. Herein, we reexamine the Au_2MP_2 q1D system (formerly, M = Hg, Tl, and Pb) and extend the range of M substituents to $Pb_{0.53}Bi_{0.43}$ and Bi. Remarkably, this q1D system resists changing its highly anisotropic structure type over a range of three valence electrons per formula unit. However, at the highest valence electron count, we find that Au_2BiP_2 exhibits polymorphism: in addition to the previously reported orthorhombic phase, a slight distortion generates a closely related monoclinic structure type. Analysis of local packing tensions in the orthorhombic phase reveals strains within the $[Au_2P_2]$ framework hold open channel spaces for the chains of M atoms, which are relatively free to move as a group within the channels. Consistent with this picture, the calculated phonon dispersions show that the monoclinic distortion in Au_2BiP_2 resolves imaginary phonon frequencies seen in the orthorhombic structure type. Using DFT computations, we determine that this structural change is driven through rectifying both electronic and atomic packing frustrations. Furthermore, electronic transport measurements substantiate calculations of the band structures and density of states of these materials, which suggest that the compositions within this series can be tuned to band structure and property design.

Status: published work in Chemistry of Materials 2024, **36**, 8217

Challenges in High-Throughput Inorganic Materials Prediction and Autonomous Synthesis

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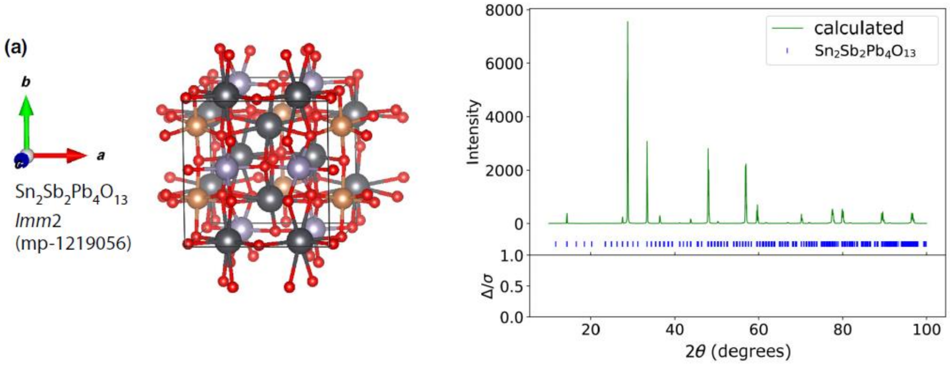
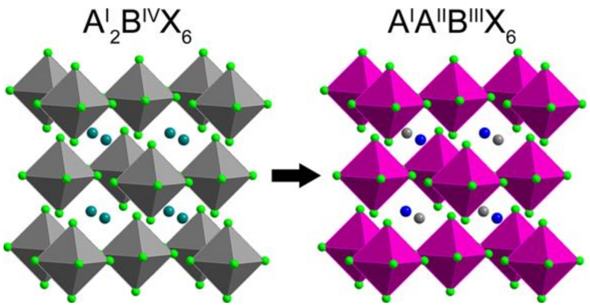


Materials discovery lays the foundation for many technological advancements. The prediction and discovery of new materials are not simple tasks. Here, we outline some basic principles of solid-state chemistry, which might help to advance both, and discuss pitfalls and challenges in materials discovery. We discuss problems that can arise in unsupervised materials discovery and hope that by addressing these, autonomous materials discovery can be brought closer to reality. We discuss 43 synthetic products and point out four common shortfalls in the analysis. We conclude that there are two important points of improvement that require future work from the community, as follows. (i) Automated Rietveld analysis of powder x-ray diffraction data is not yet reliable. (ii) We find that disorder in materials is often neglected in predictions. The predicted compounds investigated herein have all their elemental components located on distinct crystallographic positions but in reality, elements can share crystallographic sites, resulting in higher-symmetry space groups and—very often—known alloys or solid solutions. This error might be related to the difficulty of modeling disorder in a computationally economical. We highlight important issues in materials discovery, computational chemistry, and autonomous interpretation of x-ray diffraction. We discuss concepts of materials discovery from an experimentalist point of view, which we hope will be helpful for the community to further advance this important new aspect of our field.

Status: published work in PRX Enegry 2024, **3**, 011002

Expanding the Family of Magnetic Vacancy-Ordered Halide Double Perovskites

Kurt P. Lindquist, Teresa Lee, Xianghan Xu, and Robert J. Cava
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States



Vacancy-ordered halide double perovskites, with the general formula $A_2^{I}B^{IV}X_6$, can accommodate a wide variety of tetravalent B-site cations. However, few examples containing trivalent B-site cations exist, limiting the variety of magnetic cations that can comprise this structure type. Here, we incorporate divalent A-site cations to form the vacancy-ordered double perovskites $A^{I}A^{II}B^{III}Cl_6$ (A^{I} = Na, K, Rb, Cs; A^{II} = Sr, Ba; B^{III} = Ti, V, Cr, Ir) and $Ba_{1.5}B^{III}Cl_6$ (B^{III} = V, Cr). By tuning the radius of the A-site through cation substitution, we form four structure-types with these formulas, including a K_2PtCl_6-type structure, a low-temperature K_2SnCl_6-type structure, a novel derivative with ordered A^{1+}/A^{2+} cations, and a second novel derivative with ordered A-site vacancies. This structural diversity, which includes 22 unique compositions, allows us to study the effect of structure and composition on the magnetic properties of these solids, which show antiferromagnetic coupling of weak-to-moderate strength and signatures of frustrated long-range ordering. Furthermore, our studies of temperature-dependent magnetism and heat capacity reveal that the magnetic coupling strength decreases with octahedral tilting, consistent with expectations; in contrast, the coupling strength counterintuitively increases from B^{III} = Ti to Cr to V, which we speculate may be a result of competing antiferromagnetic and ferromagnetic interactions. By substituting divalent A-site cations into vacancy-ordered halide double perovskites, we further expand the already rich phase space of these structures to include magnetic trivalent transition metals and deepen our understanding of structure−magnetism relationships in metal halides.

Status: published work in Chemistry of Materials 2024, **36**, 7610

Unraveling magneto-elastoresistance in the Dirac nodal-line semi-metal ZrSiSe

J. F. Linnartz[1], A. Kool[1], J. P. Lorenz[2], C. S. A. Müller[1], M.R. van Delft[1], R. Singha[3,4], L. M. Schoop[3], N. E. Hussey[1,5], A. de Visser[2] and S. Wiedmann[1]

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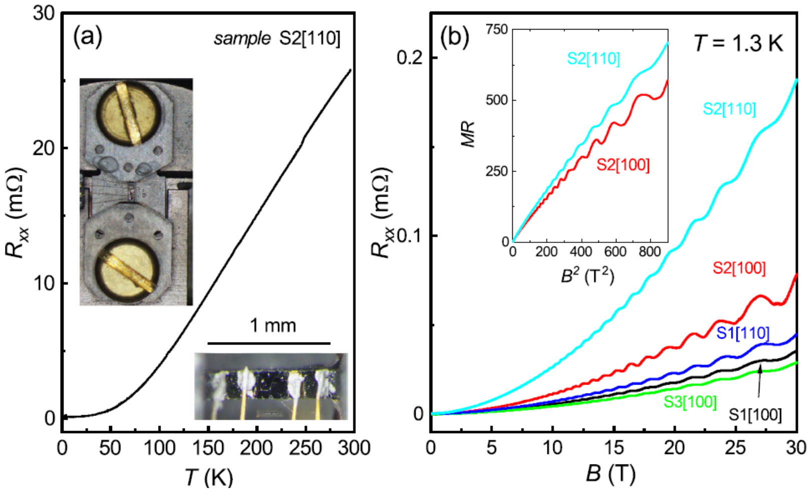

Quantum materials are often characterized by a marked sensitivity to minute changes in their physical environment, a property that can lead to new functionalities and thereby, to novel applications. One such key property is the magneto-elastoresistance (MER), the change in magnetoresistance (MR) of a metal induced by uniaxial strain. Understanding and modeling this response can prove challenging, particularly in systems with complex Fermi surfaces. Here, we present a thorough analysis of the MER in the nearly compensated Dirac nodal-line semi-metal ZrSiSe. Small amounts of strain (0.27%) lead to large changes (7%) in the MR. Subsequent analysis reveals that the MER response is driven primarily by a change in transport mobility that varies linearly with the applied strain. This study showcases how the effect of strain tuning on the electrical properties can be both qualitatively and quantitatively understood. A complementary Shubnikov-de Haas oscillation study sheds light on the root of this change in quantum mobility. Moreover, we unambiguously show that the Fermi surface consists of distinct electron and hole pockets revealed in quantum oscillation measurements originating from magnetic breakdown.

Status: published work in npj Quantum Materials 2024, **9**, 63.

Uniaxial strain effects on the Fermi surface and quantum mobility of the Dirac nodal-line semimetal ZrSiS

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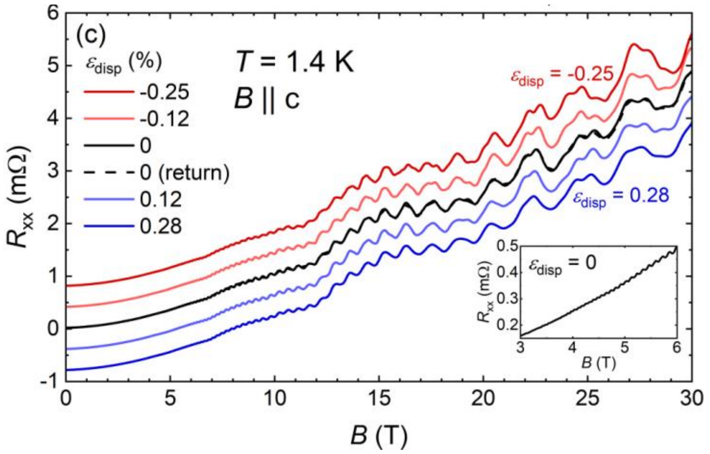

ZrSiS has been identified as an exemplary Dirac nodal-line semimetal, in which the Dirac band crossings extend along a closed loop in momentum space. Recently, the topology of the Fermi surface of ZrSiS was uncovered in great detail by quantum oscillation studies. For a magnetic field along the tetragonal c axis, a rich frequency spectrum was observed stemming from the principal electron and hole pockets and multiple magnetic breakdown orbits. In this work we use uniaxial strain as a tuning parameter for the Fermi surface and the low-energy excitations. We measure the magnetoresistance of a single crystal under tensile (up to 0.34 %) and compressive (up to −0.28 %) strain exerted along the *a* axis and in magnetic fields up to 30 T. We observe a systematic weakening of the peak structure in the Shubnikov-de Haas frequency spectrum upon changing from compressive to tensile strain. This effect may be explained by a decrease in the effective quantum mobility upon decreasing the *c/a* ratio, which is corroborated by a concurrent increase in the Dingle temperature.

Status: published work in Physical Review B 2024, **109**, 235114

Indium-Doped Crystals of $SnSe_2$

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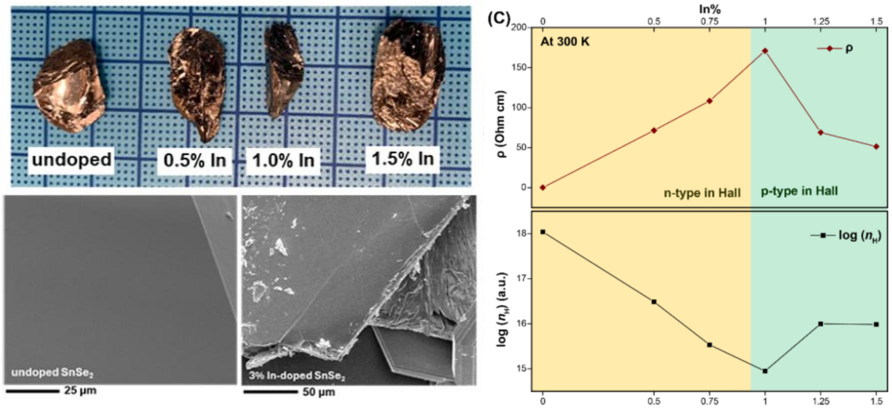

Bulk crystals of undoped and In-doped (on the order of 1%) $SnSe_2$ were synthesized using a solid-state temperature-gradient method and characterized by diffuse reflection, Raman scattering, ARPES and STM studies. An n-to-p crossover was observed as a function of the indium concentration in Hall measurements at 300 K, but the Seebeck coefficient is n-type at that temperature for all studied indium concentrations. The measured resistivity at 300 K reaches a maximum at the minimum carrier concentration. Our results suggest a multiband semiconducting nature for doped $SnSe_2$, which provides insight into the exploration of enhanced thermoelectric performance and exotic electric behavior.

Status: published work in Journal of Physical Chemistry C 2024, **128**, 11054.

A calcium aluminum rhenium sodalite with reducible rhenium in the sodalite cage

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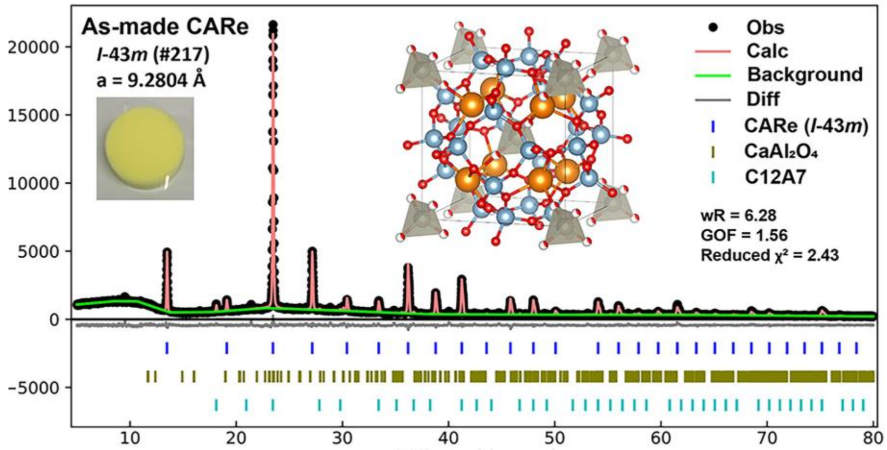

An unreported rhenium-based calcium aluminum sodalite (CARe sodalite) has been synthesized by a traditional solid-state method. The rhenium is located in the sodalite β-cage and can be reduced under 5% H_2 forming gas without breaking the cage framework. Preliminary characterizations of the structural, optical, and magnetic properties are reported.

Status: published work in MRS Communication 2024, **14**, 372

A butadiene-derived semicrystalline polyolefin with two-tiered chemical recyclability

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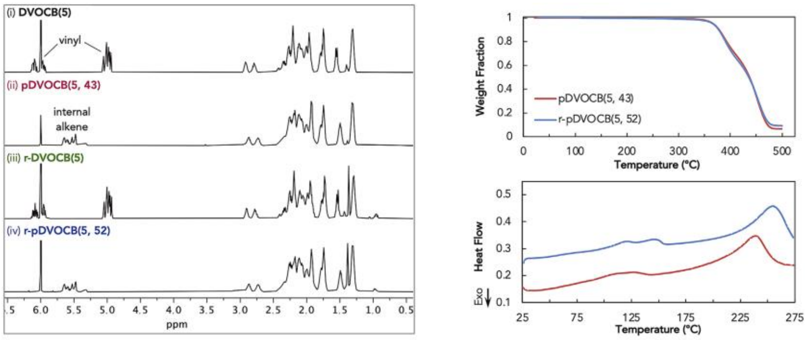

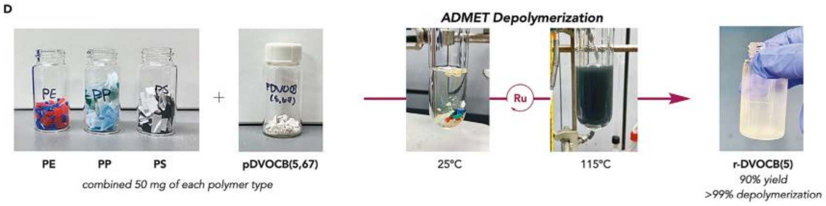

Commodity polyolefins account for the majority of plastic waste but are challenging to depolymerize or upcycle due to the high thermal and chemical stability of hydrocarbon polymer backbones. Here, we report a class of polyolefin that undergoes clean and selective chemical recycling at both the oligomeric and polymeric stages. Iron-catalyzed [2+2] cycloaddition of the monomer butadiene formed telechelic oligomers (1,n'-divinyl)-oligocyclobutane (DVOCB) that undergo deoligomerization back to butadiene. From the oligomer DVOCB, chain extension using acyclic diene metathesis (ADMET) yielded the polyolefin pDVOCB. Reverse ADMET of pDVOCB enabled full recovery of the telechelic oligomer. pDVOCB polymers are semicrystalline hydrocarbon polymers with high melting temperatures ($T_m > 230^oC$) that have excellent chemical and hydrolytic stability and comparable mechanical properties to commodity polyolefins, such as polypropylene and polyethylene. Thus, this work demonstrates a class of semicrystalline polyolefins that offers two tiers of chemical recycling.

Status: published work in Chem 2024, **10**, 698

Chemical Bonding Induces One-Dimensional Physics in Bulk Crystal $BiIr_4Se_8$

Connor J. Pollak[1], Grigorii Skorupskii[1], Martin Gutierrez-Amigo[2,3], Ratnadwip Singha[1], Joseph W. Stiles[1], Franziska Kamm[4], Florian Pielnhofer[4], N. P. Ong[5], Ion Errea[3,4,7], Maia G. Vergniory[4,8], and Leslie M. Schoop[1]

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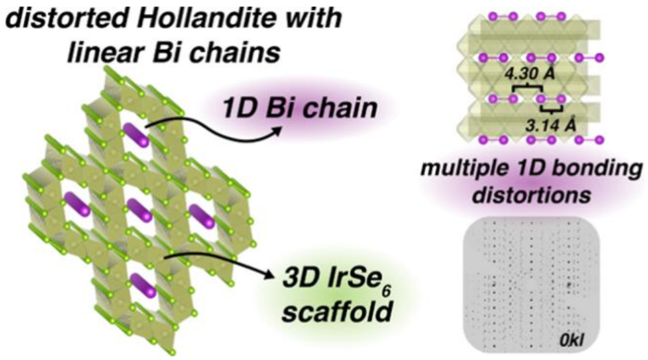

One-dimensional (1D) systems are very interesting because of the rich physics that emerges from constrained degrees of freedom. A desirable route to harness the properties therein is to grow bulk single crystals of a physically three-dimensional (3D) but electronically 1D compound. Most bulk compounds which approach the electronic 1D limit still deviate from the 1D models. In this paper, we lay out chemical concepts to realize the physics of 1D models in 3D crystals. We present $BiIr_4Se_8$, a bulk crystal consisting of linear Bi^{2+} chains within a scaffolding of $IrSe_6$ octahedra, as a prime example. Through crystal structure analysis, density functional theory calculations, X-ray diffraction, and physical property measurements, we demonstrate the unique 1D electronic configuration in $BiIr_4Se_8$. This configuration at ambient temperature is a gapped Su-Schriefer-Heeger system, generated by way of a canonical Peierls distortion involving Bi dimerization that relieves instabilities in a 1D metallic state. At 190 K, an additional 1D charge density wave distortion emerges, which affects the Peierls distortion. The experimental evidence validates our design principles and distinguishes $BiIr_4Se_8$ among other quasi-1D bulk compounds. We thus show that it is possible to realize unique electronically 1D materials applying chemical concepts.

Status: published work in J. Am. Chem. Soc. 2024, **146**, 6784.

Synthesis and Stability Phase Diagram of Topological Semimetal Family $LnSb_xTe_{2-x-\delta}$

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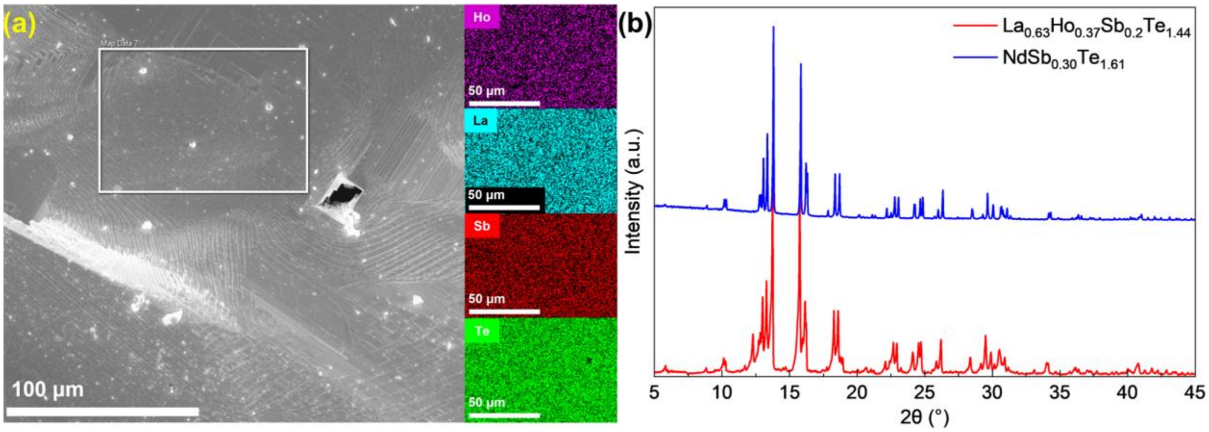

The solid solution $LnSb_xTe_{2-x-\delta}$ (Ln = lanthanide) is a family of square-net topological semimetals that exhibit tunable charge density wave (CDW) distortions and band filling dependent on x, offering broad opportunities to examine the interplay of topological electronic states, CDW, and magnetism. While several Ln series have been characterized, gaps in the literature remain, inviting a systematic survey of the remaining composition space that is synthetically accessible. We present our efforts to synthesize $LnSb_xTe_{2-x-\delta}$ across the remaining lanthanides via chemical vapor transport. Compiling our results with the reported literature, we generate a stability phase diagram across the ranges of Ln and x. We find a stability boundary for intermediate x beyond Tb, while x = 1 and x = 0 can be isolated up to Ho and Dy, respectively. SEM and XRD analyses of unsuccessful reactions indicated the formation of several stable binary phases. The presence of structurally related $LnTe_3$ in samples suggests that stability is limited by the size of Ln, due to increasing compressive strain along the layer stacking axis with decreasing size. Finally, we demonstrate that late Ln can be stabilized in $LnSb_xTe_{2-x-\delta}$ via substitution into larger Ln members, synthesizing $La_{1-y}Ho_ySb_xTe_{2-x-\delta}$ as a proof of concept.

Status: published work in Chemistry of Materials 2024, **36**, 11873.

Anisotropic and High-Mobility Electronic Transport in a Quasi 2D Antiferromagnet $NdSb_2$

Ratnadwip Singha[1], Fang Yuan[1], Scott B. Lee[1], Graciela V. Villalpando[1], Guangming Cheng[2], Birender Singh[3], Suchismita Sarker[4], Nan Yao[2], Kenneth S. Burch[3], and Leslie M. Schoop[1]
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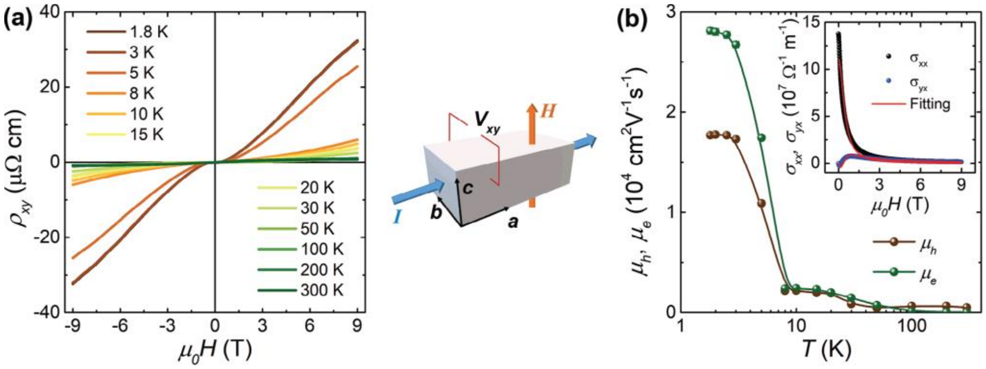

Advancements in low-dimensional functional device technology heavily rely on the discovery of suitable materials which have interesting physical properties as well as can be exfoliated down to the 2D limit. Exfoliable high-mobility magnets are one such class of materials that, not due to lack of effort, has been limited to only a handful of options. So far, most of the attention has been focused on the van der Waals (vdW) systems. However, even within the non-vdW, layered materials, it is possible to find all these desirable features. Using chemical reasoning, it is found that $NdSb_2$ is an ideal example. Even with a relatively small interlayer distance, this material can be exfoliated down to few layers. $NdSb_2$ has an antiferromagnetic ground state with a quasi 2D spin arrangement. The bulk crystals show a very large, non-saturating magnetoresistance along with highly anisotropic electronic transport properties. It is confirmed that this anisotropy originates from the 2D Fermi pockets which also imply a rather quasi 2D confinement of the charge carrier density. Both electron and hole-type carriers show very high mobilities. The possible non-collinear spin arrangement also results in an anomalous Hall effect.

Status: published work in Adv. Funct. Mater. 2024, **34**, 2308733

Designing giant Hall response in layered topological semimetals

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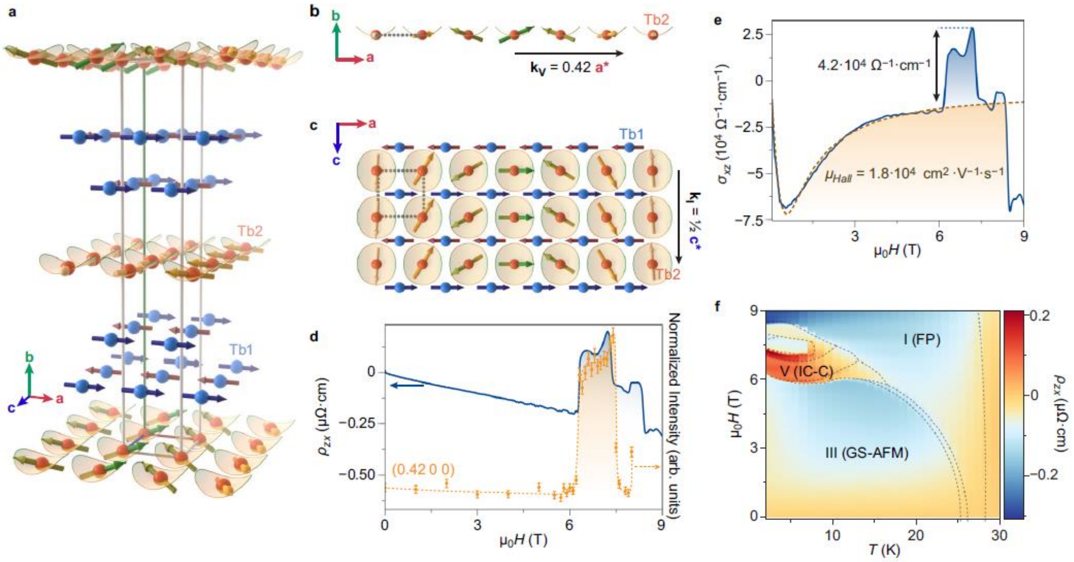

Noncoplanar magnets are excellent candidates for spintronics. However, such materials are difficult to find, and even more so to intentionally design. Here, we report a chemical design strategy that allows us to find a series of noncoplanar magnets – Ln_3Sn_7 (Ln = Dy, Tb) – by targeting layered materials that have decoupled magnetic sublattices with dissimilar single-ion anisotropies and combining those with a square-net topological semimetal sublattice. Ln3Sn7 shows high carrier mobilities upwards of 17,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$, and hosts noncoplanar magnetic order. This results in a giant Hall response with an anomalous Hall angle of 0.17 and Hall conductivity of over 42,000 $\Omega^{-1} \cdot cm^{-1}$ – a value over an order of magnitude larger than the established benchmarks in $Co_3Sn_2S_2$ and Fe thin films.

Status: published work in Nature Communications 2024, **15**, 10112

Role of Cr Redox and Dynamics in Electrochemical Cycling of $H_xCrS_{2-\delta}$

Joseph W. Stiles[1,2], Brianna Hoff[1], Maria C. Curria[3], Scott B. Lee[1], Fang Yuan[1], Guangming Cheng[2], Fatmagül Katmer[1], Grigorii Skorupskii[1], Jiaze Xie[1], Josh Leeman[4], Nan Yao[2], Claire E. White[3,5], Craig B. Arnold[2,6], and Leslie M. Schoop[1,2]

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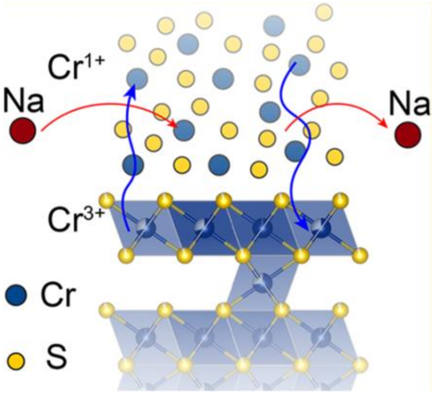

$H_xCrS_{2-\delta}$ is produced by the proton exchange of $NaCrS_2$ and features alternating layers of crystalline and amorphous lamella. It exhibits superior performance as a Na-ion battery electrode compared with its parent compound with faster Na^+ diffusion, higher capacity, and better cyclability. This work explores the nature of the unique biphasic structure of $H_xCrS_{2-\delta}$ using both powder and single-crystal X-ray diffraction, as well as electron microscopy. Additionally, ex situ characterizations using X-ray absorption spectroscopy, X-ray total scattering, and magnetometry are employed to study the mechanism by which this superiority arises. These reveal that migration of Cr does not impede battery performance and may, in fact, be crucial to the observed performance improvements. These studies show that Cr redox is not only possible but abundant in $H_xCrS_{2-\delta}$ while accessing it in $NaCrS_2$ at lower voltages results in irreversible structural transitions that limit cycling stability. Additionally, we highlight the potential of biphasic structures such as $H_xCrS_{2-\delta}$ to enable high performance in energy storage electrodes.

Status: published work in Chemistry of Materials 2024, **36**, 9469

Freestanding monolayer CrOCl through chemical exfoliation

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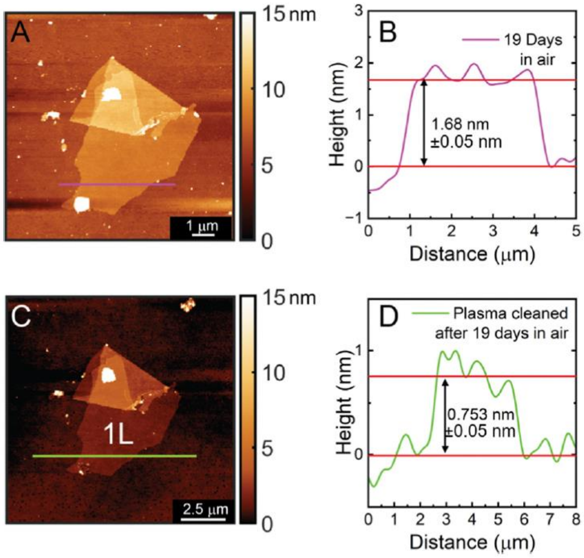

Magnetic two-dimensional (2D) materials are a unique class of quantum materials that can exhibit interesting magnetic phenomena, such as layer-dependent magnetism. The most significant barrier to 2D magnet discovery and study lies in our ability to exfoliate materials down to the monolayer limit. Therefore designing exfoliation methods that produce clean, monolayer sheets is crucial for the growth of 2D material research. In this work, we develop a facile chemical exfoliation method using lithium naphthalenide for obtaining 2D nanosheets of magnetic van der Waals material CrOCl. Using our optimized method, we obtain freestanding monolayers of CrOCl, with the thinnest measured height to date. We also provide magnetic characterization of bulk, intercalated intermediate, and nanosheet pellet CrOCl, showing that exfoliated nanosheets of CrOCl exhibit magnetic order. The results of this study highlight the tunability of the chemical exfoliation method, along with providing a simple method for obtaining 2D CrOCl.

Status: published work in Nanoscale Horizons 2024, **9**, 1766.

Accessing bands with extended quantum metric in kagome $Cs_2Ni_3S_4$ through soft chemical processing

Graciela Villalpando[1], Milena Jovanovic[1,2], Brianna Hoff[1], Yi Jiang[3], Ratnadwip Singha[1,4], Fang Yuan[1], Haoyu Hu[3], Dumitru Călugăru[5], Nitish Mathur[1], Jason F. Khoury[1,6], Stephanie Dulovic[1], Birender Singh[7], Vincent M. Plisson[7], Connor J. Pollak[1], Jaime M. Moya[1], Kenneth S. Burch[7], B. Andrei Bernevig[3,5,8], Leslie M. Schoop[1]

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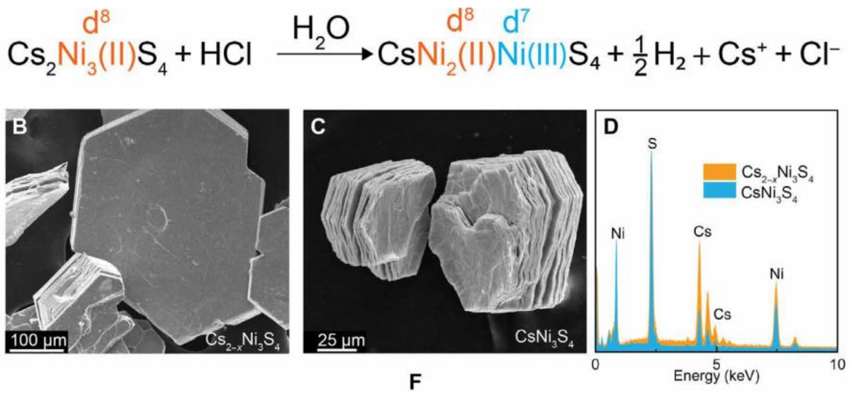

Flat bands that do not merely arise from weak interactions can produce exotic physical properties, such as superconductivity or correlated many-body effects. The quantum metric can differentiate whether flat bands will result in correlated physics or are merely dangling bonds. A potential avenue for achieving correlated flat bands involves leveraging geometrical constraints within specific lattice structures, such as the kagome lattice; however, materials are often more complex. In these cases, quantum geometry becomes a powerful indicator of the nature of bands with small dispersions. We present a simple, soft-chemical processing route to access a flat band with an extended quantum metric below the Fermi level. By oxidizing Ni-kagome material $Cs_2Ni_3S_4$ to $CsNi_3S_4$, we see a two orders of magnitude drop in the room temperature resistance. However, $CsNi_3S_4$ is still insulating, with no evidence of a phase transition. Using experimental data, density functional theory calculations, and symmetry analysis, our results suggest the emergence of a correlated insulating state of unknown origin.

Status: published work in Science Advances 2024, **10**, eadl1103.

Friends not Foes: Exfoliation of Non-van der Waals Materials

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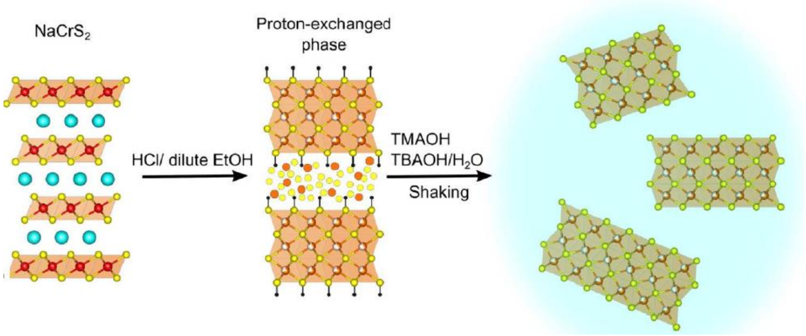

Two-dimensional materials have been a focus of study for decades, resulting in the development of a library of nanosheets made by a variety of methods. However, many of these atomically thin materials are exfoliated from van der Waals (vdW) compounds, which inherently have weaker bonding between layers in the bulk crystal. A particular class of non-vdW compounds that may be amenable to exfoliation are the ionically bonded layered materials, which have alkali ions intercalated between the layers. Although initially they may have been more difficult to exfoliate due to a lack of methodology beyond mechanical exfoliation, many synthesis techniques have been developed that have been used successfully in exfoliating non-vdW materials. In fact, as we will show, in some cases it has even proven to be advantageous to start the exfoliation from a non-vdW compound. The method we will highlight here is chemical exfoliation. Encompassing many methods, such as acid/base reactions, solvent reactions, and oxidative extractions, chemical exfoliation can be tailored to the delamination of non-vdW materials. To exemplify this, we will discuss our group's work on the synthesis of a 1T'-WS_2 monolayer ink. By starting with $K_{0.5}WS_2$, the exfoliated 1T'-WS_2 nanosheets obtained were larger and more uniform in thickness than those from previous syntheses beginning with vdW materials. We will also show how soft chemical methods can be used to make new phases from existing compounds, such as H_xCrS_2 from $NaCrS_2$. This material was found to have alternating amorphous and crystalline layersFrom these and other examples, we will see how chemical exfoliation of non-vdW materials compares to other methods, as well as how this technique can be further extended to known compounds that can be deintercalated electrochemically and to quasi-one-dimensional crystals.

Status: published work in Accounts of Chemical Research 2024, **57**, 2490.

Chemical exfoliation of 1-dimensional antiferromagnetic nanoribbons from a non-van der Waals material

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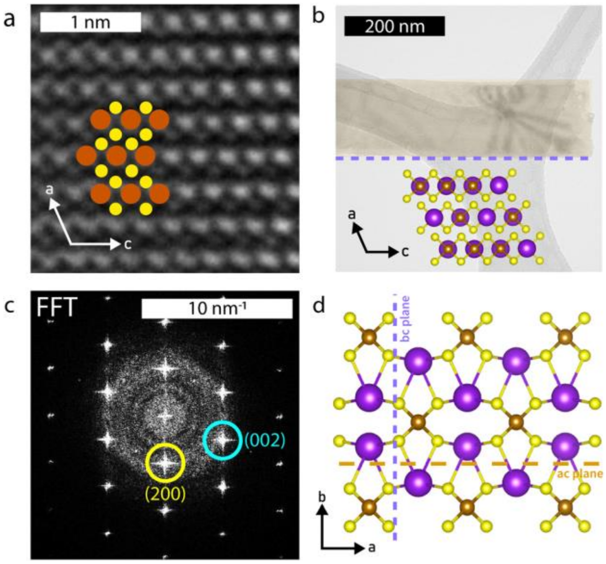

As the demand for increasingly varied types of 1-dimensional (1D) materials grows, there is a greater need for new methods to synthesize these types of materials in a simple and scalable way. Chemical exfoliation is commonly used to make 2-dimensional (2D) materials, often in a way that is both straightforward and suitable for making larger quantities, yet this method has thus far been underutilized for synthesizing 1D materials. In the few instances when chemical exfoliation has been used to make 1D materials, the starting compound has been a van der Waals material, thus excluding any structures without these weak bonds inherently present. We demonstrate here that ionically bonded crystals can also be chemically exfoliated to 1D structures by choosing KFeS2 as an example. Using chemical exfoliation, antiferromagnetic 1D nanoribbons can be yielded in a single step. The nanoribbons are crystalline and closely resemble the parent compound both in structure and in intrinsic antiferromagnetism. The facile chemical exfoliation of an ionically bonded crystal shown in this work opens up opportunities for the synthesis of both magnetic and non-magnetic 1D nanomaterials from a greater variety of starting structures.

Status: published work in Nanoscale Horizons 2024, **9**, 479.

Rotator Phases in Chemically Recyclable Oligocyclobutanes

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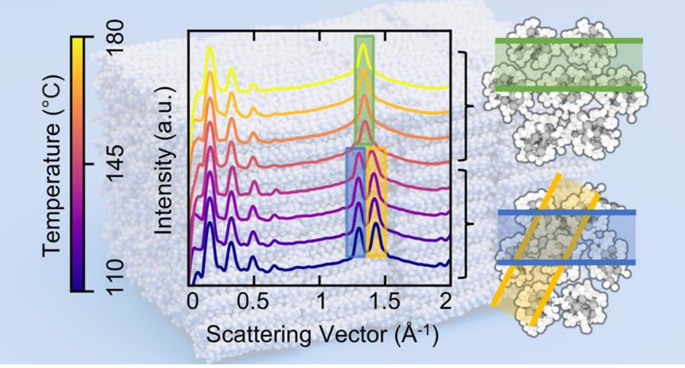

Rotator phases are rotationally disordered yet crystalline stable states found in many materials. The presence of a rotator phase leads to unique properties that influence processing methods and offer potential applications in areas such as thermal energy storage, lubrication, and sensing. Recently, a novel family of chemically recyclable oligomers, (1,n′-divinyl)-oligocyclobutane (DVOCB(*n*)), has shown evidence of rotator phases. This study combines experimental characterization and molecular dynamics simulations to confirm and elucidate the rotator phases in DVOCB(*n*). Compared with well-studied n-alkanes, DVOCB(*n*) exhibits distinct structural, thermodynamic, and dynamical characteristics. The crystal-torotator phase transition of DVOCB(*n*) involves a shift from stretched to isotropic hexagonal lamellar packing, captured by a rotational order parameter tracking local chain orientations orthogonal to the chain axis. Unlike *n*-alkanes, where rotational relaxation times are constant and long in the crystal phase before dropping dramatically during the crystal-to-rotator phase transition, relaxation times decrease more gradually upon heating in DVOCB(*n*), including continuously throughout the transition. This behavior is attributed to its unique enchained-ring architecture, which allows for semi-independent rotation of chain segments that promotes overall rotational disorder. This work provides a fundamental understanding of rotator phases in DVOCB(*n*) and highlights differences from those of conventional materials. The analyses and insights herein will inform future studies and applications of DVOCB(*n*) as well as other materials with rotator phases.

Status: published work in Chemistry of Materials 2024, **36**, 11596.

Department of Electrical and Computer Engineering

Design and fabrication of robust hybrid photonic crystal cavities

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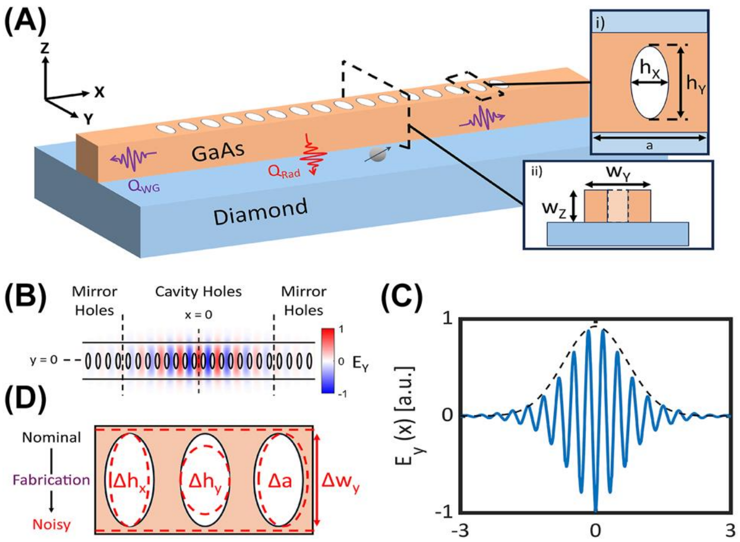

Heterogeneously integrated hybrid photonic crystal cavities enable strong light–matter interactions with solid state, optically addressable quantum memories. A key challenge to realizing high quality factor (Q) hybrid photonic crystals is the reduced index contrast on the substrate compared to suspended devices in air. This challenge is particularly acute for color centers in diamond because of diamond's high refractive index, which leads to increased scattering loss into the substrate. Here, we develop a design methodology for hybrid photonic crystals utilizing a detailed understanding of substrate-mediated loss, which incorporates sensitivity to fabrication errors as a critical parameter. Using this methodology, we design robust, high-Q, GaAs-on-diamond photonic crystal cavities, and by optimizing our fabrication procedure, we experimentally realize cavities with Q approaching 30,000 at a resonance wavelength of 955 nm.

Status: published work in Nanophotonics 2024, aop

Mitigating Iodine Diffusion by a MoO$_3$−Organic Composite Hole Transport Layer for Stable Perovskite Solar Cells

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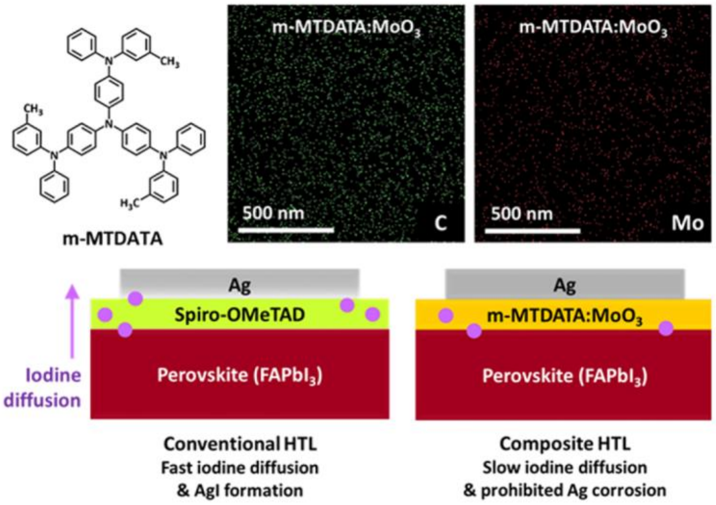

Halide perovskite solar cells (PSCs) exhibit commercialization potential, but long-term stability still must be addressed. Among various products of perovskite decomposition, iodine species are of considerable concern due to their high vapor pressure and corrosive nature. To address this, a small-molecule hole transport layer (HTL), 4,4′,4″-tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA), is used; mixing it with molybdenum trioxide (MoO$_3$) p-dopes the layer and slows iodine permeation. We demonstrate that m-MTDATA:MoO$_3$ HTLs employed in PSCs improve stability under both thermal and voltage bias stress compared to devices with a conventional doped 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD) HTL.

Status: published work in ACS Energy Letters 2023, **8**, 4984

Iodine Modulates the MACl-Assisted Growth of FAPbI$_3$ for High Efficiency Perovskite Solar Cells

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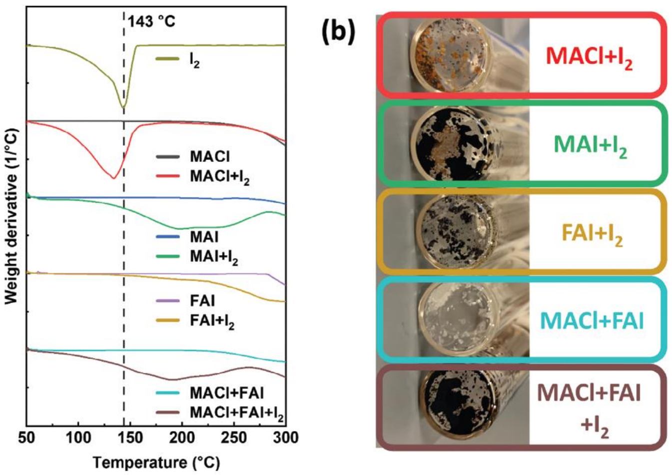

The preferential growth of α-phase formamidinium perovskite (α-FAPbI$_3$) at low temperatures can be achieved with the incorporation of chloride-based additives, with methylammonium chloride (MACl) being the most common example. However, compared to other less-volatile chloride additives, MACl only remains in the growing perovskite film for a short time before evaporating during annealing. In addition, evaporation of MACl as methylamine (MA^0) and HCl can introduce a side reaction between MA^0 and formamidinium (FA), undermining the compositional purity and phase stability of α-FAPbI$_3$. In this study, it is demonstrated that addition of iodine (I$_2$) into the FAPbI$_3$ precursor solution containing MACl suppresses the MA-FA side reaction during annealing. Additionally, MACl evaporation is delayed owing to strong interaction with triiodide. The added I$_2$ facilitates spontaneous growth of α-FAPbI$_3$ prior to annealing, with an improved bottom morphology. Perovskite solar cells derived from an I$_2$-incorporated solution deliver a champion power conversion efficiency of 25.2%.

Status: published work in Advanced Energy Materials 2024, **14**, 2400500

Evidence for Topological Protection Derived from Six-Flux Composite Fermions

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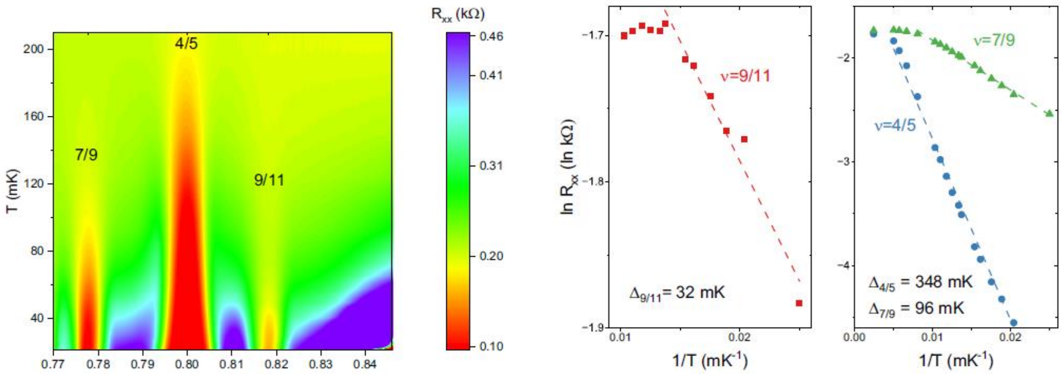

The composite fermion theory opened a new chapter in understanding many-body correlations through the formation of emergent particles. The formation of two-flux and four-flux composite fermions is well established. While there are limited data linked to the formation of six-flux composite fermions, topological protection associated with them is conspicuously lacking. Here we report evidence for the formation of a quantized and gapped fractional quantum Hall state at the filling factor $\nu = 9/11$, which we associate with the formation of six-flux composite fermions. Our result provides evidence for the most intricate composite fermion with six fluxes and expands the already diverse family of highly correlated topological phases with a new member that cannot be characterized by correlations present in other known members. Our observations pave the way towards the study of higher order correlations in the fractional quantum Hall regime.

Status: published work in Nature Communications 2024, **15**, 1461

Discovery of Crystallizable Organic Semiconductors with Machine Learning

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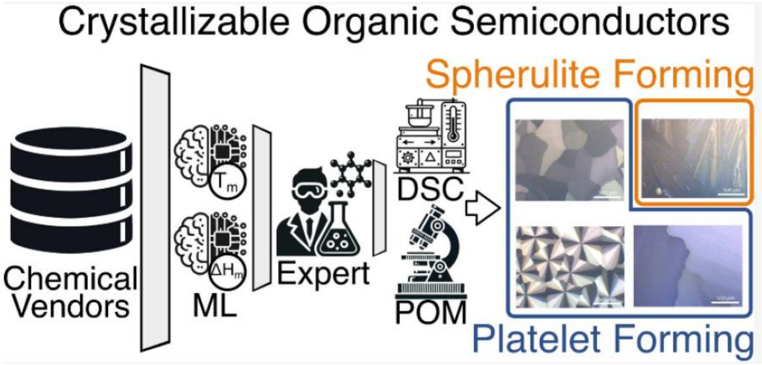

Crystalline organic semiconductors are known to have improved charge carrier mobility and exciton diffusion length in comparison to their amorphous counterparts. Certain organic molecular thin films can be transitioned from initially prepared amorphous layers to large-scale crystalline films via abrupt thermal annealing. Ideally, these films crystallize as platelets with long-range-ordered domains on the scale of tens to hundreds of microns. However, other organic molecular thin films may instead crystallize as spherulites or resist crystallization entirely. Organic molecules that have the capability of transforming into a platelet morphology feature both high melting point (T_m) and crystallization driving force (ΔG_c). In this work, we employed machine learning (ML) to identify candidate organic materials with the potential to crystallize into platelets by estimating the aforementioned thermal properties. Six organic molecules identified by the ML algorithm were experimentally evaluated; three crystallized as platelets, one crystallized as a spherulite, and two resisted thin film crystallization. These results demonstrate a successful application of ML in the scope of predicting thermal properties of organic molecules and reinforce the principles of T_m and ΔG_c as metrics that aid in predicting the crystallization behavior of organic thin films.

Status: published work in J. Am. Chem. Soc. 2024, **146**, 21583

Flat-band localization and interaction-induced delocalization of photons

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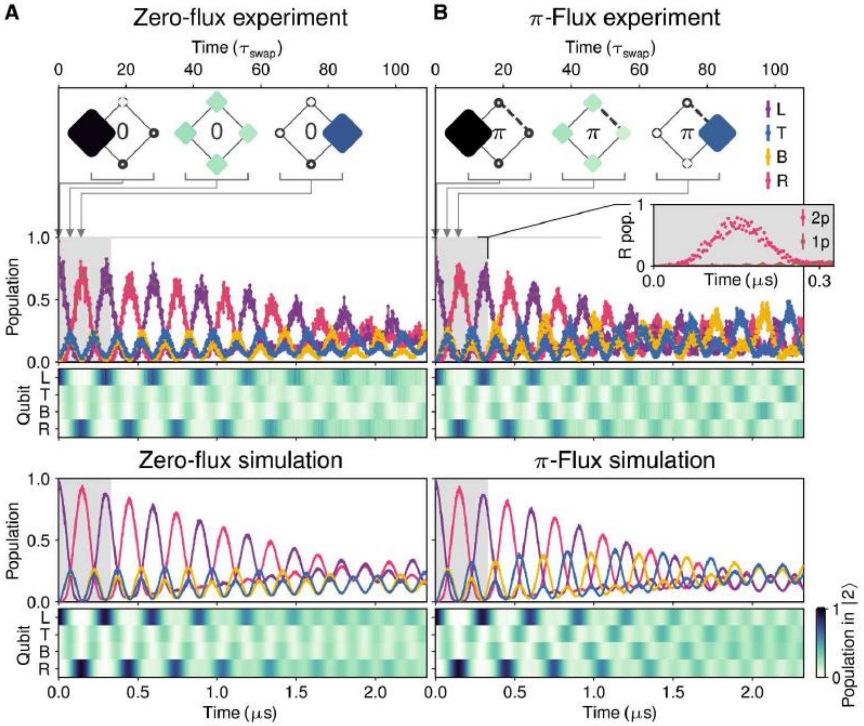

Lattices with dispersionless, or flat, energy bands have attracted substantial interest in part due to the strong dependence of particle dynamics on interactions. Using superconducting circuits, we experimentally study the dynamics of one and two particles in a single plaquette of a lattice whose band structure consists entirely of flat bands. We first observe strictly localized dynamics of a single particle, the hallmark of all-bands-flat physics. Upon initializing two particles on the same site, we see an interaction-enabled delocalized walk across the plaquette. We further find localization in Fock space for two particles initialized on opposite sides of the plaquette. These results mark the first experimental observation of a quantum walk that becomes delocalized due to interactions and establishes a key building block in superconducting circuits for studying flat-band dynamics with strong interactions.

Status: published work in Science Advances 2024, **9**, eadj7195

Diamond surface functionalization via visible light–driven C–H activation for nanoscale quantum sensing

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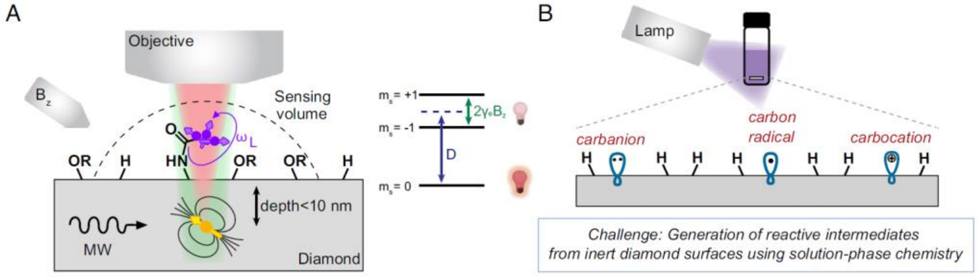

Nitrogen-vacancy (NV) centers in diamond are a promising platform for nanoscale NMR sensing. Despite significant progress in using NV centers to detect nuclear spins down to the single spin level, NV-based spectroscopy of individual, intact, arbitrary target molecules remains elusive. Such sensing requires that target molecules are immobilized within nanometers of NV centers with long spin coherence. In this work, we report a versatile strategy to directly functionalize C–H bonds on single-crystal diamond surfaces under ambient conditions using visible light, forming C–F, C–Cl, C–S, and C–N bonds at the surface. This method is compatible with NV centers within 10 nm of the surface with spin coherence times comparable to the state of the art. As a proof-of-principle demonstration, we use shallow ensembles of NV centers to detect nuclear spins from surface-bound functional groups. Our approach to surface functionalization opens the door to deploying NV centers as a tool for chemical sensing and single-molecule spectroscopy.

Status: published work in Proc. Nat. Acad. Sci. 2024, **121**, e2316032121

Nanoscale diamond quantum sensors for many-body physics

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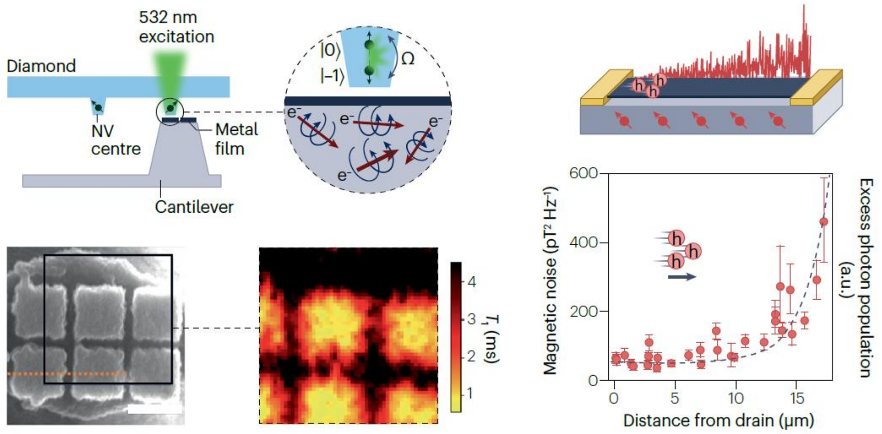

Nitrogen vacancy (NV) centre quantum sensors provide unique opportunities in studying condensed matter systems, as they are quantitative, non-invasive, physically robust, offer nanoscale resolution and may be used across a wide range of temperatures. These properties have been exploited in recent years to obtain nanoscale resolution measurements of static magnetic fields arising from spin order and current flow in condensed matter systems. Compared with other nanoscale magnetic-field sensors, NV centers have the advantage that they can probe quantities that go beyond average magnetic fields. Leveraging techniques from magnetic resonance, NV centers can perform high-precision noise sensing and have given access to diverse systems, such as fluctuating electrical currents in simple metals and graphene, as well as magnetic dynamics in yttrium iron garnet. In this Technical Review, we provide an overview of NV sensing platforms and modalities and discuss the connections between specific NV measurements and important physical characteristics in condensed matter, such as correlation functions and order parameters, that are inaccessible by other techniques. We conclude with our perspectives on the new insights that may be opened up by NV sensing in condensed matter.

Status: published work in Nature Reviews Physics 2024, **6**, 753

Correlating Halide Segregation with Photolysis in Mixed-Halide Perovskites via *In situ* Opto-gravimetric Analysis

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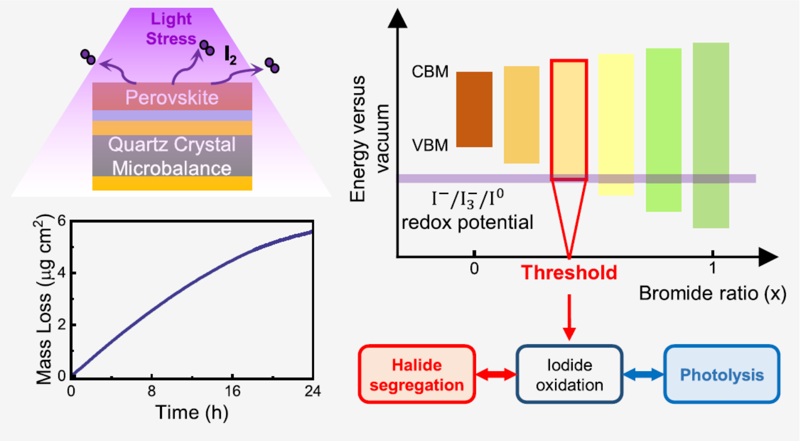

Halide oxidation plays a fundamental role in halide segregation and the degradation of halide perovskites, yet quantitative measurement of halide oxidation in solid-state perovskite samples remains challenging. Herein, we demonstrate that in situ opto-gravimetric measurements based on a quartz crystal microbalance can quantify the photolysis kinetics of solid-state perovskites. By investigating a series of mixed bromide/iodide perovskites with varying halide ratios, we demonstrate identical compositional thresholds ($x \sim 0.4$ in the $CsPb(Br_xI_{1-x})_3$ system) for iodide oxidation, light-induced halide segregation, and photolysis. Our findings reveal the correlation between these light-induced instabilities and unambiguously explain the photolysis mechanism of mixed-halide perovskites. We also show that photolysis renders the perovskite film more n-type without involving lead reduction. This study introduces a powerful methodology for quantitatively analyzing the mass loss kinetics of halide perovskites under both practical operational and accelerated aging conditions, offering deeper insights into the mechanisms of perovskite degradation.

Status: published work in J. Am. Chem. Soc. 2024, **146**, 33368.

Pseudospin polarization of composite fermions under uniaxial strain

Shuai Yuan[1], Jiaojie Yan[1,2], Ke Huang[1,3], Zhimou Chen[1], Haoran Fan[1], L. N. Pfeiffer[4], K. W. West[4], Yang Liu[1], and Xi Lin,[1,5,6]

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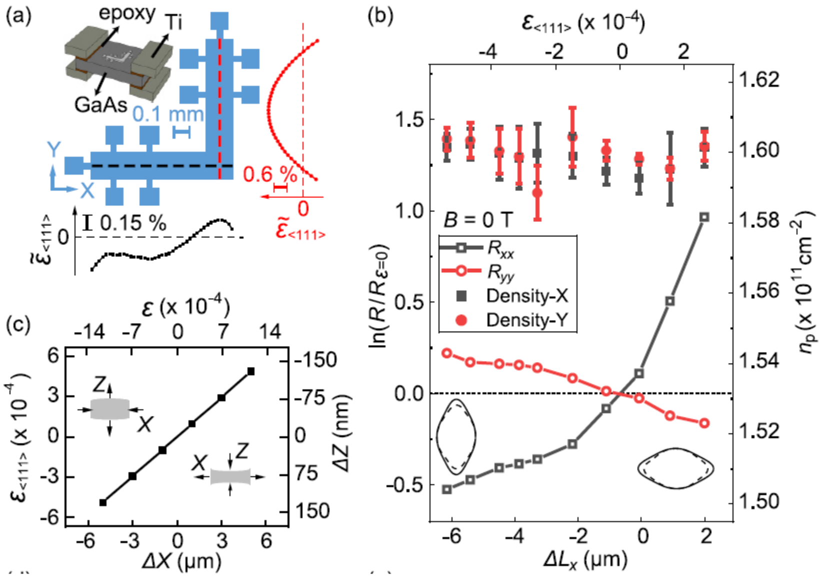

A two-dimensional system with extra degrees of freedom, such as spin and valley, is of great interest in the study of quantum phase transitions. The critical condition when a transition between different multicomponent fractional quantum Hall states appears is one of the very few junctions for many-body problems between theoretical calculations and experiments. In this work, we present that uniaxial strain induces pseudospin transitions of composite fermions in a two-dimensional hole gas. Determined from transport behavior, strain along ‹111› effectively changes pseudospin energy levels. We deduce that diagonal strain dominates these variations. Our experiment provides a wedge for manipulating two-dimensional interacting systems mechanically.

Status: published work in Physical Review B 2024, **109**, L081110.

Evolution of the Electronic and Excitonic Properties in 2D Ruddlesden–Popper Perovskites Induced by Bifunctional Ligands

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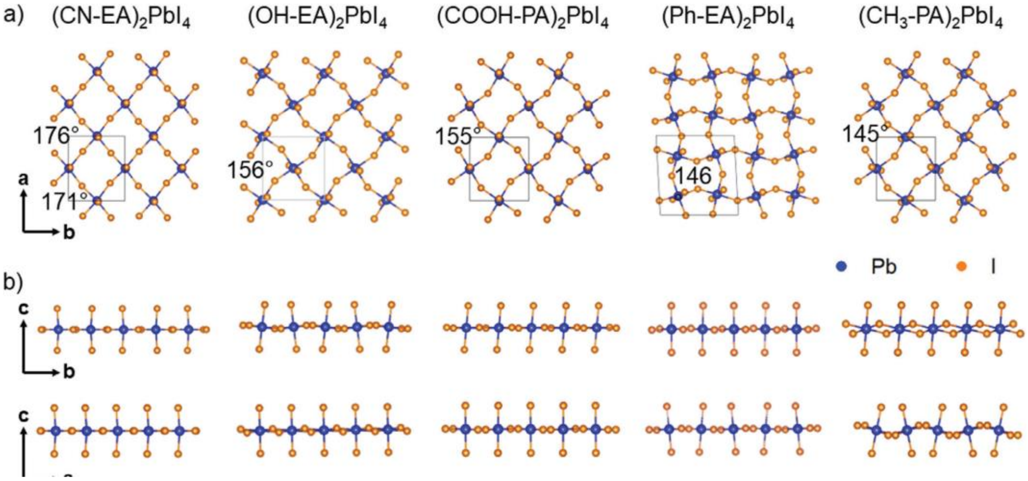

2D Ruddlesden–Popper metal-halide perovskites exhibit structural diversity due to a variety of choices of organic ligands. Incorporating bifunctional ligands in such materials is particularly intriguing since it can result in novel electronic properties and functions. However, an in-depth understanding of the effects of bifunctional ligands on perovskite structures is still lacking. Here, n = 1 2D perovskites built with organic ligands containing -CN, -OH, -COOH, -phenyl (Ph), and -CH_3 functional groups are investigated using ultraviolet and inverse photoemission spectroscopies, density functional theory calculations, and tight-binding model analyses. The experimentally determined electronic gaps of the -CN, -COOH, -Ph, and CH_3 based perovskites exhibit a strong correlation with the in-plane Pb-I-Pb bond angle, while the -OH based perovskite deviates from the linear trend. These results highlight the complex and diverse impacts of organic ligands on electronic properties, especially in terms of the involvement of strong interlayer electronic coupling. The impact of the bifunctional ligands on the evolution of the exciton binding energy is also addressed.

Status: published work in Advanced Energy Materials 2024, **14**, 2304345.

Department of Geosciences

Shallow carbonate geochemistry in the Bahamas since the last interglacial period

Stacey Edmonsond[1,2], Matthew D. Nadeau[1], Andrew C. Turner[4], Ziman Wu[4], Emily C. Geyman[1,5], Anne-Sofie C. Ahma[2], Blake Dyer[2], Sergey Oleynik[1], David McGee[3], Daniel A. Stolper[4], John A. Higgins[1], and Adam C. Maloof[1]

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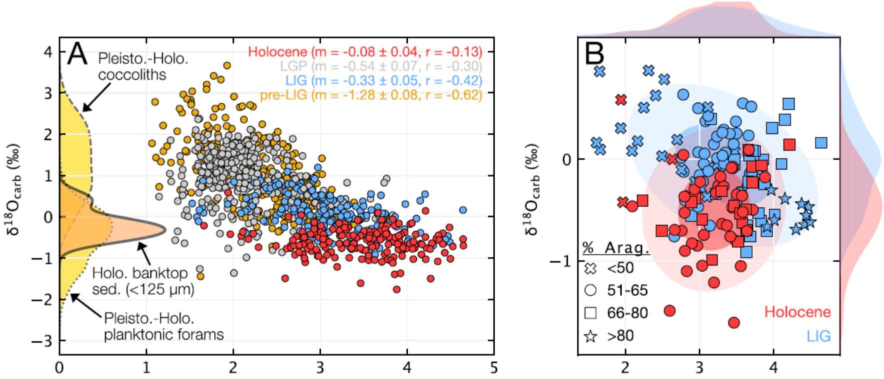

The carbon isotope composition (δ^{13}C) of ancient shallow-water carbonates frequently is used to reconstruct changes to Earth's global carbon cycle. However, previous work demonstrates that local banktop processes also exert an important control on shallow carbonate δ^{13}C as well as other isotope systems like δ^{18}O. To effectively interpret ancient δ^{13}C records, we must understand how both global carbon cycle perturbations and changes to local conditions are translated to the stratigraphic record. Shallow carbonate strata from the most recent Pleistocene glacial cycles present an opportunity to begin untangling signals of global and local processes. We study 21 short piston cores from around Bahamian platforms to quantify differences in banktop production and geochemistry. We show that mud production persists on the periplatformal slopes during the last glacial period. In contrast, Holocene and LIG carbonates show no evidence of post-depositional alteration and offer the chance to study differences in δ^{13}C and δ^{18}O between interglacials. We find that while the δ^{13}C of aragonite mud is the same during the Holocene and LIG, the LIG carbonate factory may have delivered more aragonite mud to the periplatform. In addition, the mean δ^{18}O of this mud is elevated compared to the Holocene. We posit that these differences are caused by changes to regional climate and LIG surface conditions.

Status: published work in Earth and Planetary Sciences Letters 2024, **627**, 118566

Department of Molecular Biology

Structure of a membrane tethering complex incorporating multiple SNAREs

Kevin A. DAmico, Abigail E. Stanton, Jaden D. Shirkey, Sophie M. Travis, Philip D. Jeffrey and Frederick M. Hughson
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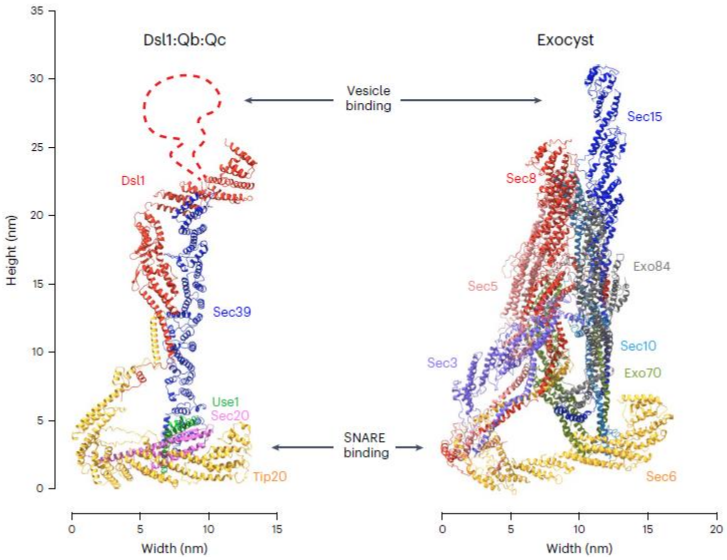

Most membrane fusion reactions in eukaryotic cells are mediated by multisubunit tethering complexes (MTCs) and SNARE proteins. MTCs are much larger than SNAREs and are thought to mediate the initial attachment of two membranes. Complementary SNAREs then form membrane-bridging complexes whose assembly draws the membranes together for fusion. Here we present a cryo-electron microscopy structure of the simplest known MTC, the 255-kDa Dsl1 complex of *Saccharomyces cerevisiae*, bound to the two SNAREs that anchor it to the endoplasmic reticulum. N-terminal domains of the SNAREs form an integral part of the structure, stabilizing a Dsl1 complex configuration with unexpected similarities to the 850-kDa exocyst MTC. The structure of the SNARE-anchored Dsl1 complex and its comparison with exocyst reveal what are likely to be common principles underlying MTC function. Our structure also implies that tethers and SNAREs can work together as a single integrated machine.

Status: published work in Nature Structural & Molecular Biology 2024, **31**, 246

SAGA1 and MITH1 produce matrix-traversing membranes in the CO$_2$-fixing pyrenoid

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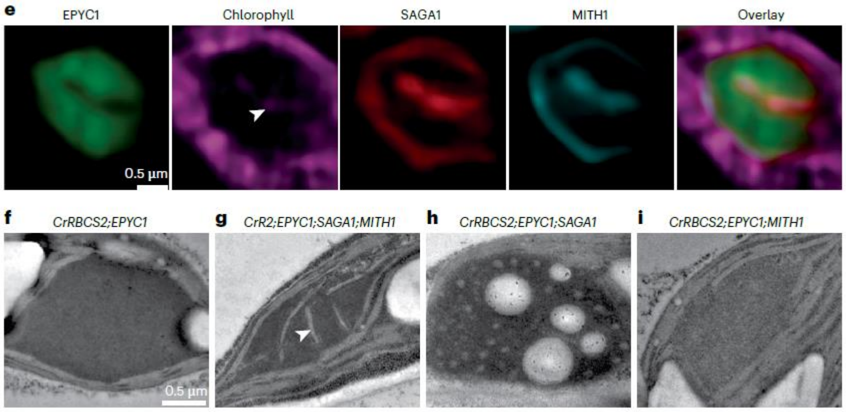

Approximately one-third of global CO$_2$ assimilation is performed by the pyrenoid. Specialized pyrenoid-traversing membranes are hypothesized to drive CO$_2$ assimilation in the pyrenoid by delivering concentrated CO$_2$, but how these membranes are made to traverse the pyrenoid matrix remains unknown. Here we show that proteins SAGA1 and MITH1 cause membranes to traverse the pyrenoid matrix in the model alga *Chlamydomonas reinhardtii*. Mutants deficient in SAGA1 or MITH1 lack matrix-traversing membranes and exhibit growth defects under CO$_2$-limiting conditions. Expression of SAGA1 and MITH1 together in a heterologous system, the model plant *Arabidopsis thaliana*, produces matrix-traversing membranes. Both proteins localize to matrix-traversing membranes. SAGA1 binds to the major matrix component, Rubisco, and is necessary to initiate matrix-traversing membranes. MITH1 binds to SAGA1 and is necessary for extension of membranes through the matrix. Our study identifies and characterizes key factors in the biogenesis of pyrenoid matrix-traversing membranes and marks a key milestone toward pyrenoid engineering into crops for improving yields.

Status: published work in Nature Plants 2024, **10**, 2038

Structural basis for human Ca$_\mathrm{v}$3.2 inhibition by selective antagonists

Jian Huang[1], Xiao Fan[1,5], Xueqin Jin[2], Chen Lyu[2], Qinmeng Guo[2], Tao Liu[2], Jiaofeng Chen[2], Amaël Davakan[3], Philippe Lory[3] and Nieng Yan[2,4]

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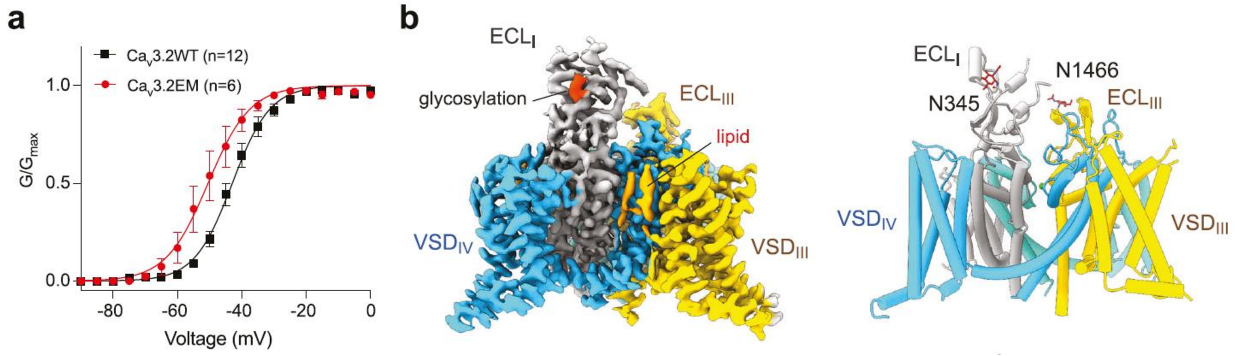

The Ca$_\mathrm{v}$3.2 subtype of T-type calcium channels has been targeted for developing analgesics and anti-epileptics for its role in pain and epilepsy. Here we present the cryo-EM structures of Ca$_\mathrm{v}$3.2 alone and in complex with four T-type calcium channel selective antagonists with overall resolutions ranging from 2.8 Å to 3.2 Å. The four compounds display two binding poses. ACT-709478 and TTA-A2 both place their cyclopropylphenyl-containing ends in the central cavity to directly obstruct ion flow, meanwhile extending their polar tails into the IV-I fenestration. TTA-P2 and ML218 project their 3,5-dichlorobenzamide groups into the II-III fenestration and place their hydrophobic tails in the cavity to impede ion permeation. The fenestration-penetrating mode immediately affords an explanation for the state-dependent activities of these antagonists. Structure-guided mutational analysis identifies several key residues that determine the T-type preference of these drugs. The structures also suggest the role of an endogenous lipid in stabilizing drug binding in the central cavity.

Status: published work in Cell Research 2024, **34**, 440

Structural biology and molecular pharmacology of voltage-gated ion channels

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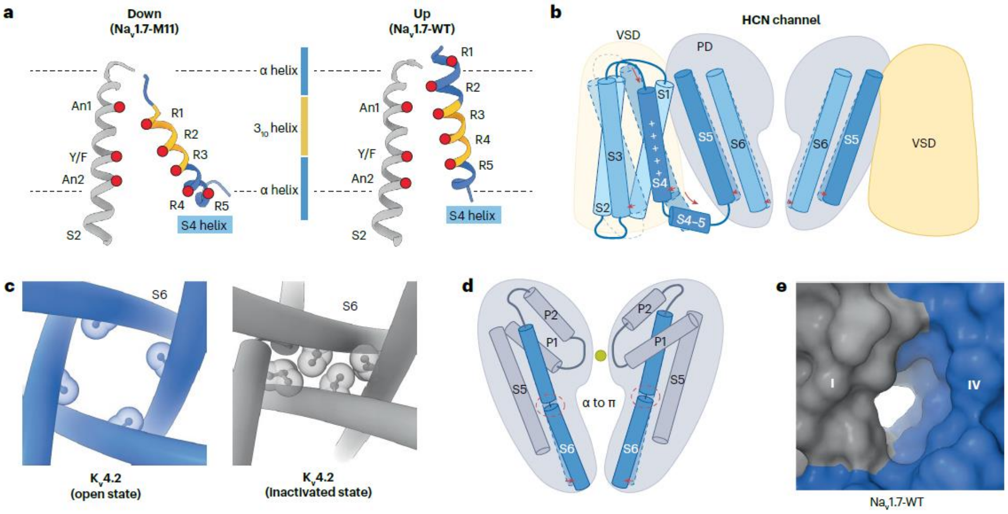

Voltage-gated ion channels (VGICs), including those for Na$^+$, Ca^{2+} and K$^+$, selectively permeate ions across the cell membrane in response to changes in membrane potential, thus participating in physiological processes involving electrical signalling, such as neurotransmission, muscle contraction and hormone secretion. Aberrant function or dysregulation of VGICs is associated with a diversity of neurological, psychiatric, cardiovascular and muscular disorders, and approximately 10% of FDA-approved drugs directly target VGICs. Understanding the structure–function relationship of VGICs is crucial for our comprehension of their working mechanisms and role in diseases. In this Review, we discuss how advances in single-particle cryo-electron microscopy have afforded unprecedented structural insights into VGICs, especially on their interactions with clinical and investigational drugs. We present a comprehensive overview of the recent advances in the structural biology of VGICs, with a focus on how prototypical drugs and toxins modulate VGIC activities. We explore how these structures elucidate the molecular basis for drug actions, reveal novel pharmacological sites, and provide clues to future drug discovery.

Status: published work in Nature Reviews Molecular Cell Biology 2024, **25**, 904.

A versatile residue numbering scheme for Na$_V$ and Ca$_V$ channels

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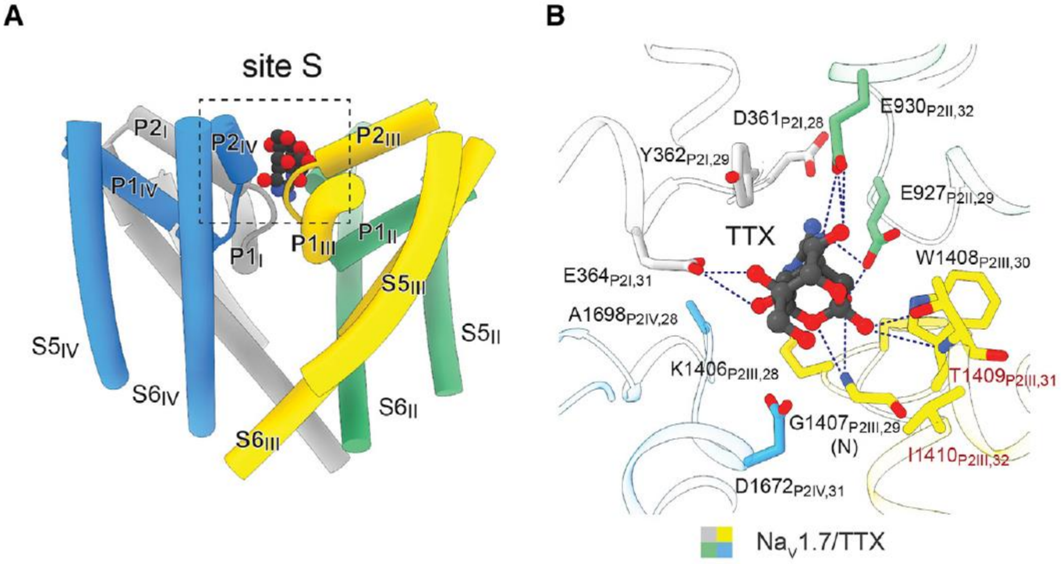

Voltage-gated sodium (Na$_V$) and calcium (Ca$_V$) channels are responsible for the initiation of electrical signals. They have long been targeted for the treatment of various diseases. The mounting number of cryoelectron microscopy (cryo-EM) structures for diverse subtypes of Na$_V$ and Ca$_V$ channels from multiple organisms necessitates a generic residue numbering system to establish the structure-function relationship and to aid rational drug design or optimization. Here we suggest a structure-based residue numbering scheme, centering around the most conserved residues on each of the functional segments. We elaborate the generic numbers through illustrative examples, focusing on representative drug-binding sites of eukaryotic Na$_V$ and Ca$_V$ channels. We also extend the numbering scheme to compare common disease mutations among different Nav subtypes. Application of the generic residue numbering scheme affords immediate insights into hotspots for pathogenic mutations and critical loci for drug binding and will facilitate drug discovery targeting Na$_V$ and Ca$_V$ channels.

Status: published work in Cell Chemical Biology 2024, **31**, 1394.

Princeton Neuroscience Institute

Fast imaging of millimeter-scale areas with beam deflection transmission electron microscopy

Zhihao Zheng[1], Christopher S. Own[2], Adrian A. Wanner[1], Randal A. Koene[2], Eric W. Hammerschmith[1], William M. Silversmith[1], Nico Kemnitz[1], Ran Lu[1], David W. Tank[1] & H. Sebastian Seung[1]

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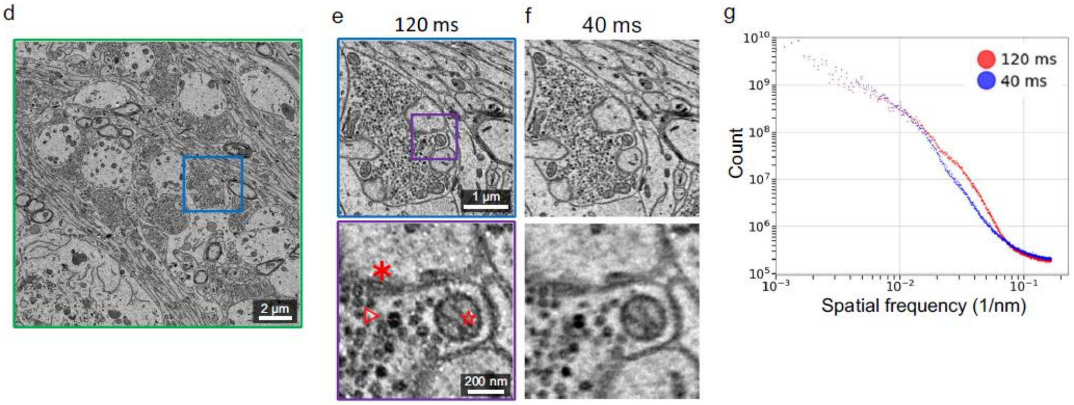

Serial section transmission electron microscopy (TEM) has proven to be one of the leading methods for millimeter-scale 3D imaging of brain tissues at nanoscale resolution. It is important to further improve imaging efficiency to acquire larger and more brain volumes. We report here a threefold increase in the speed of TEM by using a beam deflecting mechanism to enable highly efficient acquisition of multiple image tiles (nine) for each motion of the mechanical stage. For millimeter-scale areas, the duty cycle of imaging doubles to more than 30%, yielding a net average imaging rate of 0.3 gigapixels per second. If fully utilized, an array of four beam deflection TEMs should be capable of imaging a dataset of cubic millimeter scale in five weeks.

Status: published work in Nature Communication 2024, **15**, 6860.

Princeton Center for Complex Materials

Obstructed swelling and fracture of hydrogels

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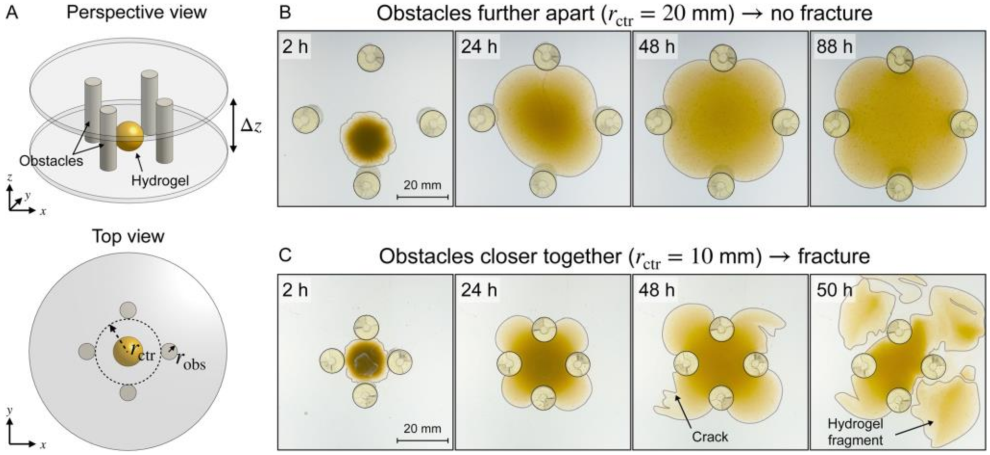

Obstructions influence the growth and expansion of bodies in a wide range of settings—but isolating and understanding their impact can be difficult in complex environments. Here, we study obstructed growth/expansion in a model system accessible to experiments, simulations, and theory: hydrogels swelling around fixed cylindrical obstacles with varying geometries. When the obstacles are large and widely-spaced, hydrogels swell around them and remain intact. In contrast, our experiments reveal that when the obstacles are narrow and closely-spaced, hydrogels fracture as they swell. We use finite element simulations to map the magnitude and spatial distribution of stresses that build up during swelling at equilibrium in a 2D model, providing a route toward predicting when this phenomenon of self-fracturing is likely to arise. Applying lessons from indentation theory, poroelasticity, and nonlinear continuum mechanics, we also develop a theoretical framework for understanding how the maximum principal tensile and compressive stresses that develop during swelling are controlled by obstacle geometry and material parameters. These results thus help to shed light on the mechanical principles underlying growth/expansion in environments with obstructions.

Status: published work in Soft Matter 2024, **20**, 1425

Department of Physics

Strong electron–phonon coupling in magic-angle twisted bilayer graphene

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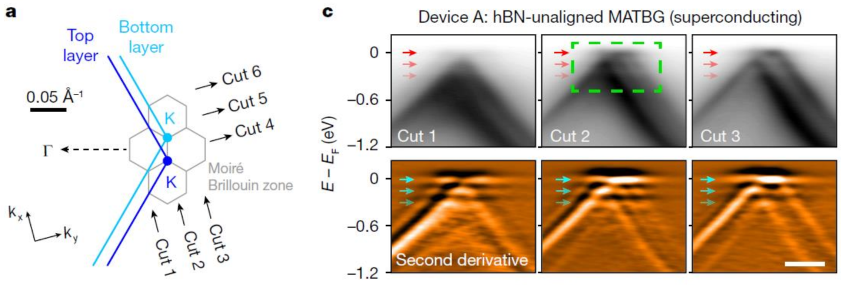

The unusual properties of superconductivity in magic-angle twisted bilayer graphene (MATBG) have sparked considerable research interest. However, despite the dedication of intensive experimental efforts and the proposal of several possible pairing mechanisms, the origin of its superconductivity remains elusive. Here, by utilizing angle-resolved photoemission spectroscopy with micrometre spatial resolution, we reveal flat-band replicas in superconducting MATBG, where MATBG is unaligned with its hexagonal boron nitride substrate. These replicas show uniform energy spacing, approximately 150 ± 15 meV apart, indicative of strong electron–boson coupling. Strikingly, these replicas are absent in non-superconducting twisted bilayer graphene (TBG) systems. Calculations suggest that the formation of these flat-band replicas in superconducting MATBG are attributed to the strong coupling between flat-band electrons and an optical phonon mode at the graphene K point. These findings, unravel the electronic structure inherent in superconducting MATBG, thereby providing crucial information for understanding the unusual electronic landscape from which its superconductivity is derived.

Status: published work in Nature 2024, **636**, 342

“Quantum Geometric Nesting” and Solvable Model Flat-Band Systems

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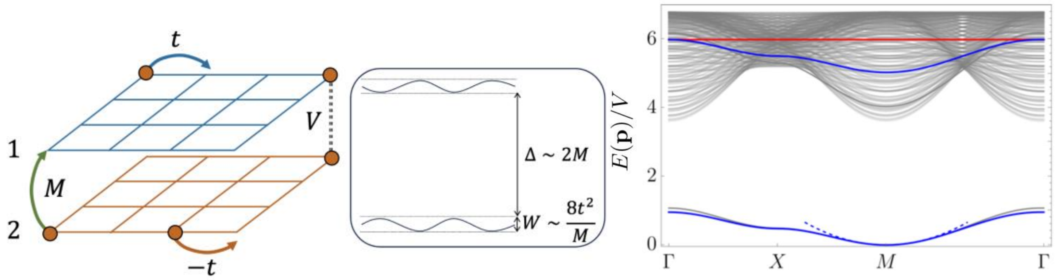

We introduce the concept of “quantum geometric nesting” (QGN) to characterize the idealized ordering tendencies of certain flat-band systems implicit in the geometric structure of the flat-band subspace. Perfect QGN implies the existence of an infinite class of local interactions that can be explicitly constructed and give rise to solvable ground states with various forms of possible fermion bilinear order, including flavor ferromagnetism, density waves, and superconductivity. For the ideal Hamiltonians constructed in this way, we show that certain aspects of the low-energy spectrum can also be exactly computed including, in the superconducting case, the phase stiffness. Examples of perfect QGN include flat bands with certain symmetries (e.g., chiral or time reversal) and non-symmetry-related cases exemplified with an engineered model for pair-density wave. Extending this approach, we obtain exact superconducting ground states with nontrivial pairing symmetry.

Status: published work in Physical Review X 2024, **14**, 041004

Interacting topological quantum chemistry in 2D with many-body real space invariants

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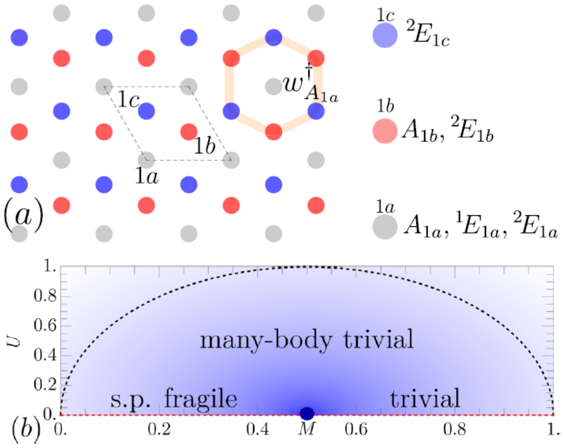

The topological phases of non-interacting fermions have been classified by their symmetries, culminating in a modern electronic band theory where wavefunction topology can be obtained from momentum space. Recently, Real Space Invariants (RSIs) have provided a spatially local description of the global momentum space indices. The present work generalizes this real space classification to interacting 2D states. We construct many-body local RSIs as the quantum numbers of a set of symmetry operators on open boundaries, but which are independent of the choice of boundary. Using the $U(1)$ particle number, they yield many-body fragile topological indices, which we use to identify which single-particle fragile states are many-body topological or trivial at weak coupling. To this end, we construct an exactly solvable Hamiltonian with single-particle fragile topology that is adiabatically connected to a trivial state through strong coupling. We then define global many-body RSIs on periodic boundary conditions. They reduce to Chern numbers in the band theory limit, but also identify strongly correlated stable topological phases with no single-particle counterpart. Finally, we show that the many-body local RSIs appear as quantized coefficients of Wen-Zee terms in the topological quantum field theory describing the phase.

Status: published work in Nature Communications 2024, **15**, 1171

Moiré fractional Chern insulators. II. First-principles calculations and continuum models of rhombohedral graphene superlattices

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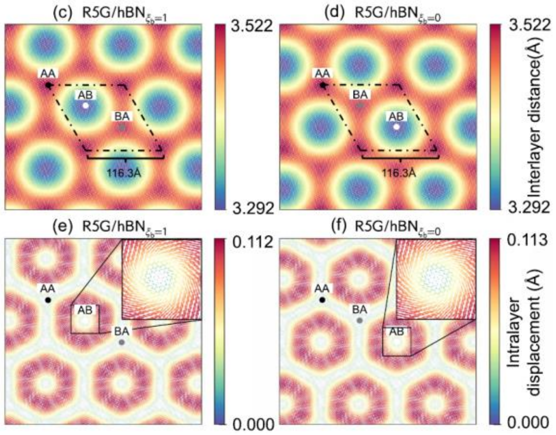

The experimental discovery of fractional Chern insulators (FCIs) in rhombohedral pentalayer graphene twisted on hexagonal boron nitride (hBN) has preceded theoretical prediction. Supported by large-scale first-principles relaxation calculations at the experimental twist angle of 0.77°, we obtain an accurate continuum model of n = 3, 4, 5, 6, 7 layer rhombohedral graphene-hBN moiré systems. We analytically explain the robust |C| = 0, 5 Chern numbers seen in the low-energy single-particle bands, making use of a minimal two-flavor continuum Hamiltonian derived from the full model. We then predict nonzero valley Chern numbers at the ν = −4, 0 insulators observed in experiment. Our analysis makes clear the importance of displacement field and the moiré potential in producing localized “heavy fermion” charge density in the top valence band. Lastly, we study doubly aligned devices as additional platforms for moiré FCIs with higher Chern number bands.

Status: published work in Physical Review B 2024, **109**, 205122.

Quantum transport response of topological hinge modes

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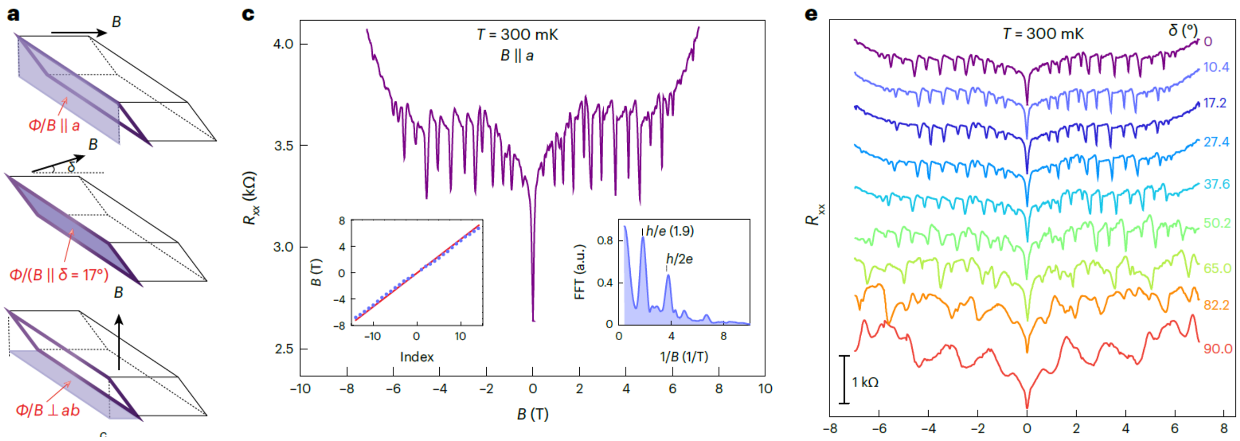

Electronic topological phases are typified by the conducting surface states that exist on the boundary of an insulating three-dimensional bulk. While the transport response of the two-dimensional surface states has been studied, the quantum response of the one-dimensional hinge modes has not been demonstrated. Here we provide evidence for quantum transport in gapless topological hinge states existing within the insulating bulk and surface energy gaps in the intrinsic topological insulator α-Bi_4Br_4. Our magnetoresistance measurements reveal pronounced Aharonov–Bohm oscillations that are periodic in h/e (where h denotes Planck's constant and e is the electron charge). The observed periodicity evinces quantum interference of electrons circumnavigating around the hinges. We also demonstrate that the h/e oscillations evolve as a function of magnetic field orientation, following the interference paths along the hinge modes that are allowed by topology and symmetry. Our findings reveal the quantum transport response of topological hinge modes with both topological nature and quantum coherence, which can eventually be applied to the development of efficient topological electronic devices.

Status: published work in Nature Physics 2024, **20**, 776

Surface-confined two-dimensional mass transport and crystal growth on monolayer materials

Yanyu Jia[1], Fang Yuan[2], Guangming Cheng[3], Yue Tang[1], Guo Yu[1,4], Tiancheng Song[1], Pengjie Wang[1], Ratnadwip Singha[2], Ayelet J. Uzan-Narovlansky[1], Michael Onyszczak[1], Kenji Watanabe[5], Takashi Taniguchi[6], Nan Yao[3], Leslie M. Schoop[2] and Sanfeng Wu[1]
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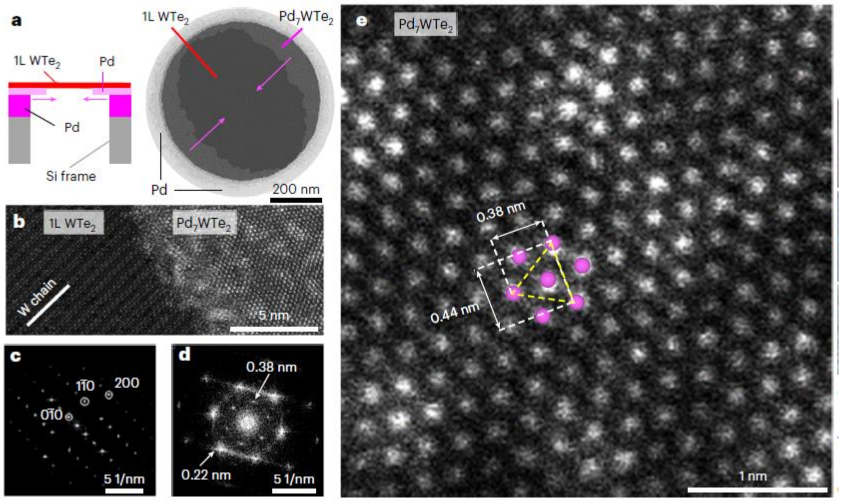

Conventional vapour deposition or epitaxial growth of two-dimensional (2D) materials and heterostructures is conducted in a large chamber in which masses transport from the source to the substrate. Here we report a chamber-free, on-chip approach for growing 2D crystalline structures directly in a nanoscale surface-confined 2D space. The method is based on the surprising discovery of the rapid, long-distance, non-Fickian transport of a uniform layer of atomically thin palladium on a monolayer crystal of tungsten ditelluride at temperatures well below the known melting points of all the materials involved. The nanoconfined growth realizes the controlled formation of a stable 2D crystalline material, Pd_7WTe_2, when the monolayer seed is either free-standing or fully encapsulated in a van der Waals stack. The approach is generalizable and compatible with nanodevice fabrication, promising to greatly expand the library of 2D materials and their functionalities.

Status: published work in Nature Synthesis 2024, **3**, 386

Moiré fractional Chern insulators. I. First-principles calculations and continuum models of twisted bilayer $MoTe_2$

Yujin Jia[1,2], Jiabin Yu[3], Jiaxuan Liu[1,2], Jonah Herzog-Arbeitman[3], Ziyue Qi[1,2], Hanqi Pi[1,2], Nicolas Regnault[3,4], Hongming Weng[1,2,5], B. Andrei Bernevig[3,6,7], and Quansheng Wu[1,2].
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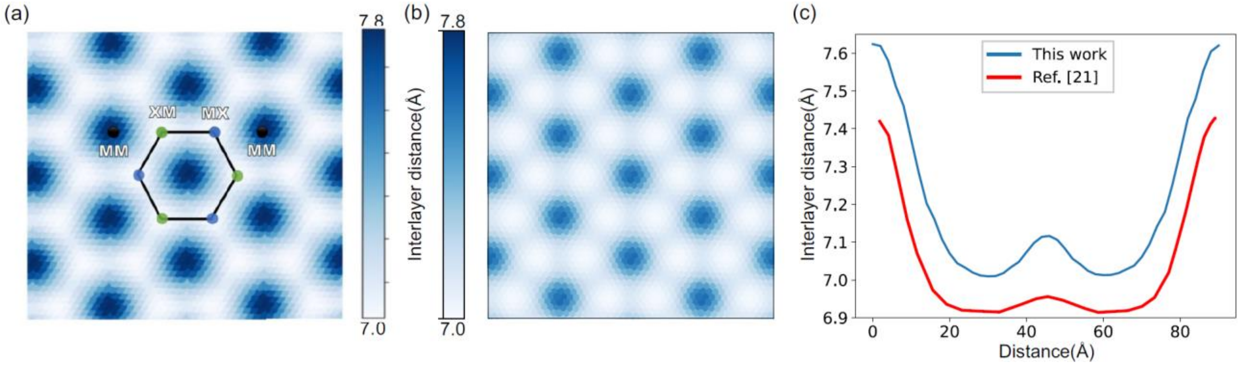

Recent experiments observed fractional Chern insulators (FCI) in twisted bilayer $MoTe_2$ at zero magnetic field, yet even the single-particle model of this material is controversial, leading to unreliable predictions of the experimental phase diagram. In this light, we revisit the single-particle model of twisted bilayer $MoTe_2$. Utilizing large-scale density functional theory, we calculate the band structure of twisted AA-stacked bilayer $MoTe_2$ at various twist angles relevant to experiment. We find that a band inversion occurs near 4.41^o between the second and third bands in one valley. Our ab initio band structure is in qualitative agreement with the earlier study, but shows important differences in the remote bands and in the Γ valley. We incorporate two higher harmonic terms into the continuum model to capture the highest three valence bands per valley. We confirm that the two highest valence bands per valley have opposite Chern numbers with $|C| = 1$ for experimentally relevant angles, and also use our model to predict a variety of Chern states in the remote bands accessible by displacement field. We also perform DFT calculations and build models for the AB-stacking configuration. Our paper serves as a foundation for accurate determination of the correlated phases in twisted bilayer $MoTe_2$.

Status: published work in Physical Review B 2024, **109**, 205121.

Superconductivity from On-Chip Metallization on 2D Topological Chalcogenides

Yanyu Jia[1], Guo Yu[1,2], Tiancheng Song[1], Fang Yuan[3], Ayelet J. Uzan[1], Yue Tang[1], Pengjie Wang[1], Ratnadwip Singha[3], Michael Onyszczak[1], Zhaoyi Joy Zheng[1,2], Kenji Watanabe[4], Takashi Taniguchi[5], Leslie M. Schoop[3], and Sanfeng Wu[1]

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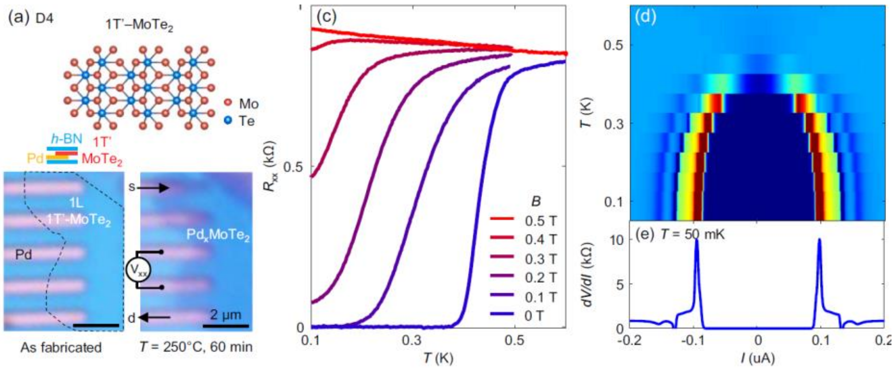

Two-dimensional (2D) transition metal dichalcogenides (TMDs) is a versatile class of quantum materials of interest to various fields. Tailoring the electronic properties of TMDs is essential to their applications. Here, we report that a highly controllable and uniform on-chip 2D metallization process converts a class of atomically thin TMDs into robust superconductors, a property belonging to none of the starting materials. As examples, we demonstrate the introduction of superconductivity into a class of 2D air-sensitive topological TMDs, including monolayers of T_d-WTe_2, 1T'-$MoTe_2$, and 2H-$MoTe_2$, as well as their natural and twisted bilayers, metallized with an ultrathin layer of palladium. This class of TMDs is known to exhibit intriguing topological phases ranging from topological insulator, Weyl semimetal to fractional Chern insulator. The unique, high-quality two-dimensional metallization process is based on our recent findings of the long-distance, non-Fickian in-plane mass transport and chemistry in 2D that occur at relatively low temperatures and in devices fully encapsulated with inert insulating layers. Highly compatible with existing nanofabrication techniques for van der Waals stacks, our results offer a route to engineering superconductivity and topological phases in a class of correlated 2D materials.

Status: published work in Physical Review X 2024, **14**, 021051.

Edge supercurrent reveals competition between condensates in a Weyl superconductor

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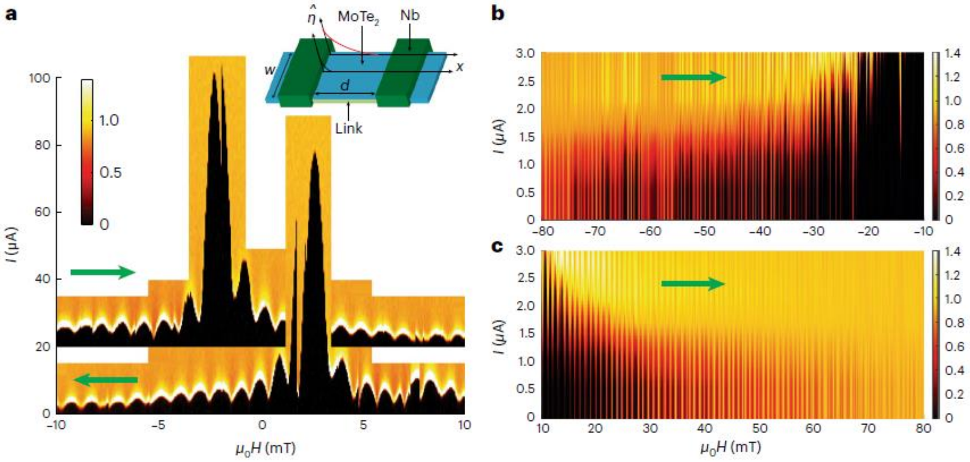

In topological materials, the edge states are readily distinguished from the bulk states. The situation where a topological semimetal becomes superconducting so that Cooper pairs occupy both the bulk and the edge states is not well understood. In particular, we do not know if we can force their pairing symmetries to be different. Here we show that, when supercurrent is injected into the superconducting Weyl semimetal MoTe$_2$ from Nb contacts, the invasive s-wave pairing potential from Nb is incompatible with the intrinsic Cooper pair condensate in MoTe$_2$. This incompatibility leads to strong stochasticity in the switching current and an unusual anti-hysteretic behaviour in the current – voltage loops. There is also an asymmetry in the edge oscillations where, as the magnetic field crosses zero, the phase noise switches from one with a noisy spectrum to one that is noise free. Using the noise spectrum as a guide, we track the anomalous features to field-induced switching of the device gap function between s-wave symmetry and the unconventional symmetry intrinsic to MoTe$_2$. We infer that the behaviour of the gap function along the edges is different from that in the bulk.

Status: published work in Nature Physics 2024, **20**, 261

Boundary modes of a charge density wave state in a topological material

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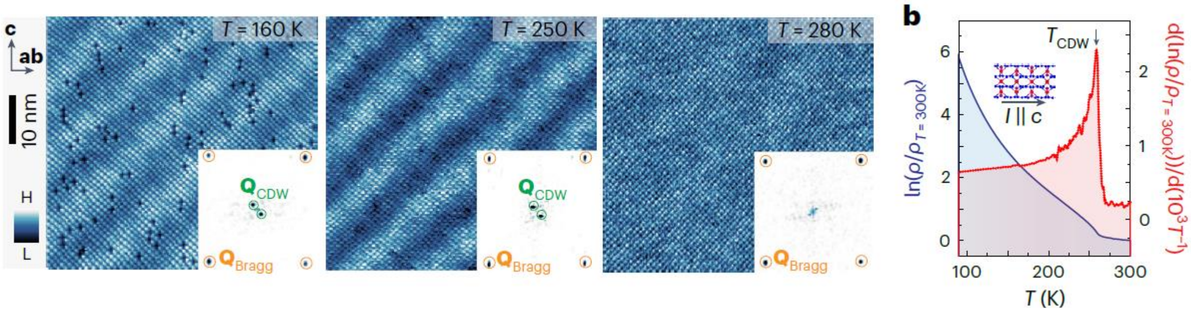

Charge density waves appear in numerous condensed matter platforms ranging from high-temperature superconductors to quantum Hall systems. Despite such ubiquity, there has been a lack of direct experimental study of boundary states that can uniquely stem from the charge order. Here we directly visualize the bulk and boundary phenomenology of the charge density wave in a topological material, Ta_2Se_8I, using scanning tunnelling microscopy. At a monolayer step edge, we demonstrate the presence of an in-gap boundary mode persisting up to the charge ordering temperature with modulations along the edge that match the charge density wave wavevector along the edge. Furthermore, these results manifesting the presence of an edge state challenge the existing axion insulator interpretation of the charge-ordered phase in this compound.

Status: published work in Nature Physics 2024, **20**, 1253

Electron–K-phonon interaction in twisted bilayer graphene

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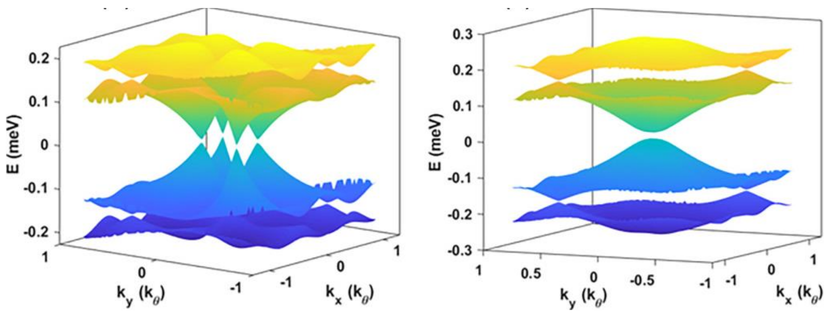

We develop an analytic theory to describe the interaction between electrons and K phonons and study its influence on superconductivity in the bare bands of twisted bilayer graphene (TBG). We find that, due to symmetry and the two-center approximation, only one optical K phonon (~160 meV) of graphene is responsible for the intervalley electron-phonon interaction. By projecting the interaction to the TBG flat bands, we perform the full symmetry analysis of the phonon-mediated attractive interaction and pairing channels in the Chern basis, and show that several channels are guaranteed to have gapless order parameters. From the linearized gap equations, we find that the highest Tc pairing induced by this phonon is a singlet gapped s-wave inter-Chern-band order parameter, followed closely by a gapless nematic d-wave intra-Chern-band order parameter. We justify these results analytically, using the topological heavy-fermion mapping of TBG which has allowed us to obtain an analytic form of a phonon-mediated attractive interaction and to analytically solve the linearized and T = 0 gap equations. For the intra-Chern-band channel, the nematic state with nodes is shown to be stabilized in the chiral flat-band limit. While the flat-band Coulomb interaction can be screened sufficiently enough—around the Van Hove singularities—to allow for electron-phonon based superconductivity, it is unlikely that this effect can be maintained in the lower density of states excitation bands around the correlated insulator states.

Status: published work in Physical Review B 2024, **110**, 045133.

Unconventional superconducting quantum criticality in monolayer WTe_2

Tiancheng Song[1], Yanyu Jia[1], Guo Yu[1,2], Yue Tang[1], Pengjie Wang[1], Ratnadwip Singha[3], Xin Gui[3], Ayelet J. Uzan-Narovlansky[1], Michael Onyszczak[1], Kenji Watanabe[4], Takashi Taniguchi[5], Robert J. Cava[3], Leslie M. Schoop[3], N. P. Ong[1] and Sanfeng Wu[1]

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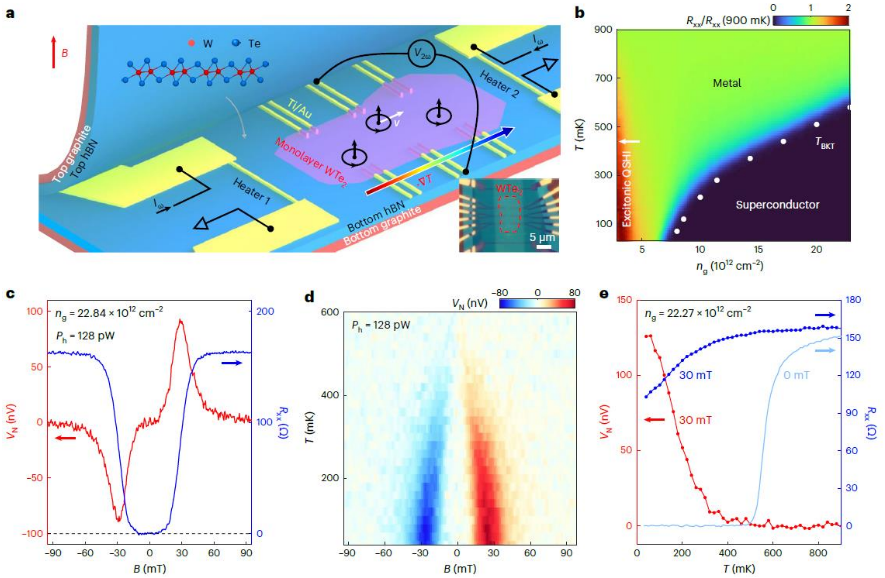

The transitions from a superconductor to a resistive state in two dimensions provide a valuable platform for studying continuous quantum phase transitions and critical phenomena. Here we uncover anomalous quantum fluctuations and identify an unconventional superconducting quantum critical point in a gate-tuned excitonic quantum spin Hall insulator, the monolayer tungsten ditelluride. We do this by extending Nernst experiments down to millikelvin temperatures. The vortex Nernst effect that we observe reveals singular superconducting fluctuations in the resistive normal state induced by magnetic fields or temperature, even well above the transition. Near the doping-induced quantum critical point, the Nernst signal driven by quantum fluctuations is large in the millikelvin regime, an indication of the proliferation of vortices. Unexpectedly, the Nernst signal abruptly disappears when the doping falls below the critical value, in contrast with conventional expectations. This series of phenomena calls for careful examination of the mechanism of the quantum critical point in the monolayer.

Status: published work in Nature Physics 2024, **20**, 269.

Anderson critical metal phase in trivial states protected by average magnetic crystalline symmetry

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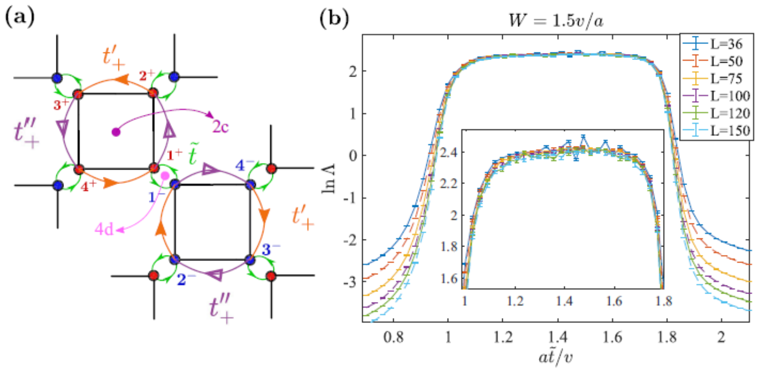

Transitions between distinct obstructed atomic insulators (OAIs) protected by crystalline symmetries, where electrons form molecular orbitals centering away from the atom positions, must go through an intermediate metallic phase. In this work, we find that the intermediate metals will become a scale-invariant critical metal phase (CMP) under certain types of quenched disorder that respect the magnetic crystalline symmetries on average. We explicitly construct models respecting average $C_{2z}T$,m, and $C_{4z}T$ and show their scale-invariance under chemical potential disorder by the finite-size scaling method. Conventional theories, such as weak anti-localization and topological phase transition, cannot explain the underlying mechanism. A quantitative mapping between lattice and network models shows that the CMP can be understood through a semi-classical percolation problem. Ultimately, we systematically classify all the OAI transitions protected by (magnetic) groups P_m, P2’, P4’, and P6’ with and without spin-orbit coupling, most of which can support CMP.

Status: published work in Nature Communications 2024, **15**, 3069.

Emergent Symmetry and Valley Chern Insulator in Twisted Double-Bilayer Graphene

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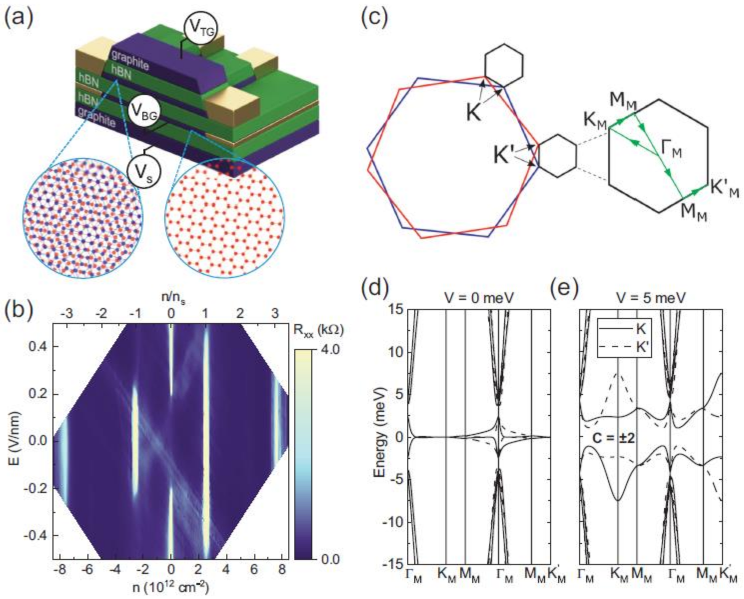

Theoretical calculations show that twisted double bilayer graphene (TDBG) under a transverse electric field develops a valley Chern number 2 at charge neutrality. Using thermodynamic and thermal activation measurements we report the experimental observation of a universal closing of the charge neutrality gap in the Hofstadter spectrum of TDBG at 1/2 magnetic flux per unit cell, in agreement with theoretical predictions for a valley Chern number 2 gap. Our theoretical analysis of the experimental data shows that the interaction energy, while larger than the flat-band bandwidth in TDBG near 1° does not alter the emergent valley symmetry or the single-particle band topology.

Status: published work in Physical Review Letters 2024, **133**, 246401.

The detection of unconventional quantum oscillations in insulating 2D materials

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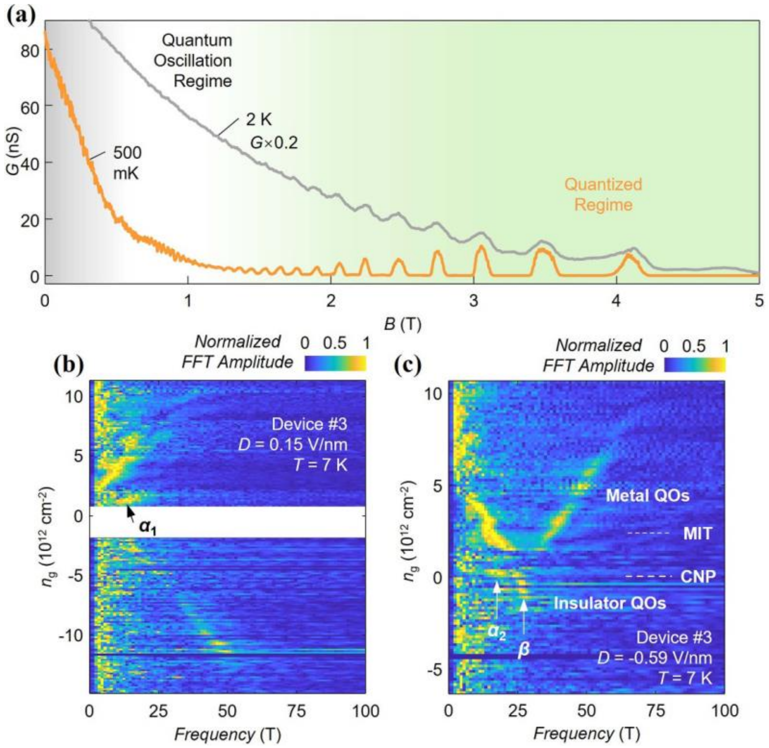

In strongly correlated quantum materials, electrons behave in ways that often extend beyond the confines of conventional Fermi-liquid theory. Interesting results include the observation of low-temperature metallic behavior in systems that are highly resistive. Here we provide an overview of experiments in which insulators exhibit characteristics of a metal such as the Shubnikov–de Haas-like quantum oscillations, focusing on recent findings in the correlated insulating states of two-dimensional WTe_2. We discuss the status of current research, clarify the debates and challenges in interpreting the experiments, rule out extrinsic explanations and discuss promising future directions.

Status: published work in 2D Materials 2024, **11**, 033004.

Charge-neutral electronic excitations in quantum insulators

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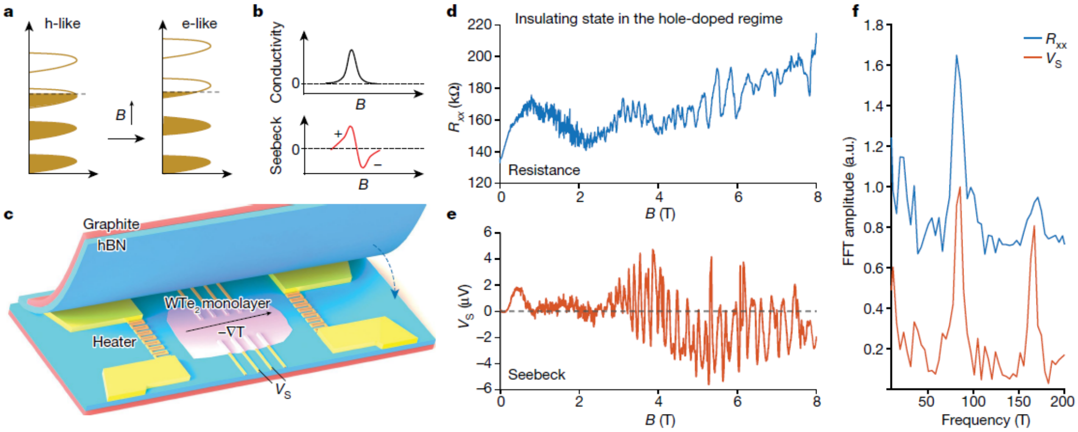

Experiments on quantum materials have uncovered many interesting quantum phases ranging from superconductivity to a variety of topological quantum matter including the recently observed fractional quantum anomalous Hall insulators. The findings have come in parallel with the development of approaches to probe the rich excitations inherent in such systems. In contrast to observing electrically charged excitations, the detection of charge-neutral electronic excitations in condensed matter remains difficult, although they are essential to understanding a large class of strongly correlated phases. Low-energy neutral excitations are especially important in characterizing unconventional phases featuring electron fractionalization, such as quantum spin liquids, spin ices and insulators with neutral Fermi surfaces. In this Perspective, we discuss searches for neutral fermionic, bosonic or anyonic excitations in unconventional insulators, highlighting theoretical and experimental progress in probing excitonic insulators, new quantum spin liquid candidates and emergent correlated insulators based on two-dimensional layered crystals and moiré materials. We outline the promises and challenges in probing and using quantum insulators and discuss exciting new opportunities for future advancements offered by ideas rooted in next-generation quantum materials, devices and experimental schemes.

Status: published work in Nature 2024, **635**, 305.

Filling-enforced obstructed atomic insulators

Yuanfeng Xu[1,2,3], Luis Elcoro[4], Zhi-Da Song[1], M. G. Vergniory[5,6,7], Claudia Felser[7], Stuart S. P. Parkin[3], Nicolas Regnault[1,8], Juan L. Mañes[4], and B. Andrei Bernevig[1,5,6]

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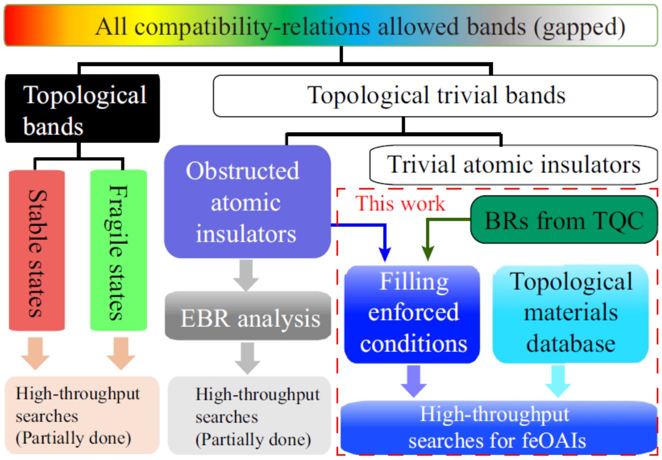

Topological band theory has achieved great success in the high-throughput search for topological band structures both in paramagnetic and magnetic crystal materials. However, a significant proportion of materials are topologically trivial insulators at the Fermi level. In this paper, we show that, remarkably, for a subset of the topologically trivial insulators, knowing only their electron number and the Wyckoff positions of the atoms we can separate them into two groups: the obstructed atomic insulator (OAI) and the atomic insulator (AI). The interesting group, the OAI, have a center of charge not localized on the atoms. Using the theory of topological quantum chemistry, in this work we first derive the necessary and sufficient conditions for a topologically trivial insulator to be a filling enforced obstructed atomic insulator (feOAI) in the 1651 Shubnikov space groups. With the help of the Topological Quantum Chemistry website, we have performed a high-throughput search for feOAIs and have found that 957 ICSD entries (638 unique materials) are paramagnetic feOAIs, among which 738 (475) materials have an indirect gap.

Status: published work in Physical Review B 2024, **109**, 165139

Catalog of topological phonon materials

Yuanfeng Xu[1,2], M. G. Vergniory[3,4], Da-Shuai Ma[5], Juan L. Mañes[6], Zhi-Da Song[2,7], B. Andrei Bernevig[2,3,8], Nicolas Regnault[9,2], Luis Elcoro[6]

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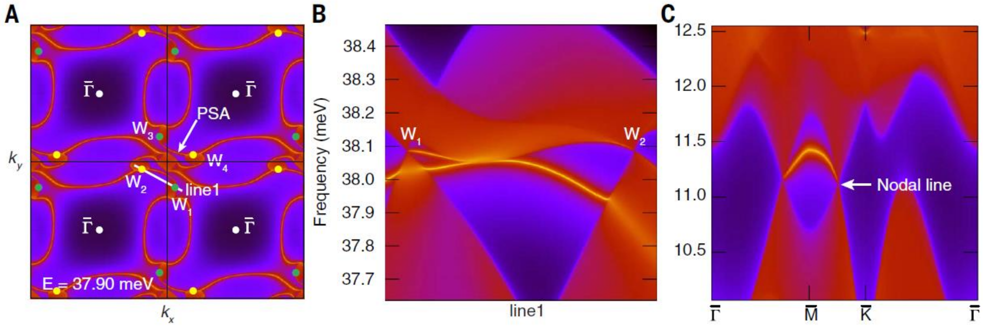

Phonons play a crucial role in many properties of solid-state systems, and it is expected that topological phonons may lead to rich and unconventional physics. On the basis of the existing phonon materials databases, we have compiled a catalog of topological phonon bands for more than 10,000 three-dimensional crystalline materials. Using topological quantum chemistry, we calculated the band representations, compatibility relations, and band topologies of each isolated set of phonon bands for the materials in the phonon databases. Additionally, we calculated the real-space invariants for all the topologically trivial bands and classified them as atomic or obstructed atomic bands. We have selected more than 1000 "ideal" nontrivial phonon materials to motivate future experiments. The datasets were used to build the Topological Phonon Database.

Status: published work in Science 2024, **384**, 638.

Topological minibands and interaction driven quantum anomalous Hall state in topological insulator based moiré heterostructures

Kaijie Yang[1], Zian Xu[2], Yanjie Feng[2], Frank Schindler[3], Yuanfeng Xu[4,5], Zhen Bi[1], B. Andrei Bernevig[5,6,7], Peizhe Tang[2,8] and Chao-Xing Liu[1,5]

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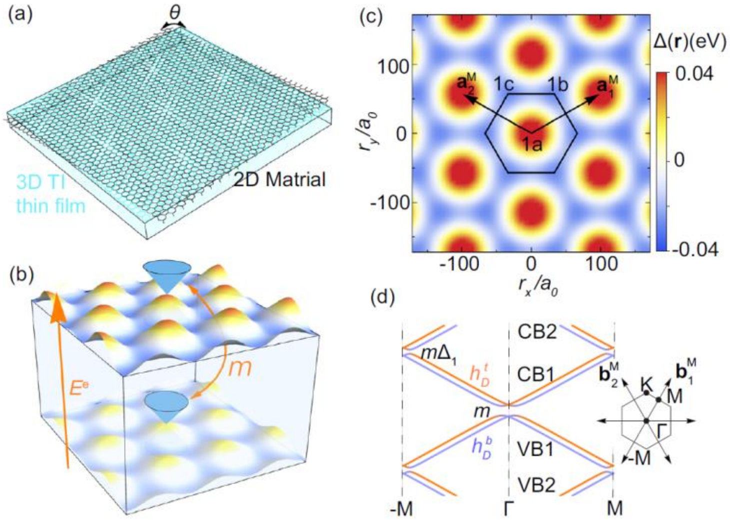

The presence of topological flatminibands in moirématerials provides an opportunity to explore the interplay between topology and correlation. In this work, we study moiré minibands in topological insulator films with two hybridized surface states under a moiré superlattice potential created by two-dimensional insulating materials. We show the lowest conduction (highest valence) Kramers' pair of minibands can be Z_2 non-trivial when the minima (maxima) of moiré potential approximately form a hexagonal lattice with six-fold rotation symmetry. Coulomb interaction can drive the non-trivial Kramers' minibands into the quantum anomalous Hall state when they are half-filled, which is further stabilized by applying external gate voltages to break inversion. We propose themonolayer Sb_2 on top of Sb_2Te_3 films as a candidate based on first principles calculations. Our work demonstrates the topological insulator based moiré heterostructure as a potential platform for studying interacting topological phases.

Status: published work in Nature Communications 2024, **15**, 2670

Non-trivial quantum geometry and the strength of electron–phonon coupling

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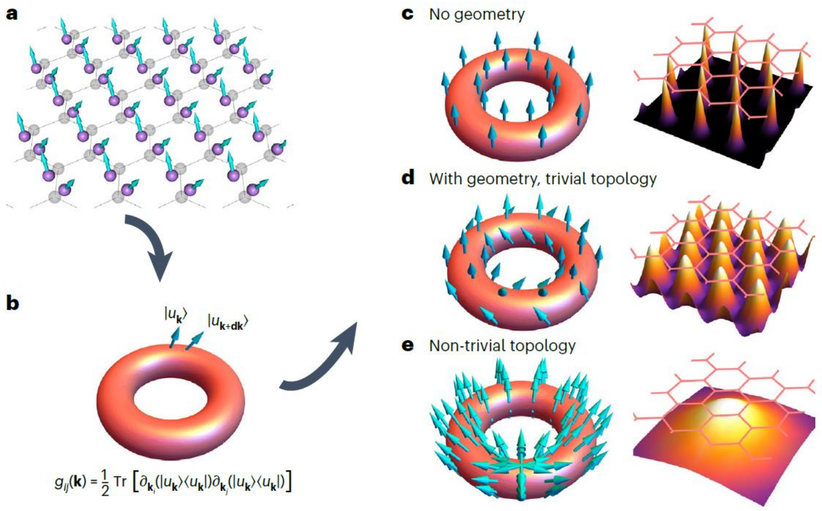


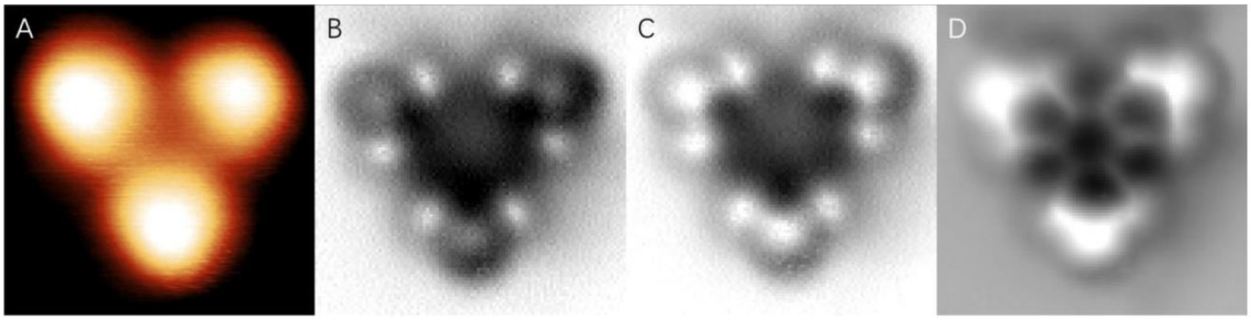
Electron–phonon coupling is crucial for the existence of various phases of matter, in particular superconductivity and density waves. Here, we devise a theory that incorporates the quantum geometry of the electron bands into the electron–phonon coupling, demonstrating the crucial contributions of the Fubini–Study metric or its orbital selective version to the dimensionless electron–phonon coupling constant. We apply the theory to two materials, that is, graphene and MgB_2, where the geometric contributions account for approximately 50% and 90% of the total electron–phonon coupling constant, respectively. The quantum geometric contributions in the two systems are further bounded from below by topological contributions. Our results suggest that the non-trivial electron band geometry or topology might favour superconductivity with a relatively high critical temperature.

Status: published work in Nature Physics 2024, **20**, 1262.

Princeton Materials Institute

Identifying a Critical Nucleus for Ice Nucleation on Hydrophilic and Hydrophobic Surfaces

Pengcheng Chen, Dingxin Fan, and Nan Yao
Princeton Materials Institute, Princeton University, Princeton, NJ, USA



Water has long served as a critical topic in science and technology thanks to its ubiquitous existence in daily life. Studies of surface-supported water clusters provide a means to obtain a rigorous molecular scale description of the initial stages of the surface-based processes. Here, we report a direct structural determination of the water clusters at the initial stages of ice nucleation on close-packed metal surfaces, represented by hydrophilic Pt(111) and hydrophobic Cu(111) surfaces using a combination of scanning tunneling microscopy (STM) and noncontact atomic force microscopy (NC-AFM). Real-space identification of the atomic structure of water clusters with precise information on the position of oxygen atoms and O-H bond orientation can be achieved using NC-AFM with a terminated tip. A series of hydrated clusters consisting of conjugated hexagon, pentagon, and heptagon rings were structurally identified through the atomically resolved NC-AFM images. We found similar structural motifs of water on both Pt(111) and Cu(111) surfaces, indicating the presence of universal starting nuclei at the initial ice growth stage on the terrace of wetting and non-wetting surfaces. Combined with first-principles density functional theory calculations, a critical nucleus comprising 15 water molecules has been identified, whereas further ice growth bifurcates to form two-dimensional (three-dimensional) layers on hydrophilic (hydrophobic) surfaces. A rigorous molecule-scale description of the initial stages of heterogeneous water nucleation is proposed.

Status: published work in Microscopy and Microanalysis 2024, **30**, 1424

Identification of a common ice nucleus on hydrophilic and hydrophobic close-packed metal surfaces

Pengcheng Chen[1], Qiuhao Xu[2], Zijing Ding[2], Qing Chen[2], Jiyu Xu[2], Zhihai Cheng[3], Xiaohui Qiu[4,5], Bingkai Yuan[6], Sheng Meng[2,5] & Nan Yao[1]

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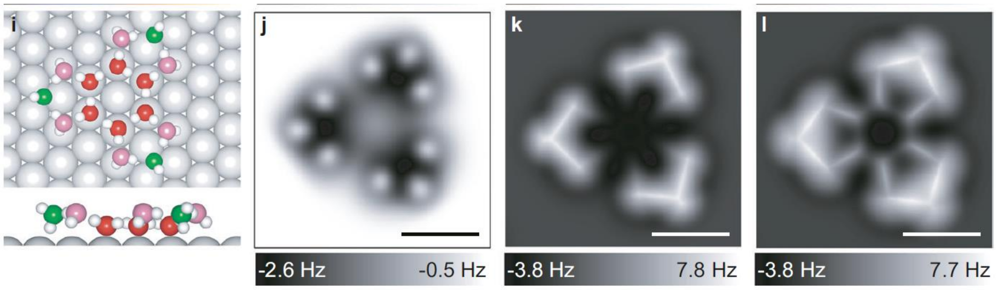

Establishing a general heterogeneous ice nucleation model has long been challenging because of the surface water structures found on different substrates. Identifying common water clusters, regardless of the underlying substrate, is one of the key steps toward solving this problem. Here, we demonstrate the presence of a common water cluster found on both hydrophilic Pt(111) and hydrophobic Cu(111) surfaces using scanning tunneling microscopy and non-contact atomic force microscopy. Water molecules self-assemble into a structure with a central flat-lying hexagon and three fused pentagonal rings, forming a cluster of 15 individual water molecules. This cluster serves as a critical nucleus during ice nucleation on both surfaces: ice growth beyond this cluster bifurcates to form two-dimensional (three-dimensional) layers on hydrophilic (hydrophobic) surfaces. Our results reveal the inherent similarity and distinction at the initial stage of ice growth on hydrophilic and hydrophobic close-packed metal surfaces; thus, these observations provide initial evidence toward a general model for water-substrate interaction.

Status: published work in Nature Communications 2023, **14**, 5813.

Atomic Resolution Imaging of Highly Air-Sensitive Twisted-Bilayer 2D Structures

Guangming Cheng, Nan Yao
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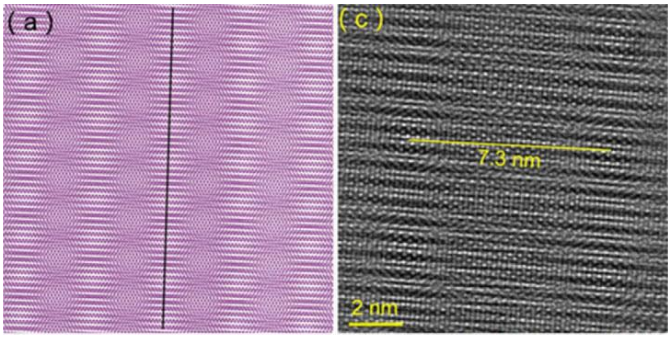

The physical properties of the majority of 2D crystals remain unexplored or poorly explored, especially those beyond the air-stable materials, such as graphene and semiconducting transition-metal dichalcogenides (TMDs). The investigation of 2D crystals requires careful processing to avoid degradation and contamination. Bulk orthorhombic Td-WTe$_2$ is a semimetal, while its monolayer counterpart is a 2D topological insulator. Recently, electronic transport resembling a Luttinger liquid state was found in twisted-bilayer WTe$_2$ with a twist angle of ~5°. Despite the strong interest in 2D WTe$_2$ systems, little experimental information about their intrinsic microstructure is available. The monolayer, and consequently twisted-bilayer WTe$_2$, are highly air-sensitive. Here, we demonstrated a robust method for atomic-resolution visualization of monolayers and twisted-bilayer WTe$_2$ obtained through mechanical exfoliation and fabrication. We observed the high crystalline quality of mechanically exfoliated WTe$_2$ samples by using high-resolution scanning transmission electron microscopy (STEM). We developed a methodology to prepare plan-view TEM samples from air-sensitive Scotch-tape-exfoliated monolayer and twisted-bilayer WTe$_2$ samples. We established that the in-plane crystal structures of monolayer WTe$_2$ are the same as its form in the bulk parent, confirmed by their identical in-plane d-spacings. We investigated the moiré patterns of twisted-bilayer WTe$_2$ with twist angles of approximately 5 and 2° and observed no noticeable lattice reconstruction. The visualization procedure described in this work deepens the understanding of the monolayer and twisted-bilayer WTe2 microstructure.

Status: published work in Microscopy and Microanalysis 2024, **30**, 1093.

Differentiating the Bonding States in Calcium Carbonate Polymorphs by Low-Loss Electron-Energy-Loss Spectroscopy

Guangming Cheng[1], Yao-Wen Yeh[2], Sobhitand Singh[2], Shiyou Xu[3], and Nan Yao[1]
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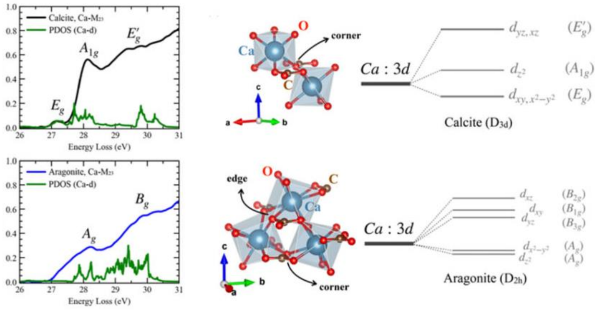

Calcium carbonate is one of the important building components in organisms, especially the two most common polymorphs, calcite and aragonite. Although their microstructures are well characterized, there is still lack of study about the electronic structures related to the bonding state (valence) in the compounds. Experimentally, the electronic structures of materials can be studied by electron energy loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS). We found that Ca-M edges showed advantages for the analysis of bonding states in the two studied $CaCO_3$ polymorphs because the spin-orbit coupling is much reduced for a 3p orbital as compared to a 2p orbital, which in turn reduces the atomic multiplet effect. This enables us to deeply explore the fine spectral features from low-loss EELS data. Here, to understand the difference in bonding state, we use scanning transmission electron microscopy (STEM) coupled with EELS to characterize the valence (low-loss) spectral region (4 – 50 eV) of calcite and aragonite. It is found that the difference in Ca M_{23} edge originating from 3p to 3d states is consistent with the change of Ca-O bonds in the two studied polymorphs. Surprisingly, the measured CaM_{23} edge is in qualitative agreement with the calculated partial density of states (PDOS) of Ca-d states in contrast to their L edges (from 2p to 3d states), which are strongly influenced by atomic multiplet effect. Our findings show insights that PDOS has great potential for the interpretation of M_{23} edge spectrum from lighter 3d transition metals such as scandium, titanium, vanadium and chromium.

Status: published work in Microscopy and Microanalysis 2024, **30**, 1157

Polymer nanocomposites: Interfacial properties and capacitive energy storage

Stavros X. Drakopoulos[1], Jiaen Wu[2], Shawn M. Maguire[2], Sneha Srinivasan[2], Katelyn Randazzo[2], Emily C. Davidson[1,2], Rodney D. Priestley[1,2]

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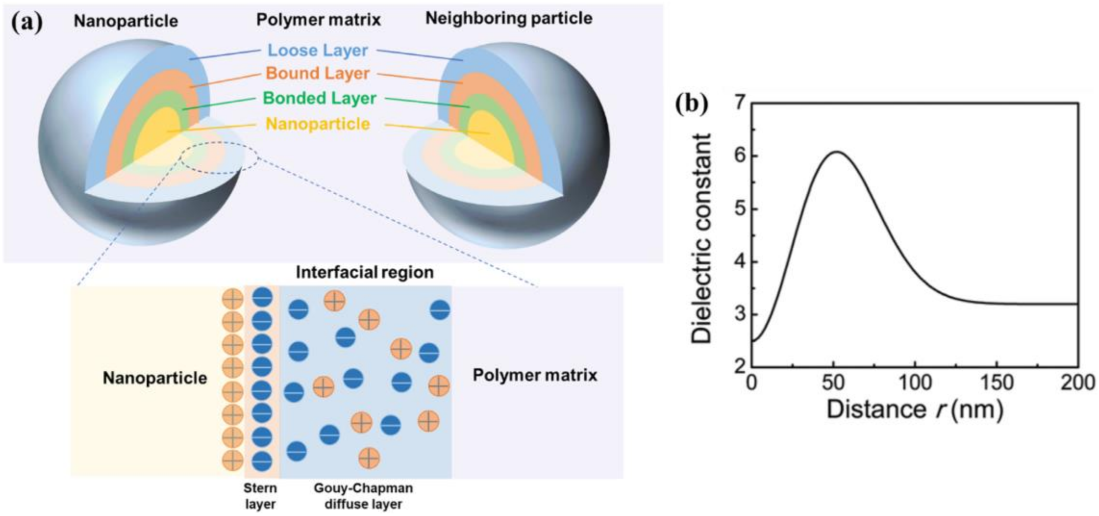

An in-depth review is presented on the interfacial phenomena of polymer nanocomposites and the role of the interface/interphase in capacitive energy storage. The interaction between polymer chains and nanofillers upon filler dispersion and glass transition temperature are discussed through the lens of the adsorbed layer or polymer-grafted nanoparticles. Moreover, fundamentals of dielectric physics are discussed regarding charge transport and charge entrapment on the interface, yielding the phenomenon of interfacial polarization. Therefore, the aim of this review is to inform the readers on the importance of the interface and highlight that both polymer chain dynamics and charge transport points of view are pivotal in the understanding of modern polymer nanodielectrics.

Status: published work in Progress in Polymer Science 2024, **156**, 101870

Atomic Force Microscopy Imaging of Individual CO Molecules Adsorbed on a Cu(111) Surface

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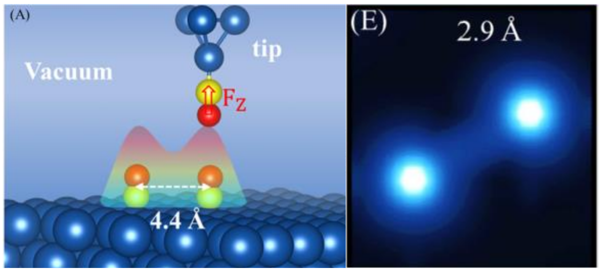

CO-functionalized atomic force microscopy (AFM) refers to attaching a single CO molecule onto a metallic Cu tip (C bonded with Cu). This CO molecule serves as a molecular probe, enabling the direct probing of atomic/subatomic features of the specimen in real space. We can only measure the relative tip height concerning a setpoint in the experiment. This accounts for why negative heights are often reported on experimental images. In theory, researchers have obtained data from different models ranging from less than 3 Å to over 15 Å. The uncertainty in tip height prevents us from precisely discerning how the tip interacts with the sample and identifying the exact nature of what we had probed. In our experiment, we constructed the system using a CO-functionalized AFM tip mounted on a qPlus sensor to perform AFM imaging of CO molecules adsorbed on a Cu(111) surface at different tip heights. Furthermore, to obtain more accurate imaging heights for each image, we conducted vertical force measurements directly above a surface CO. By comparing the experimentally measured force curve with the force curves calculated using DFT, we found that the use of local density approximation (LDA - CA) overestimates the force equilibrium tip height, while the generalized gradient approximations (GGA - PBE) underestimate the tip height. Our experimental AFM images and AFM images simulated by DFT showed good agreement. Our work demonstrates that AFM imaging can be conducted in the attractive regime and under the dominance of Pauli repulsion, accurately pinpointing the imaging height. We also elucidate why AFM images are often height-dependent and distorted at small tip heights. When imaging in the repulsive regime, we can observe additional fine structures of the specimen. Our findings can play a crucial role in advancing the capabilities of AFM in characterizing complex molecular systems

Status: published work in Microscopy and Microanalysis 2024, **30**, 1649

Reconfigurable quantum fluid molecules of bound states in the continuum

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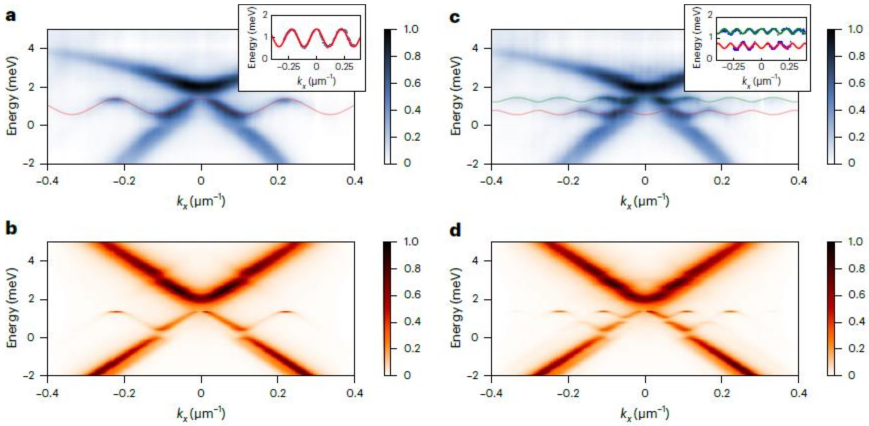

Topological bound states in the continuum are confined wave-mechanical objects that offer advantageous ways to enhance light–matter interactions in compact photonic devices. In particular, their large quality factor in the strong-coupling regime has recently enabled the demonstration of Bose–Einstein condensation of bound-state-in-the-continuum polaritons. Here we show that polariton condensation into a negative-mass bound state in the continuum exhibits interaction-induced state confinement, opening opportunities for optically reprogrammable molecular arrays of quantum fluids of light. We exploit this optical-trapping mechanism to demonstrate that such artificial molecular complexes show hybridization into macroscopic modes with unusual topological charge multiplicity. Additionally, we demonstrate the scalability of our technique by constructing extended mono- and diatomic chains of bound-state-in-the-continuum polariton fluids that display non-Hermitian band formation and the opening of a minigap. Our findings offer insights into large-scale, reprogrammable, driven, dissipative many-body systems in the strong-coupling regime.

Status: published work in Nature Physics 2024, **20**, 61

Polariton Condensation in Gap-Confined States of Photonic Crystal Waveguides

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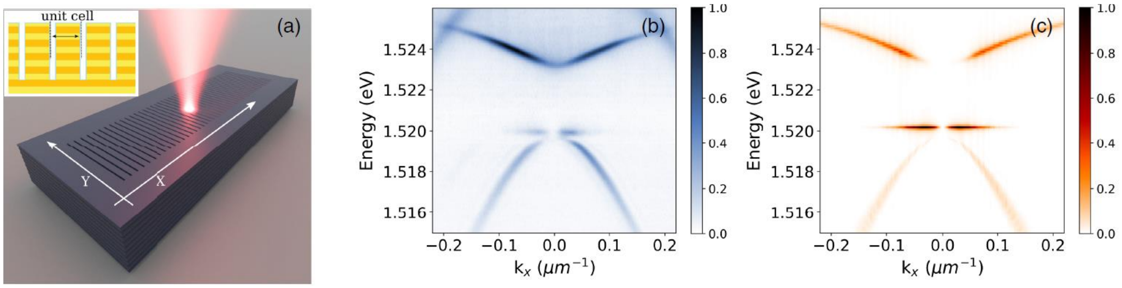

The development of patterned multiquantum well heterostructures in GaAs/AlGaAs waveguides has recently made it possible to achieve exciton-polariton condensation in a topologically protected bound state in the continuum (BIC). Polariton condensation was shown to occur above a saddle point of the two-dimensional polariton dispersion in a one-dimensional photonic crystal waveguide. A rigorous analysis of the condensation phenomenon in these systems, as well as the role of the BIC, is still missing. In the present Letter, we theoretically and experimentally fill this gap by showing that polariton confinement resulting from the negative effective mass and the photonic energy gap in the dispersion play a key role in enhancing the relaxation toward the condensed state. In fact, our results show that low-threshold polariton condensation is achieved within the effective trap created by the exciting laser spot, regardless of whether the resulting confined mode is long-lived (polariton BIC) or short-lived (lossy mode). In both cases, the spatial quantization of the polariton condensate and the threshold differences associated to the corresponding state lifetime are measured and characterized. For a given negative mass, a slightly lower condensation threshold from the polariton BIC mode is found and associated to its reduced radiative losses, as compared to the lossy one.

Status: published work in Physical Review Letters 2024, **131**, 246901.