

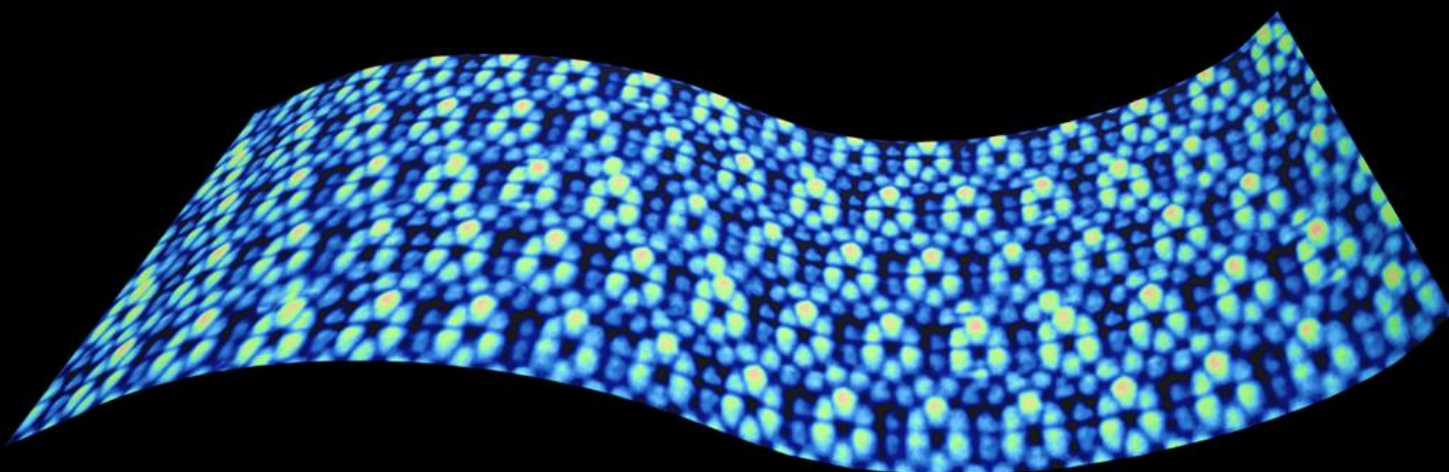
# RESEARCH REPORT

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Imaging and Analysis Center  
PMI



2023





## 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 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 5,000 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.

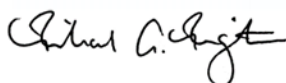
Recent IAC internal users include over 350 students and researchers from more than 90 research groups. The IAC supports ~240 research contracts worth a total of ~\$450M. In the IAC, undergraduate students are provided with the opportunity to operate various electron microscopes during class and later 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 post-docs are each provided with a unique opportunity to conduct research using the IAC's state-of-the-art instrumentation. Their research covers a diverse spectrum of topics including: improving photovoltaics, batteries, circuit-design, and cements; elucidating biochemical pathways, understanding the structures of biomolecular machines; and characterizing samples from aerodynamic wing models, pharmaceutical drug crystals, catalytic nanoparticles, and biofilms.



### Nanomaterials

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



### Biomaterials

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



### Electronic Materials

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



### Ceramics and Glasses

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



### Polymers

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



### Metal Alloys

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



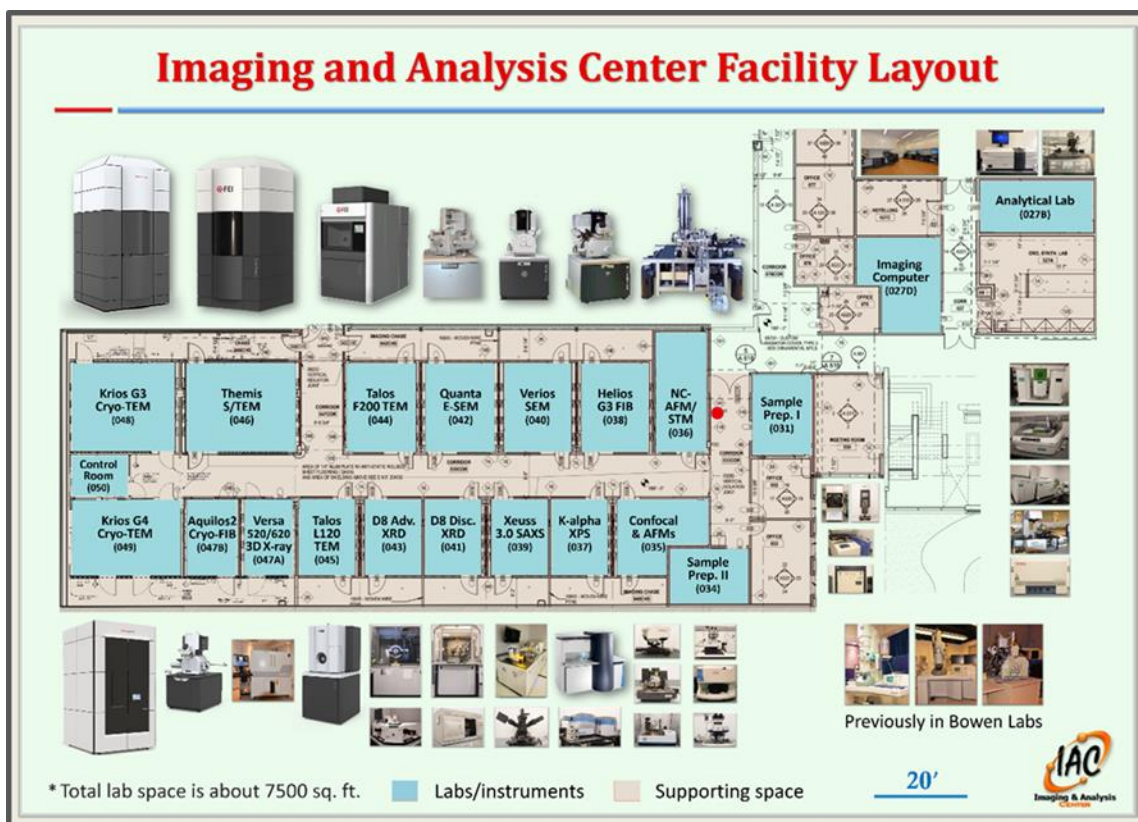
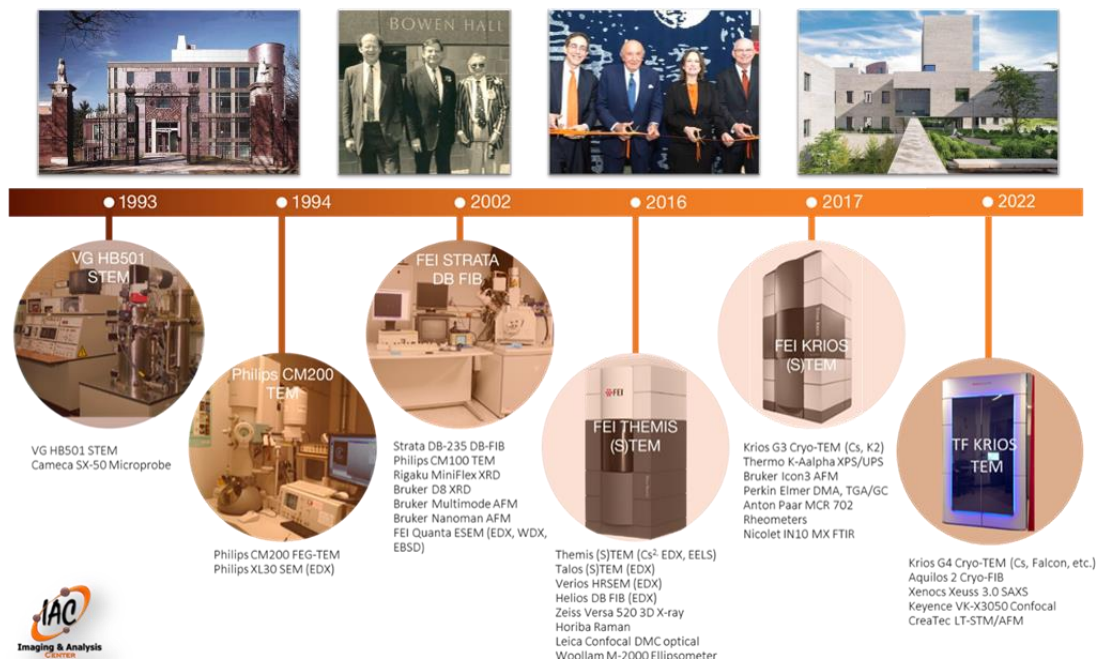
### Pharmaceutical Materials

drug coating, toothpaste, molecular crystals, etc.



## Imaging and Analysis Center (IAC)

**IAC Background:** Started in 1993 with one person and one microscope, and today, it has grown to have seven staff and become a world-leading microscopy facility for the physical and life sciences.





## IAC team members:



Nan Yao John Schreiber Paul Shao Denis Potapenko Dan McNesby Kevin Lamb Gary Cheng Pengcheng Chen

## IAC faculty users from Princeton:

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Sujit Datta

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### *Geosciences*

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Satish Myneni  
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Michael Hecht  
Greg Scholes  
Haw Yang  
Leslie M. Schoop  
Marissa Weichman  
Mohammad Seyedsayamdost  
Salvatore Torquato

### *Materials Institute*

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Zuzanna Lewicka

### *Neuroscience Institute*

Sebastian Seung

### *Physics*

Chris Tully  
Jason Petta  
Mojtaba Safabakhsh  
Phuan Ong  
Sanfeng Wu  
Zahid Hasan

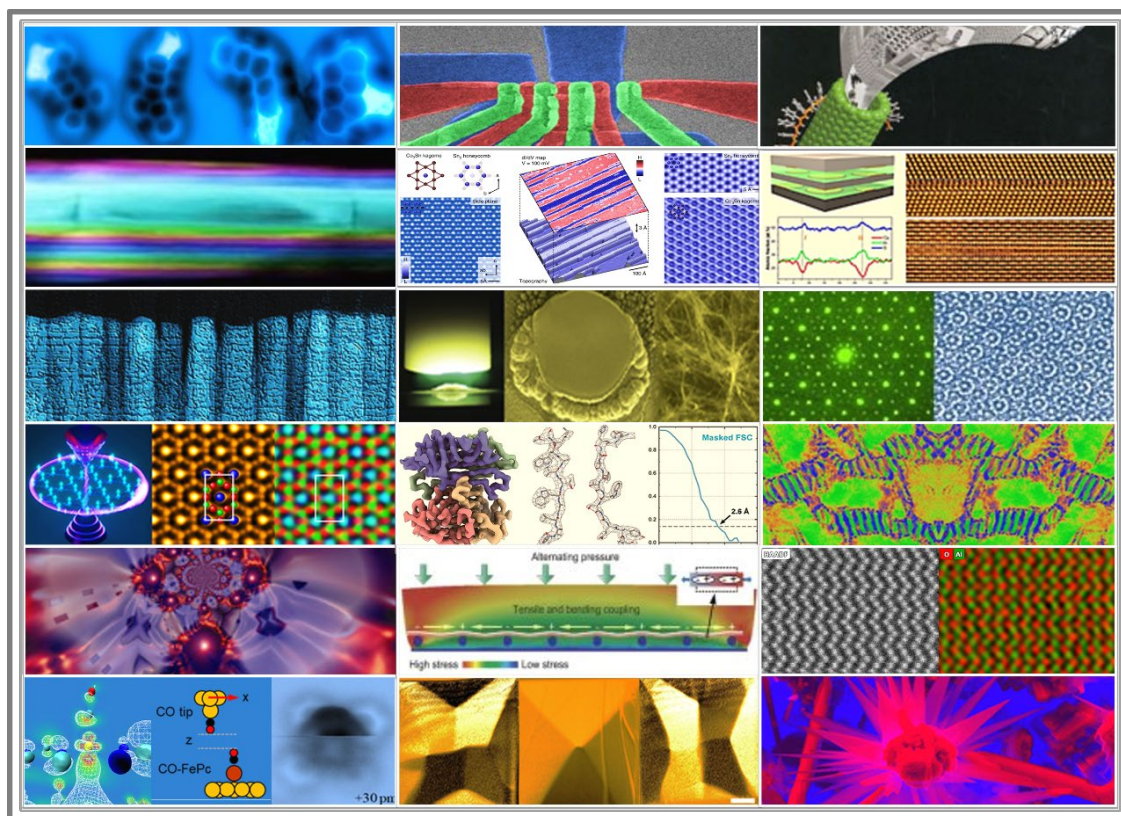
### *Plasma Physics Lab.*

Robert Goldston  
Philip Efthimion  
Yevgeny Raitses

IAC outside users from industry and other universities in recent years:



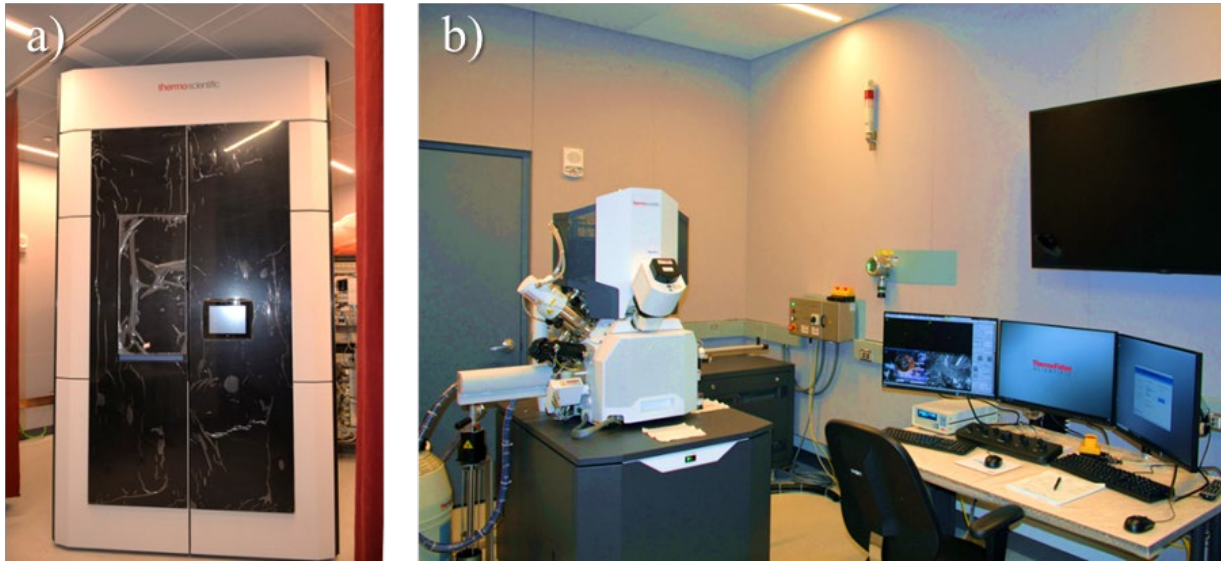
IAC research images highlight:



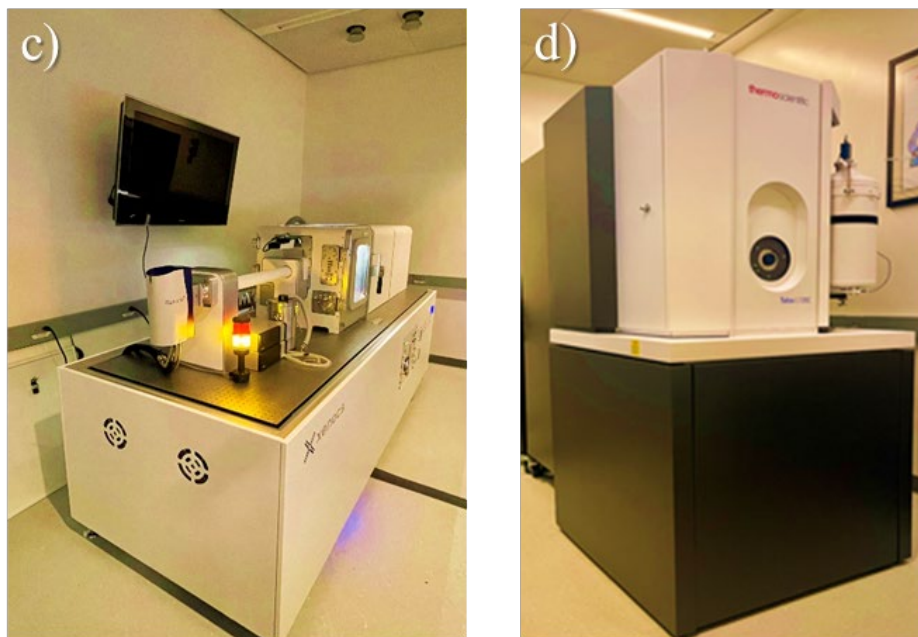


## Recent new instruments in the IAC

**a) Thermo Fisher Krios G4 Cryo-TEM**, and **b) Aquilos 2 Cryo FIB/SEM** (funds from Dean for Research, Molecule Biology Department, Princeton Materials Institute (via BMS)).



**c) Xenocs Xeuss 3.0 Small-angle X-ray Scattering System (SAXS)**, and **d) Talos L120C G2 TEM** (supported by the Princeton Center for Complex Materials (PCCM), a National Science Foundation (NSF) Materials Research Science and Engineering Center (MRSEC; DMR-2011750), and the Dean for Research, respectively).





**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.

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# RESEARCH

ADVANCING THE FRONTIERS OF KNOWLEDGE

IMAGING AND ANALYSIS CENTER

## SEEING CLEARLY

*A team led by Princeton researchers is the first to directly observe and distinguish electron orbital structures of atoms within a molecule. In the image here, captured using an atomic force microscope, iron and cobalt, which are chemically similar, can be distinguished by their shapes (the iron atom is square-like) and brightness (cobalt is brighter). "People have predicted certain orbital structures, but they have never seen them," said Professor Nan Yao, director of Princeton's Imaging and Analysis Center (IAC), where the image was produced. The research was published in the journal Nature Communications in March.*



**FOR MORE** Princeton research news visit [PAW.PRINCETON.EDU](https://www.paw.princeton.edu).

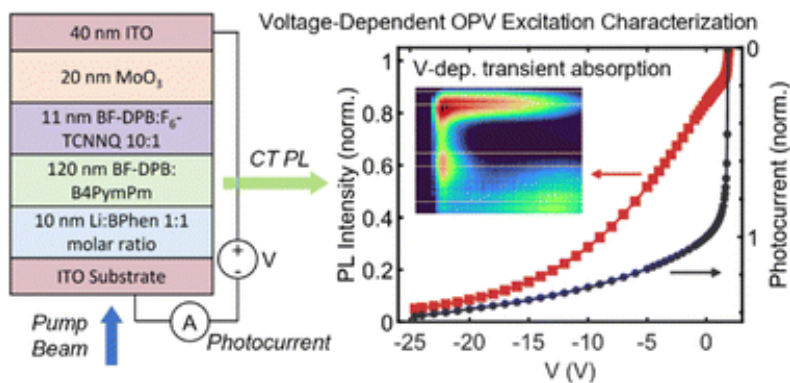
NOVEMBER 2023 PRINCETON ALUMNI WEEKLY 25

## **Andlinger Center for Energy and the Environment**

## Voltage-dependent excitation dynamics in UV-absorbing organic photovoltaics with efficient charge transfer exciton emissions

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Intermolecular charge-transfer excitons play a central role in determining the performance of organic solar cells as their voltage-dependent formation, dissociation, and recombination dynamics contribute to photocurrent generation, radiative/nonradiative voltage losses, and photovoltaic fill factor. Here, we explore the properties of brightly-emitting wide energy gap ( $>2$  eV) charge transfer excitons by measuring the voltage-dependent photoluminescence, photocurrent, and ultrafast pump–probe transient absorption spectra of organic solar cells employing five UV-absorbing donor molecules that differ only by the length of the oligophenylene or acene group at their core. We find that organic solar cells with a strong correlation between their voltage-dependent photocurrent and charge-transfer exciton photoluminescence have low photovoltaic fill factors as they require voltage to facilitate efficient charge-transfer exciton dissociation. In contrast, solar cells that are efficient can readily generate charges without an applied field and have a separate population of tightly-bound charge-transfer excitons that are responsible for emission. Considering that the sum of all excitation loss rates (i.e., recombination and charge extraction) must be equal to the excitation generation rate in the steady state, these voltage-dependent data allow us to solve for the voltage-dependent fate of all excitations in the solar cells and estimate upper and lower bounds for geminate and non-geminate recombination, respectively.

**Status:** published work in Energy Environ. Sci. 2023, **16**, 1742



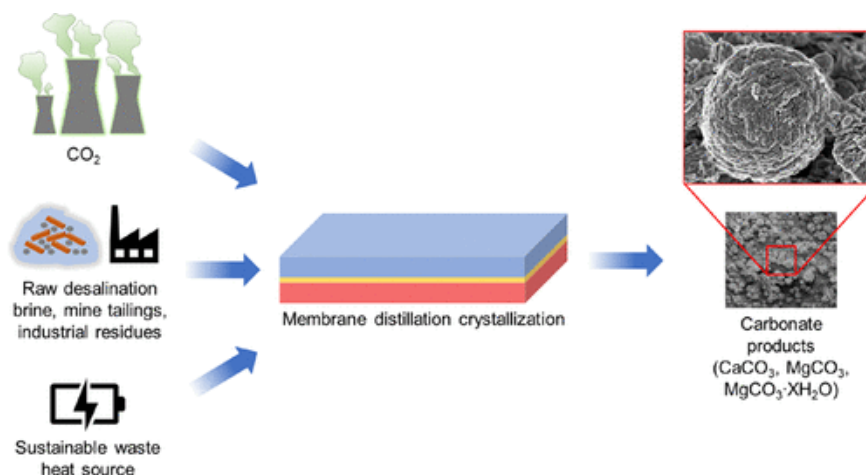
# Membrane Distillation–Crystallization for Sustainable Carbon Utilization and Storage

Kofi S. S. Christie,<sup>1,2</sup> Allyson McGaughey,<sup>1,3</sup> Samantha A. McBride,<sup>3</sup> Xiaohui Xu,<sup>3</sup> Rodney D. Priestley,<sup>3</sup> and Zhiyong Jason Ren<sup>1,2</sup>

<sup>1</sup>Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States;

<sup>2</sup>Department of Civil and Environmental Engineering, Princeton University, Princeton, New Jersey, United States;

<sup>3</sup>Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, United States.



Anthropogenic greenhouse gas emissions from power plants can be limited using postcombustion carbon dioxide capture by amine-based solvents. However, sustainable strategies for the simultaneous utilization and storage of carbon dioxide are limited. In this study, membrane distillation–crystallization is used to facilitate the controllable production of carbonate minerals directly from carbon dioxide-loaded amine solutions and waste materials such as fly ash residues and waste brines from desalination. To identify the most suitable conditions for carbon mineralization, we vary the membrane type, operating conditions, and system configuration. Membranes with lower surface energy and greater roughness are found to more rapidly promote mineralization due to up to 20% greater vapor flux. Lower operating temperature improves membrane wetting tolerance by 96.2% but simultaneously reduces crystal growth rate by 48.3%. Sweeping gas membrane distillation demonstrates a 71.6% reduction in the mineralization rate and a marginal improvement (37.5%) on membrane wetting tolerance. Mineral identity and growth characteristics are presented, and the analysis is extended to explore potential improvements for carbon mineralization and the feasibility of future implementation.

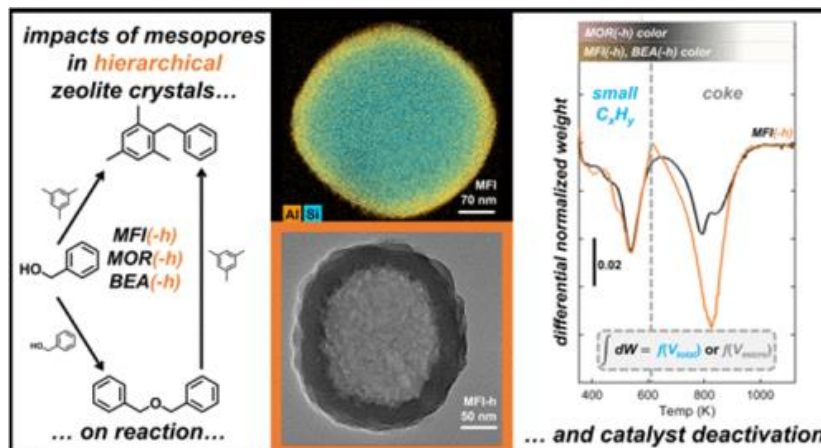
**Status:** published work in Environ. Sci. Technol. 2023, **57**, 16628–16640

## **Department of Chemical and Biological Engineering**

# Underpinnings of Carbonaceous Deposition among Structurally Diverse Hierarchical Zeolites during Hydrocarbon Upgrading

Hayat I. Adawi, Yiteng Zheng, and Michele L. Sarazen

Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, USA



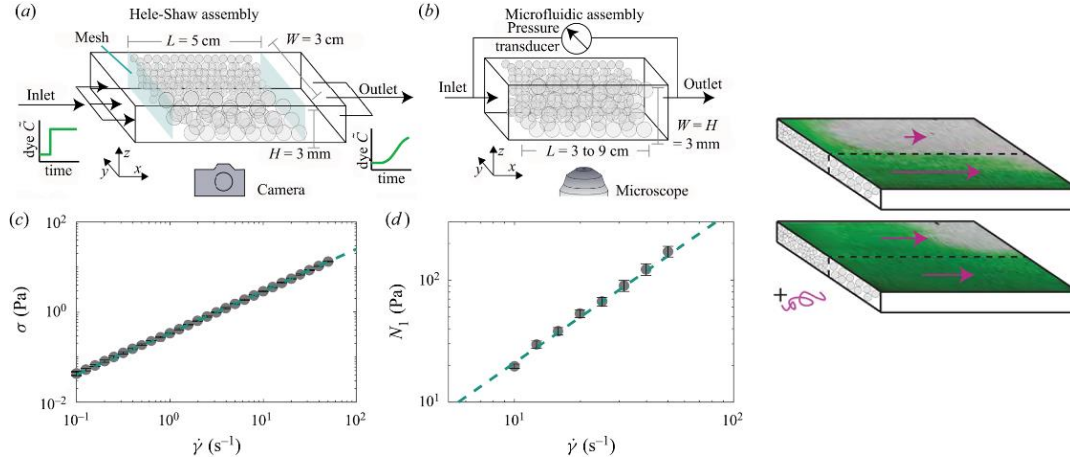
This work examines how engineered hierarchical (microporous–mesoporous) zeolites influence deactivation during hydrocarbon upgrading. Accumulations of carbonaceous deposits in microporous (MFI, MOR BEA), hierarchical (MFI-h, MOR-h, BEA-h), and mesoporous (Al-MCM-41) aluminosilicates at differing crystal size regimes and pore topologies are evaluated as functions of overarching material descriptors like surface areas and pore volumes after liquid-phase, batch alkylation of 1,3,5-trimethylbenzene with benzyl alcohol. Thermogravimetric analysis of spent catalysts shows that total foulant accumulation increases linearly with BET surface area, even absent considerations of physical nuances, chemical nuances, among diverse hierarchical zeolites prepared by demetalation or recrystallization. Comparing calcination (O<sub>2</sub>) to pyrolysis (inert) in TGA reveals two foulant classes that preferentially deposit in micropores or mesopores: low organics decomposing at 353–623 K and coke combusting at 623–1073 K. Mass spectrometry of foulants and Raman spectroscopy of catalysts show that low organics are strongly adsorbed reaction species from the alkylation network, while coking involves occlusion of undesired graphitic products of polyalkylation and dehydration. These investigations yield general insights into fouling behaviors of zeolites having broad synthetic diversity.

**Status:** published work in *Crystal Growth & Design* 2023, **23**, 2675–2688

# Homogenizing fluid transport in stratified porous media using an elastic flow instability

Christopher A. Browne, Richard B. Huang, Callie W. Zheng and Sujit S. Datta

Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA



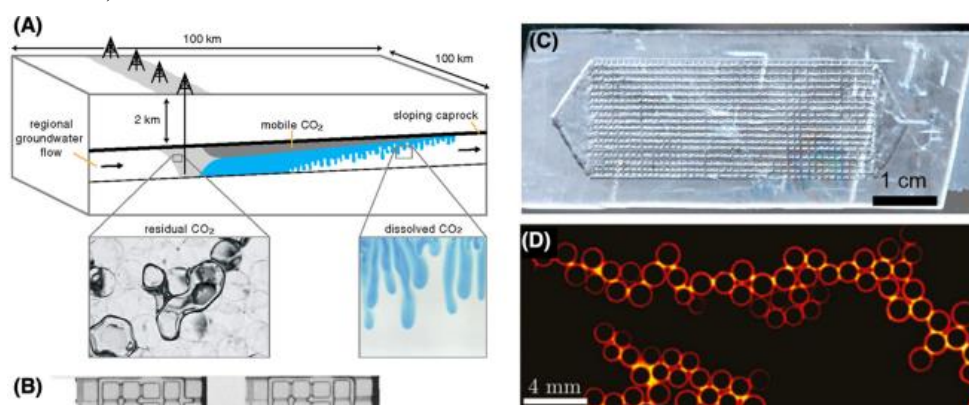
Many key environmental, industrial and energy processes rely on controlling fluid transport within subsurface porous media. These media are typically structurally heterogeneous, often with vertically layered strata of distinct permeabilities – leading to uneven partitioning of flow across strata, which can be undesirable. Here, using direct in situ visualization, we demonstrate that polymer additives can homogenize this flow by inducing a purely elastic flow instability that generates random spatio-temporal fluctuations and excess flow resistance in individual strata. In particular, we find that this instability arises at smaller imposed flow rates in higher-permeability strata, diverting flow towards lower-permeability strata and helping to homogenize the flow. Guided by the experiments, we develop a parallel-resistor model that quantitatively predicts the flow rate at which this homogenization is optimized for a given stratified medium. Thus, our work provides a new approach to homogenizing fluid and passive scalar transport in heterogeneous porous media

**Status:** published work in J. Fluid Mech. 2023, **963**, A30

## Lab on a chip for a low-carbon future

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Transitioning our society to a sustainable future, with low or net-zero carbon emissions to the atmosphere, will require a wide-spread transformation of energy and environmental technologies. In this perspective article, we describe how lab-on-a-chip (LoC) systems can help address this challenge by providing insight into the fundamental physical and geochemical processes underlying new technologies critical to this transition, and developing the new processes and materials required. We focus on six areas: (I) subsurface carbon sequestration, (II) subsurface hydrogen storage, (III) geothermal energy extraction, (IV) bioenergy, (V) recovering critical materials, and (VI) water filtration and remediation. We hope to engage the LoC community in the many opportunities within the transition ahead, and highlight the potential of LoC approaches to the broader community of researchers, industry experts, and policy makers working toward a low-carbon future

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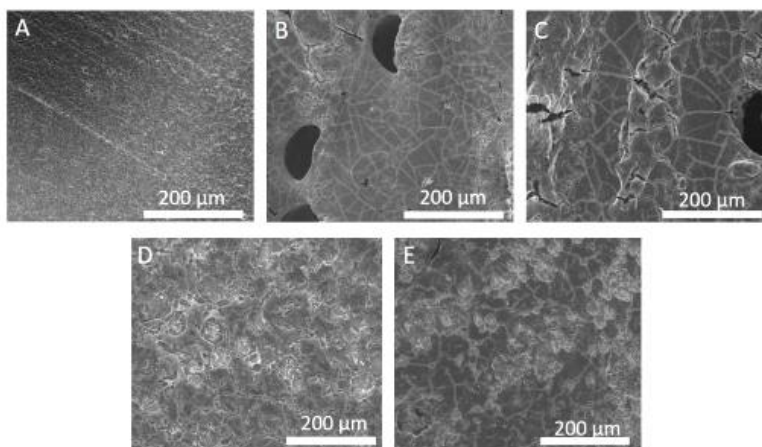


## Air Stabilization of $\text{Li}_7\text{P}_3\text{S}_{11}$ Solid-State Electrolytes through Laser-Based Processing

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All-solid-state batteries (ASSBs) that employ solid-state electrolytes (SSEs) have the potential to replace more conventional batteries that employ liquid electrolytes due to their inherent safety, compatibility with lithium metal and reputable ionic conductivity.  $\text{Li}_7\text{P}_3\text{S}_{11}$  is a promising SSE with reported ionic conductivities in the order of 10 mS/cm. However, its susceptibility to degradation through oxidation and hydrolysis limits its commercial viability. In this work, we demonstrate a laser-based processing method for SSEs to improve humidity stability. It was determined that laser power and scanning speed greatly affect surface morphology, as well as the resulting chemical composition of  $\text{Li}_7\text{P}_3\text{S}_{11}$  samples. Electrochemical impedance spectroscopy revealed that laser treatment can produce SSEs with higher ionic conductivities than pristine counterparts after air exposure. Further examination of chemical composition revealed an optimal laser processing condition that reduces the rate of  $\text{P}_2\text{S}_7^{4-}$  degradation. This work demonstrates the ability of laser-based processing to be used to improve the stability of SSEs.

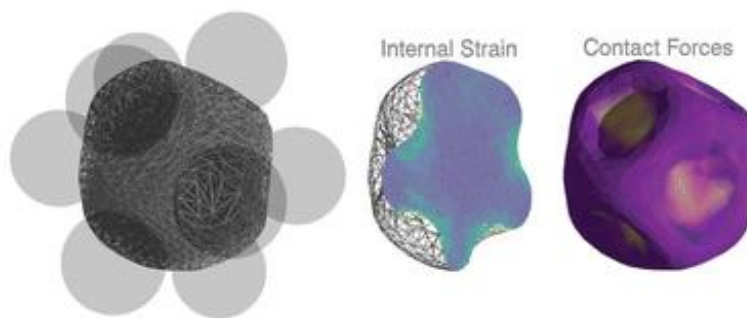
**Status:** published work in *Nanomaterials* 2023, **13**, 2210

## An energy-optimization method to study gel-swelling in confinement

Chaitanya Joshi,<sup>1</sup> Mathew Q. Giso,<sup>1</sup> Jean-François Louf,<sup>2</sup> Sujit S. Datta,<sup>3</sup> and Timothy J. Atherton<sup>1</sup>

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Simulating swollen hydrogels under confinement using *Morpho*



We recast the problem of hydrogel swelling under physical constraints as an energy optimization problem. We apply this approach to compute equilibrium shapes of hydrogel spheres confined within a jammed matrix of rigid beads and interpret the results to determine how confinement modifies the mechanics of swollen hydrogels. In contrast to the unconfined case, we find a spatial separation of strains within the bulk of the hydrogel as the strain becomes localized to an outer region. We also explore the contact mechanics of the gel, finding a transition from Hertzian behavior to non-Hertzian behavior as a function of swelling. Our model, implemented in the *Morpho* shape optimization environment and validated against an experimentally demonstrated prototypical scenario, can be applied in any dimension, readily adapted to diverse swelling scenarios and extended to use other energies in conjunction

**Status:** published work in *Soft Matter* 2023, **19**, 7184

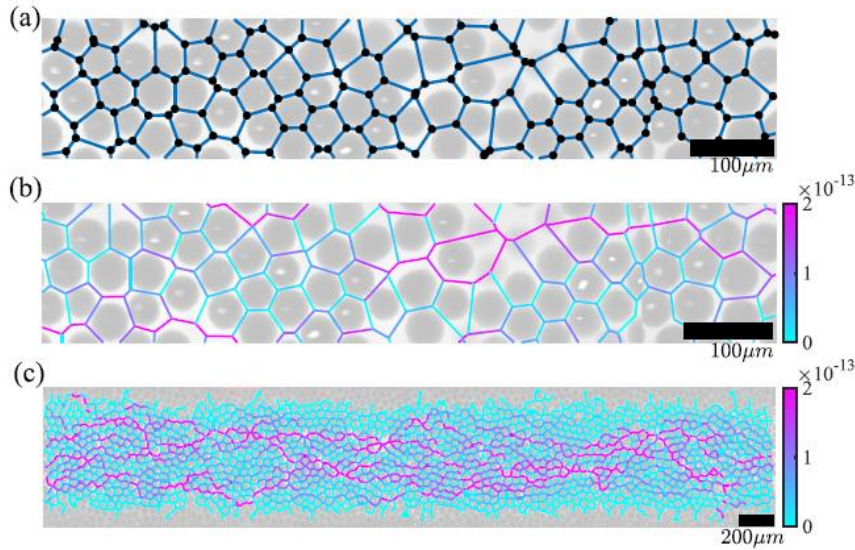
# Modeling the Transition between Localized and Extended Deposition in Flow Networks through Packings of Glass Beads

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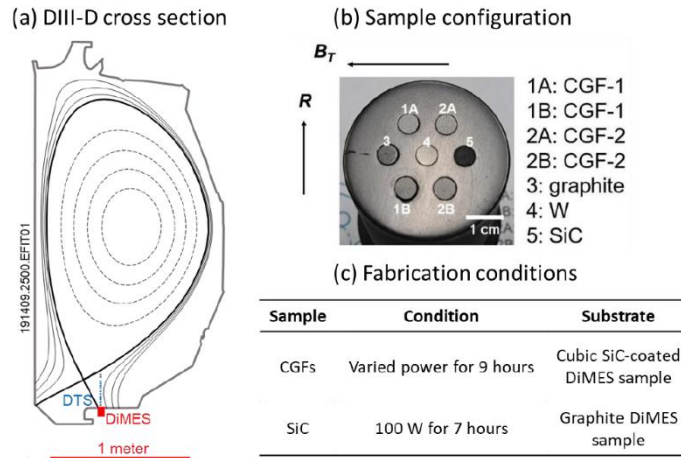
We use a theoretical model to explore how fluid dynamics, in particular, the pressure gradient and wall shear stress in a channel, affect the deposition of particles flowing in a microfluidic network. Experiments on transport of colloidal particles in pressure-driven systems of packed beads have shown that at lower pressure drop, particles deposit locally at the inlet, while at higher pressure drop, they deposit uniformly along the direction of flow. We develop a mathematical model and use agent-based simulations to capture these essential qualitative features observed in experiments. We explore the deposition profile over a two-dimensional phase diagram defined in terms of the pressure and shear stress threshold, and show that two distinct phases exist. We explain this apparent phase transition by drawing an analogy to simple one-dimensional mass-aggregation models in which the phase transition is calculated analytically.

**Status:** published work in Physical Review Letters 2023, **130**, 128204

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

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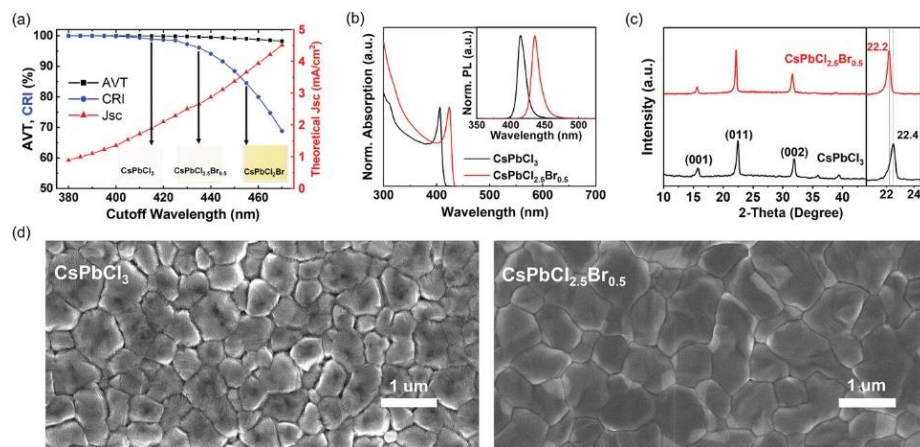
W-SiC composite material is a promising alternative due to the low neutron activation, low impurity radiation, and ductility of SiC at high temperatures while leveraging the high erosion resistance of the W armor. The present study addresses the synthesis and performance of compositionally graded W-SiC 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 L-mode 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.

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# Highly Transparent, Scalable, and Stable Perovskite Solar Cells with Minimal Aesthetic Compromise

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Transparent photovoltaics (TPVs) can be integrated into the surfaces of buildings and vehicles to provide point-of-use power without impacting aesthetics. Unlike TPVs that target the photon-rich near-infrared portion of the solar spectrum, TPVs that harvest ultraviolet (UV) photons can have significantly higher transparency and color neutrality, offering a superior solution for low-power electronics with stringent aesthetic tolerance. In addition to being highly transparent and colorless, an ideal UV-absorbing TPV should also be operationally stable and scalable over large areas while still outputting sufficient power for its specified application. None of today's TPVs meet all these criteria simultaneously. Here, the first UV-absorbing TPV is demonstrated that satisfies all four criteria by using CsPbCl<sub>2.5</sub>Br<sub>0.5</sub> as the absorber. By precisely tuning the halide ratio during thermal co-evaporation, high-quality large-area perovskite films can be accessed with an ideal absorption cutoff for aesthetic performance. The resulting TPVs exhibit a record average visible transmittance of 84.6% and a color rendering index of 96.5, while maintaining an output power density of 11 W m<sup>-2</sup> under one-sun illumination. Further, the large-area prototypes up to 25 cm<sup>2</sup> are demonstrated, that are operationally stable with extrapolated lifetimes of >20 yrs under outdoor conditions.

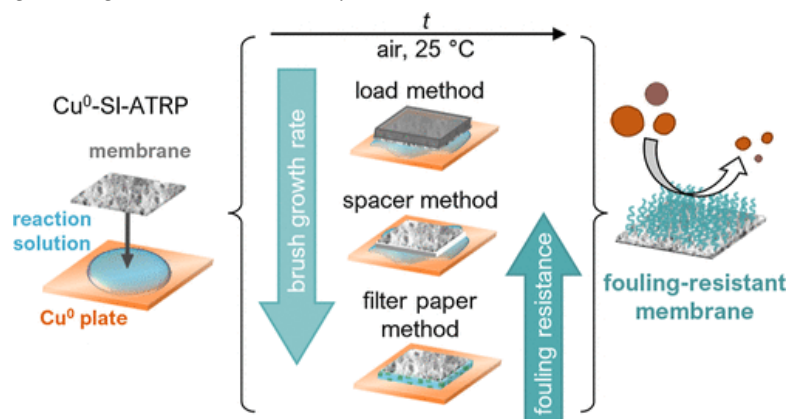
**Status:** published work in Adv. Energy Mater. 2022, 2200402



# Scalable Zwitterionic Polymer Brushes for Antifouling Membranes via Cu<sup>0</sup>-Mediated Atom Transfer Radical Polymerization

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<sup>1</sup>Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA; <sup>2</sup>Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA; <sup>3</sup>Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ, USA



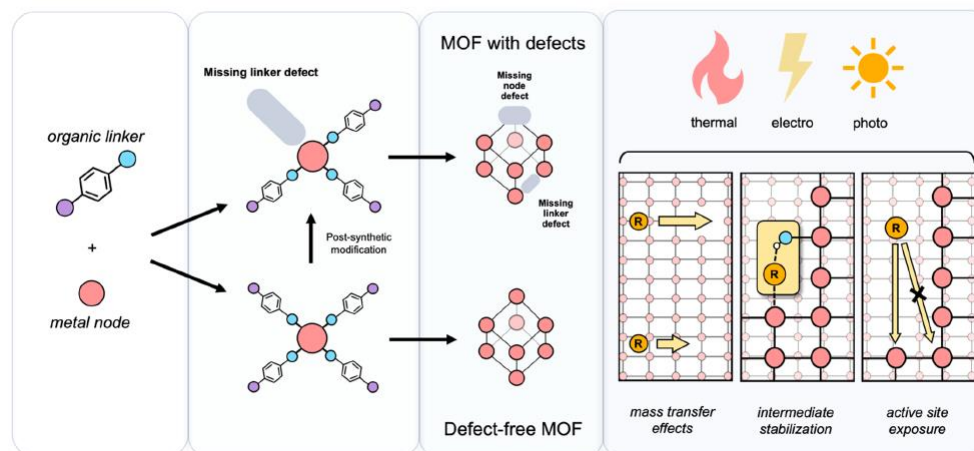
Polymer brush layers have attracted significant interest for versatile, controlled surface modification enabling fabrication and functionalization of membranes for water treatment and reuse applications. However, there are significant challenges associated with commercial scale-up of traditional fabrication methods. In this work, we demonstrate scalable grafting of zwitterionic polymer brushes from microfiltration membrane substrates under ambient conditions, and with low chemical consumption, for the first time, via Cu<sup>0</sup>-mediated surface-initiated atom transfer radical polymerization (Cu<sup>0</sup>-SI-ATRP). We demonstrate that Cu<sup>0</sup>-SI-ATRP is effective for brush grafting from porous membrane substrates, including samples of up to 150 cm<sup>2</sup>. Furthermore, we systematically investigate the effect of polymerization in confinement on brush growth kinetics and fouling resistance, using colloid probe force microscopy and dynamic fouling experiments. Results demonstrate that Cu<sup>0</sup>-SI-ATRP results in poly(sulfobetaine methacrylate) brush layers that significantly improve fouling resistance; however, polymerization methods significantly impact fouling resistance. We identify polymerization methods that enhance fouling resistance even for thin brush layers. The results of this study provide pathways to the scalable fabrication and design of robust, antifouling membranes.

**Status:** published work in ACS Appl. Polym. Mater. 2023, **5**, 4921–4932

# Kinetic Impacts of Defect Sites in Metal–Organic Framework Catalysts under Varied Driving Forces

Samuel C. Moore,<sup>1</sup> Michael R. Smith,<sup>2</sup> James L. Trettin,<sup>1</sup> Rachel A. Yang,<sup>1</sup> and Michele L. Sarazen.<sup>1</sup>

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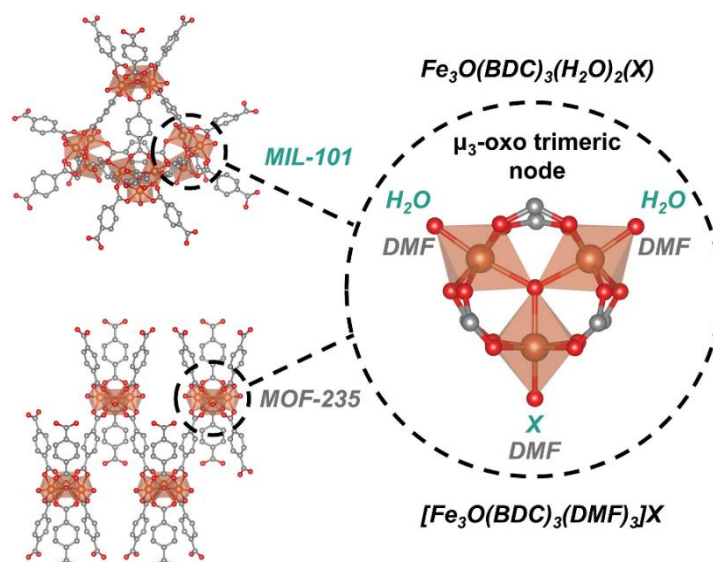
Defects in metal–organic frameworks (MOFs) primarily manifest as missing linkers or metal nodes induced through synthesis, post-synthetic modification, and/or exposure to reaction conditions. By changing the nature of active site(s) and perturbing crystalline frameworks, defects confer physicochemical alterations to MOF catalysts that may promote or inhibit intrinsic reactivity, electron transfer and excitation, and mass transport. However, the complexity and dynamic character of defects often obfuscate the structure–function relations needed to permit rational catalyst design. Here, highlights of recent studies examining the impact of MOF defects in thermo-, photo-, and electrocatalytic systems pertinent to energy applications demonstrate progress toward identifying defect impacts on MOF catalysis, particularly for widely studied zirconium-based frameworks. Moreover, the combination of ex situ and operando/in situ defect identification and quantification will be paramount in future research to improve the mechanistic understanding of MOF-catalyzed systems for energy conversion but also extends to MOF energy storage, photovoltaics, and gas separations/storage applications.

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## Stability and kinetics of iron-terephthalate MOFs with diverse structures in aqueous pollutant degradation

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Synthesized iron-terephthalate metal–organic frameworks (MOFs), MIL-101 and MOF-235, with contrasting morphologies are examined to elucidate the role of structural arrangement in catalytic aqueous pollutant degradation. MIL-101 demonstrates a larger pseudo-first order rate constant than MOF-235 ( $3.5 \pm 0.2 \text{ molFe}^{-1} \cdot \text{s}^{-1}$  vs.  $0.84 \pm 0.07 \text{ molFe}^{-1} \cdot \text{s}^{-1}$ ) toward oxidation of methylene blue (MB) dye with excess hydrogen peroxide at ambient temperature, likely due to intrinsic differences in ligand coordination at their metal nodes. However, despite continued activity upon reuse, both MOFs undergo structural alterations resulting in formation of leached species active for MB degradation that have been obfuscated in previous studies. Detailed stability testing and ex situ characterization of recovered catalyst, examinations that remain underreported in Fe-MOF studies for pollutant oxidation, indicate that water plays a prominent role in the breakdown of these frameworks. This work informs the interpretation and use of common Fe-MOFs for aqueous applications, relating material changes to observed reaction phenomena.

**Status:** published work in AICHE Journal 2023, **69**, e18205.

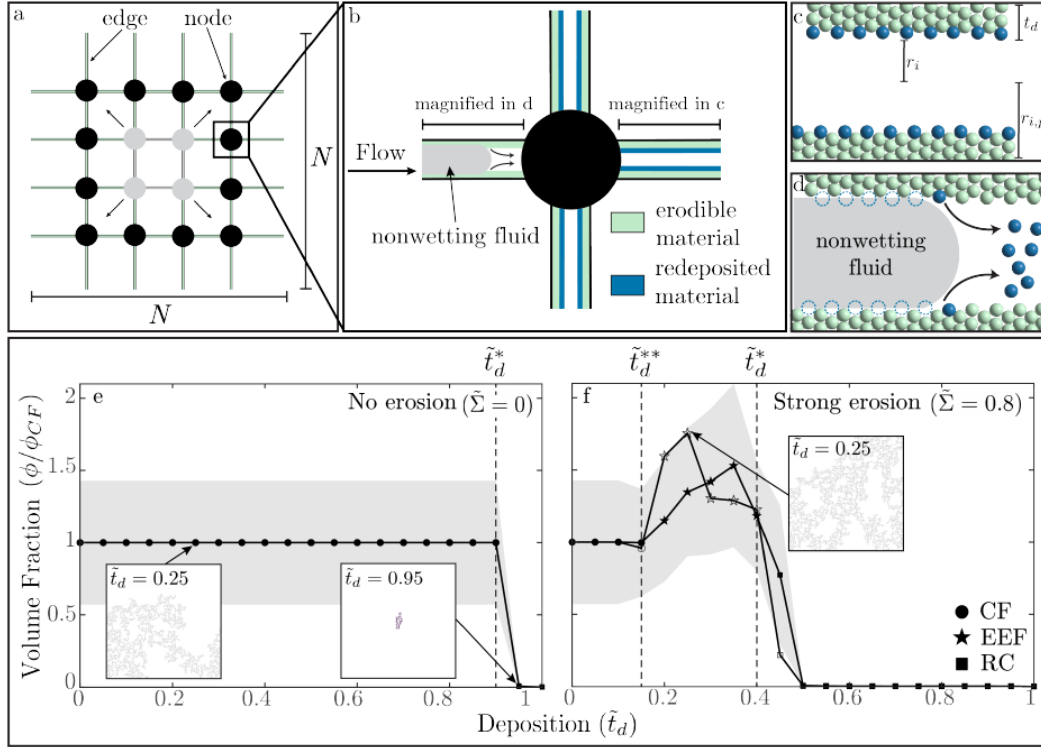
## Fluid drainage in erodible porous media

Joanna Schneider,<sup>1</sup> Christopher A. Browne,<sup>1</sup> Malcolm Slutzky,<sup>2</sup> Cecilia A. Quirk,<sup>3</sup> Daniel B. Amchin,<sup>1</sup> Sujit S. Datta<sup>1</sup>

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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 new drainage behaviors with markedly different characteristics, and quantitatively delineate the conditions under which they arise. Our results thereby help expand current understanding of these rich physics, with implications for applications of drainage in industry and the environment.

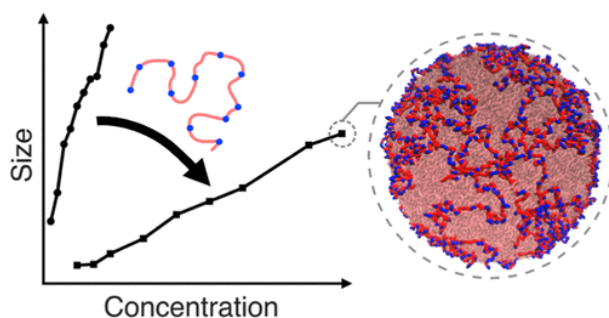
**Status:** work posted on arXiv.org: 2303.01260, 2023



## Rapid Precipitation of Ionomers for Stabilization of Polymeric Colloids

Douglas M. Scott,<sup>1</sup> Arash Nikoubashman,<sup>2</sup> Richard A. Register,<sup>1,3</sup> Rodney D. Priestley,<sup>1,3</sup> Robert K. Prud'homme<sup>1</sup>

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Polymeric colloids have shown potential as “building blocks” in applications ranging from formulations of Pickering emulsions and drug delivery systems to advanced materials, including colloidal crystals and composites. However, for applications requiring tunable properties of charged colloids, obstacles in fabrication can arise through limitations in process scalability and chemical versatility. In this work, the capabilities of flash nanoprecipitation (FNP), a scalable nanoparticle (NP) fabrication technology, are expanded to produce charged polystyrene colloids using sulfonated polystyrene ionomers as a new class of NP stabilizers. Through experimental exploration of formulation parameters, increases in the ionomer content are shown to reduce the particle size, mitigating a significant trade-off between the final particle size and inlet concentration; thus, expanding the processable material throughput of FNP. Further, the degree of sulfonation is found to impact stabilization with optimal performance achieved by selecting ionomers with intermediate (2.45–5.2 mol %) sulfonation. Simulations of single ionomer chains and their arrangement in multicomponent NPs provide molecular insights into the assembly and structure of NPs wherein the partitioning of ionomers to the particle surface depends on the polymer molecular weight and degree of sulfonation. By combining the insights from simulations with diffusion-limited growth kinetics and parametric fits to experimental data, a simple design formulation relation is proposed and validated. This work highlights the potential of ionomer-based stabilizers for controllably producing charged NP dispersions in a scalable manner.

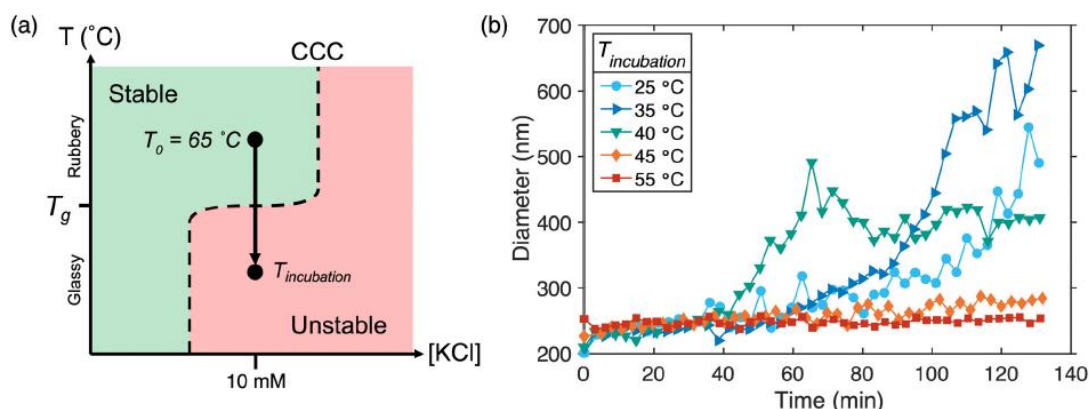
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## Effects of the polymer glass transition on the stability of nanoparticle dispersions

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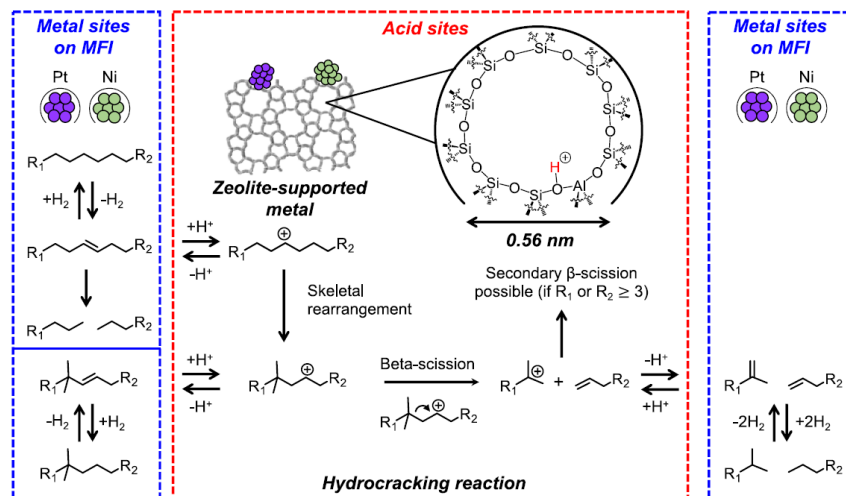
In addition to the repulsive and attractive interaction forces described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, many charged colloid systems are stabilized by non-DLVO contributions stemming from specific material attributes. Here, we investigate non-DLVO contributions to the stability of polymer colloids stemming from the intra-particle glass transition temperature ( $T_g$ ). Flash nanoprecipitation is used to fabricate nanoparticles (NPs) from a library of polymers and dispersion stability is studied in the presence of both hydrophilic and hydrophobic salts. When adding KCl, stability undergoes a discontinuous decrease as  $T_g$  increases above room temperature, indicating greater stability of rubbery NPs over glassy NPs. Glassy NPs are also found to interact strongly with hydrophobic phosphonium cations ( $PR_4^+$ ), yielding charge inversion and intermediate aggregation while rubbery NPs resist ion adsorption. Differences in the lifetime of ionic structuration within mobile surface layers is presented as a potential mechanism underlying the observed phenomenon.

**Status:** published work in Soft Matter, 2023, **19**, 1212–1218

# Conversion of polyethylene waste to short chain hydrocarbons under mild temperature and hydrogen pressure with metal-free and metal-loaded MFI zeolites

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Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States



Catalytic hydrocracking on supported metal zeolites promisingly converts waste plastics into more valuable hydrocarbons. Although the presence of metal sites on solid acids is typically considered necessary for C-C bond cleavage of alkanes at modest temperatures, we show that polyethylene (PE) depolymerization on metal-free MFI zeolites proceeds at higher rates than analogous metal-loaded MFI zeolites (Pt, Ni) under mild reaction conditions. Higher rates on metal-free MFI are consistent with higher ratios of alkenes to alkanes, leading to subsequent alkene-mediated beta-scission events that form smaller molecules. Under varied reaction conditions (e.g., temperature, pressure, H<sub>2</sub> versus N<sub>2</sub>), both metal-free and metal-loaded MFI catalysts demonstrate high selectivity to C<sub>3</sub>-C<sub>7</sub> gaseous hydrocarbons, likely due to the 10-MR channel structure. Collectively, these findings demonstrate the importance of deconvoluting metal and acid sites contributions for PE hydrocracking, which has significant implications on rates and product selectivities of plastic upcycling reactions.

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Xiaohui Xu,<sup>1</sup> N  h  mie Guillomaitre,<sup>1,2</sup> Kofi S. S. Christie,<sup>3,4</sup> R. K  nane Bay,<sup>1</sup> Navid Bizmark,<sup>1,5</sup>  
Sujit S. Datta,<sup>1</sup> Zhiyong Jason Ren,<sup>3,4</sup> and Rodney D. Priestley<sup>1,5</sup>

The diagram illustrates the mechanism of the L-PNIPAm-based smart membrane for oil-water separation. The top part shows the L-PNIPAm network in its swollen state, with an inset showing a hydration layer and water flow. The bottom part shows the transition to the collapsed state (LSAG) upon heating ( $T > LCST$ ), which leads to rapid water release and antifouling properties. A graph shows mass change over time, and a SEM image shows the membrane structure.

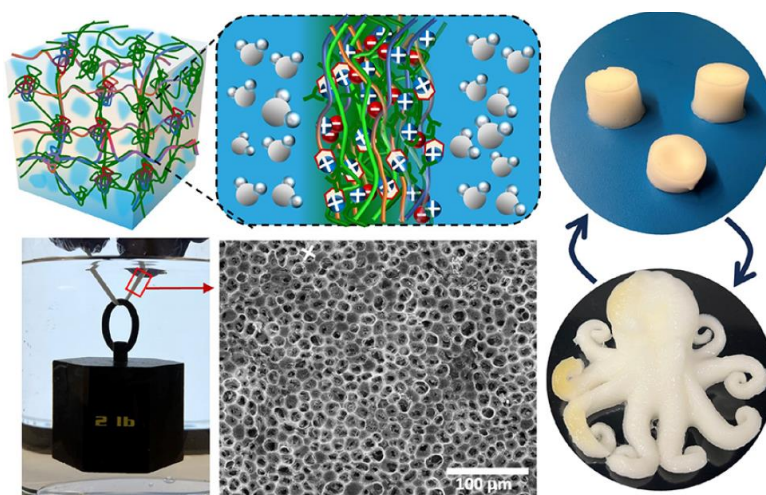
**Status:** published work in ACS Central Science 2023, **9**, 177-185



## Tough and Recyclable Phase-Separated Supramolecular Gels via a Dehydration–Hydration Cycle

Xiaohui Xu,<sup>1</sup> Yannick L. Eatmon,<sup>2</sup> Kofi S. S. Christie,<sup>3,4</sup> Allyson L. McGaughey,<sup>3,4</sup> Néhémie Guillomaitre,<sup>1,2</sup> Sujit S. Datta,<sup>1</sup> Zhiyong Jason Ren,<sup>3,4</sup> Craig Arnold,<sup>2</sup> and Rodney D. Priestley<sup>1,5</sup>

<sup>1</sup>Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA; <sup>2</sup>Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA; <sup>3</sup>Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ, USA; <sup>4</sup>Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA; <sup>5</sup>Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, NJ, USA.



Hydrogels are compelling materials for emerging applications including soft robotics and autonomous sensing. Mechanical stability over an extensive range of environmental conditions and considerations of sustainability are enduring challenges. To make progress on these challenges, we designed a dehydration-hydration approach to transform soft and weak hydrogels into tough and recyclable supramolecular phase-separated gels (PSGs) using water as the only solvent. The dehydration–hydration approach led to phase separation and the formation of domains consisting of strong polymer–polymer interactions. The phase-separated segments acted as robust, physical cross-links to strengthen PSGs, which exhibited enhanced toughness and stretchability in its fully swollen state. PSGs are not prone to overswelling or severe shrinkage in wet conditions and show environmental tolerance in harsh conditions, e.g., solutions with pH between 1 and 14. Finally, we demonstrate the use of PSGs as strain sensors in air and aqueous environments.

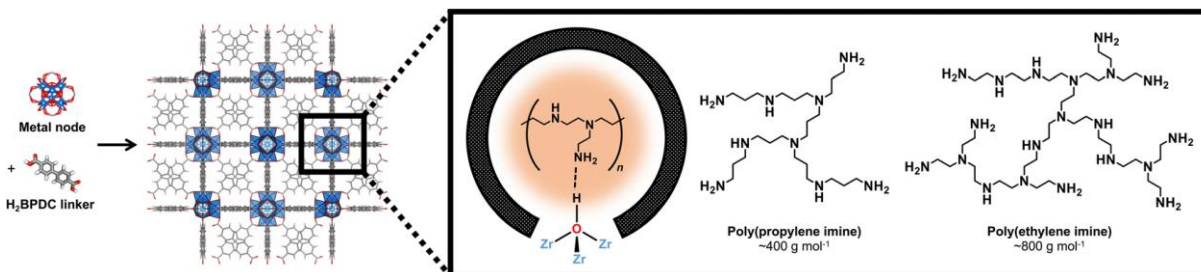
**Status:** published work in J. Am. Chem. Soc. Au 2023, **3**, 2772

## Investigation of storage environments on aminopolymer stabilization within UiO-67(Zr) for CO<sub>2</sub> capture

Rachel A. Yang,<sup>1</sup> Darius R. Ganza,<sup>1</sup> Michael R. Smith,<sup>1,2</sup> Stanley Cho,<sup>1</sup> Jacqueline A. Vandermel,<sup>1</sup> Elizabeth Jiang,<sup>1</sup> and Michele L. Sarazen.<sup>1</sup>

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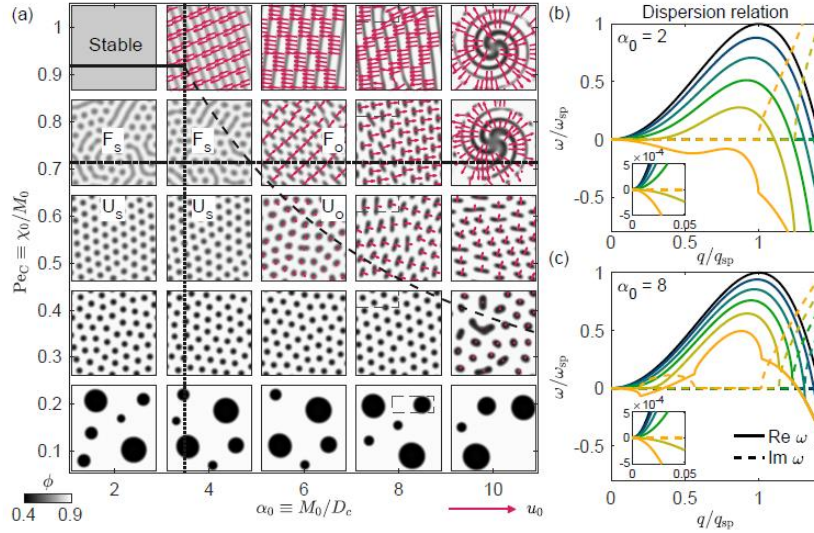
Aminopolymers, poly(ethylene imine) (PEI) and poly(propylene imine) (PPI), are supported within nanoporous UiO-67(Zr) and evaluated for CO<sub>2</sub> capture from simulated flue gas (10% CO<sub>2</sub>) and air (400 ppm CO<sub>2</sub>). N<sub>2</sub> physisorption and Fourier-transform infrared spectroscopy indicate that PEI and PPI are physisorbed in UiO-67(Zr) voids but not tethered to metal nodes or carboxylate backbones. Mass-normalized CO<sub>2</sub> capacity increases with repeated CO<sub>2</sub> uptake-regeneration cycles for 30–50 wt% PPI, suggesting CO<sub>2</sub> diffusion limitations at these higher loadings. 20 wt% PPI/UiO-67(Zr) and 20 wt% PEI/UiO-67(Zr) exposed to ambient air for 7 days demonstrate higher oxidative degradation in PEI than PPI, though PEI oxidation is reduced when stabilized within UiO-67(Zr) relative to when unconfined. Exposure of composites to liquid storage environments of varying polarity, hydrogen-bonding capability, and size indicate that 20 wt% PPI/UiO-67(Zr) amine efficiencies are minimally affected by solvent-induced aminopolymer conformational changes. Conversely, 20 wt% PEI/UiO-67(Zr) is more sensitive to surrounding solvent environments, exhibiting the greatest amine efficiency in methanol and the lowest in acetone due to solvent-induced aminopolymer swelling and reaction, respectively. Overall, this work provides insight into CO<sub>2</sub> capture efficacies and chemical stabilities of composite PEI and PPI materials under various storage environments to inform future adsorbent and system design.

**Status:** published work in Materials Advances 2023, **4**, 901

## Chemotactic motility-induced phase separation

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Collectives of actively-moving particles can spontaneously separate into dilute and dense phases – a fascinating phenomenon known as motility-induced phase separation (MIPS). MIPS is well-studied for randomly-moving particles with no directional bias. However, many forms of active matter exhibit collective chemotaxis, directed motion along a chemical gradient that the constituent particles can generate themselves. Here, using theory and simulations, we demonstrate that collective chemotaxis strongly competes with MIPS – in some cases, arresting or completely suppressing phase separation, or in other cases, generating fundamentally new dynamic instabilities. We establish quantitative principles describing this competition, thereby helping to reveal and clarify the rich physics underlying active matter systems that perform chemotaxis, ranging from cells to robots.

**Status:** published work in Phys. Rev. Lett. 2023, **131**, 118301

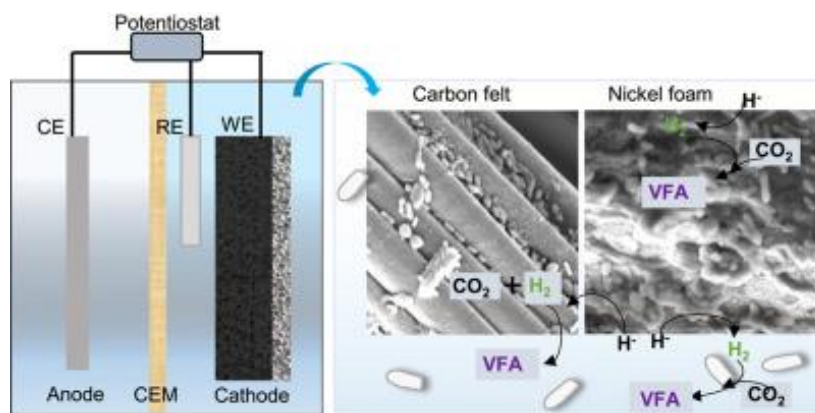
## **Department of Civil and Environmental Engineering**

## H<sub>2</sub> mediated mixed culture microbial electrosynthesis for high titer acetate production from CO<sub>2</sub>

Yanhong Bian,<sup>1,2</sup> Aaron Leininger,<sup>1,2</sup> Harold D. May,<sup>2</sup> Zhiyong Jason Ren<sup>1,2</sup>

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Microbial electrosynthesis (MES) converts CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. Here we report high acetate titers can be achieved via improved in situ H<sub>2</sub> supply by nickel foam decorated carbon felt cathode in mixed community MES systems. Acetate concentration of 12.5 g L<sup>-1</sup> was observed in 14 days with nickel-carbon cathode at a poised potential of -0.89 V, which was much higher than cathodes using stainless steel (5.2 g L<sup>-1</sup>) or carbon felt alone (1.7g L<sup>-1</sup>) with the same projected surface area. A higher acetate concentration of 16.0 g L<sup>-1</sup> 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<sup>-1</sup>) was also found in the abiotic anode chamber. We observed the low Faradaic efficiencies in acetate production, attributed to partial H<sub>2</sub> utilization for electrosynthesis. The selective acetate production with high titer demonstrated in this study shows the H<sub>2</sub>-mediated electron transfer with common cathode materials carries good promise in MES development.

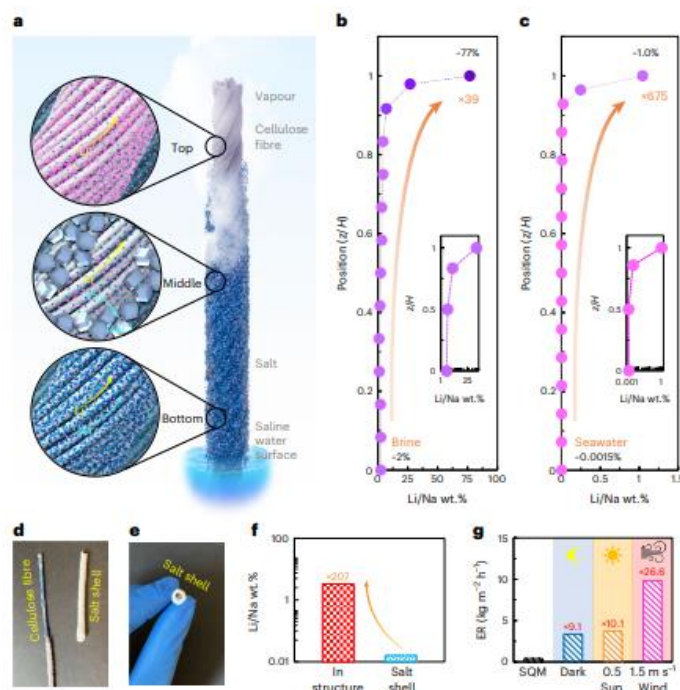
**Status:** published work in Environmental Science and Ecotechnology 2024, **19**, 100324



# Spatially separated crystallization for selective lithium extraction from saline water

Xi Chen,<sup>1,2</sup> Meiqi Yang,<sup>1,2</sup> Sunxiang Zheng,<sup>1,2</sup> Fernando Temprano-Coletto,<sup>2,3</sup> Qi Dong,<sup>4</sup> Guangming Cheng,<sup>5</sup> Nan Yao,<sup>5</sup> Howard A. Stone,<sup>3</sup> Liangbing Hu,<sup>4</sup> & Zhiyong Jason Ren<sup>1,2</sup>

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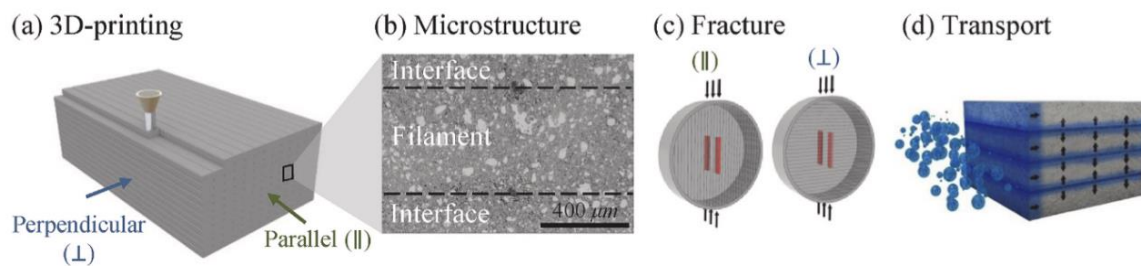
Limited lithium supply is hindering the global transformation towards electrification and decarbonization. Current lithium mining can be energy, chemical and land intensive. Here we present an efficient and self-concentrating crystallization method for the selective extraction of lithium from both brine and seawater. The sequential and separable crystallization of cation species with different concentrations and solubilities was enabled by a twisted and slender 3D porous natural cellulose fibre structure via capillary and evaporative flows. The process exhibited an evaporation rate as high as  $9.8 \text{ kg m}^{-2} \text{ h}^{-1}$ , and it selectively concentrated lithium by orders of magnitude. The composition and spatial distribution of crystals were characterized, and a transport model deciphered the ion re-distribution process in situ. We also demonstrated system scalability via a 100-crystallizer array.

**Status:** published work in Nature Water 2023, **1**, 808–817

# Fracture and transport analysis of heterogeneous 3D-Printed lamellar cementitious materials

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This paper investigates the spatial characteristics of microstructural phases in relation to the fracture toughness in Mode-I/II and transport behavior in two orthogonal directions of lamellar 3D-printed cement paste compared to cast counterparts. Using segmentation techniques, it was found that intact 3D-printed materials represent porous interfaces and microchannels. A modified partial-notch Brazil-Nut test was proposed to characterize the Mode-I/II fracture toughness. A new laser-notching process was proposed to generate a sharp notch and account for the sensitivity of fracture processes to microstructural heterogeneities in 3D-printed materials. Unlike Mode-I, significantly higher Mode-II fracture toughness was found in 3D-printed material in the perpendicular direction compared to the cast, owing to the in/out-of-plane crack deflection along the interfaces. The porous interfacial regions were hypothesized to govern the crack initiation in both Mode-I/II. Water transport was characterized by absorption using Neutron Radiography, where interfacial heterogeneities act as capillary breaks, hence directionally influences water absorption and transport.

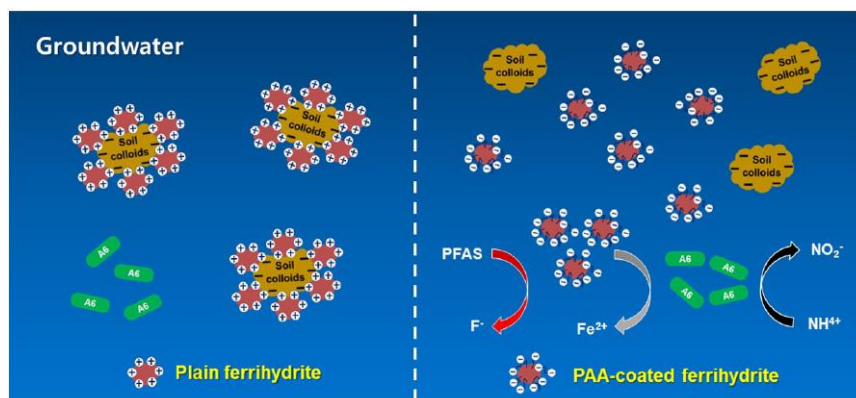
**Status:** Published work in Cement and Concrete Composites 2023, **140**, 105034

## Enhanced Feammox activity and perfluorooctanoic acid (PFOA) degradation by *Acidimicrobium* sp. Strain A6 using PAA-coated ferrihydrite as an electron acceptor

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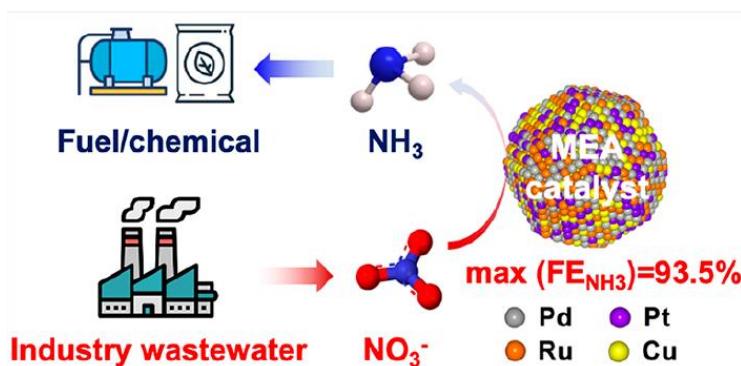
*Acidimicrobium* sp. Strain A6 (A6) can degrade perfluoroalkyl acids (PFAAs) by oxidizing  $\text{NH}_4^+$  while reducing Fe(III). However, supplying and distributing Fe(III) phases in sediments is challenging since surface charges of Fe(III)-phases are typically positive while those of sediments are negative. Therefore, ferrihydrite particles were coated with polyacrylic acid (PAA) with four different molecular weights, resulting in a negative zeta potential on their surface. Zeta potential was determined as a function of pH and PAA loading, with the lowest value observed when the PAA/ferrihydrite ratio was  $> 1/5$  (w/w) at a pH of 5.5. Several 50-day incubations with an A6-enrichment culture were conducted to determine the effect of PAA-coated ferrihydrite as the electron acceptor of A6 on the Feammox activity and PFOA degradation.  $\text{NH}_4^+$  oxidation, PFOA degradation, production of shorter-chain PFAS, and  $\text{F}^-$  were observed in all PAA-coated samples. The 6 K and 450 K treatments exhibited significant reductions in PFOA concentration and substantial  $\text{F}^-$  production compared to incubations with bare ferrihydrite. Electrochemical impedance spectroscopy showed lowered charge transfer resistance in the presence of PAA-coated ferrihydrite, indicating that PAAs facilitated electron transfer to ferrihydrite. This study highlights the potential of PAA-coated ferrihydrite in accelerating PFAS defluorination, providing novel insights for A6-based bioremediation strategies.

**Status:** published work in Journal of Hazardous Materials 2023, **459**, 132039

# Highly Selective Electrochemical Nitrate to Ammonia Conversion by Dispersed Ru in a Multielement Alloy Catalyst

Meiqi Yang,<sup>1,2</sup> Boyang Li,<sup>3</sup> Shuke Li,<sup>4</sup> Qi Dong,<sup>4</sup> Zhennan Huang,<sup>4</sup> Sunxiang Zheng,<sup>1,2</sup> Ying Fang,<sup>3</sup> Guangye Zhou,<sup>1,2</sup> Xi Chen,<sup>1,2</sup> Xiaobo Zhu,<sup>1,2</sup> Tangyuan Li,<sup>4</sup> Miaofang Chi,<sup>5</sup> Guofeng Wang,<sup>3</sup> Liangbing Hu,<sup>4</sup> and Zhiyong Jason Ren<sup>1,2</sup>

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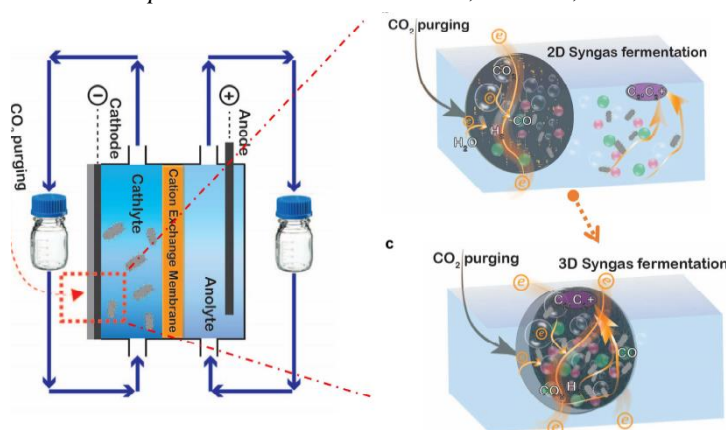
Electrochemical reduction of nitrate to ammonia (NH<sub>3</sub>) converts an environmental pollutant to a critical nutrient. However, current electrochemical nitrate reduction operations based on monometallic and bimetallic catalysts are limited in NH<sub>3</sub> selectivity and catalyst stability, especially in acidic environments. Meanwhile, catalysts with dispersed active sites generally exhibit a higher atomic utilization and distinct activity. Herein, we report a multielement alloy nanoparticle catalyst with dispersed Ru (Ru-MEA) with other synergistic components (Cu, Pd, Pt). Density functional theory elucidated the synergy effect of Ru-MEA than Ru, where a better reactivity (NH<sub>3</sub> partial current density of  $-50.8 \text{ mA cm}^{-2}$ ) and high NH<sub>3</sub> faradaic efficiency (93.5%) is achieved in industrially relevant acidic wastewater. In addition, the Ru-MEA catalyst showed good stability (e.g., 19.0% decay in FE<sub>NH3</sub> in three hours). This work provides a potential systematic and efficient catalyst discovery process that integrates a data-guided catalyst design and novel catalyst synthesis for a range of applications.

**Status:** published work in Nano Letters 2023, **23**, 7733-7742

## Syngas mediated microbial electrosynthesis for CO<sub>2</sub> to acetate conversion using *Clostridium ljungdahlii*

Xiaobo Zhu,<sup>1,2</sup> Joshua Jack,<sup>1,2</sup> Aaron Leininger,<sup>1,2</sup> Meiqi Yang,<sup>1,2</sup> Yanhong Bian,<sup>1,2</sup> Jonathon Lo,<sup>3</sup> Wei Xiong,<sup>3</sup> Nicolas Tsesmetzis,<sup>4</sup> Zhiyong Jason Ren,<sup>1,2</sup>

<sup>1</sup>Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544; <sup>2</sup>Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544; <sup>3</sup>Department of Energy, National Renewable Energy Laboratory, Biosciences Center, Golden, CO 80401; <sup>4</sup>New Energies Research and Technology, Shell International Exploration and Production Inc., Houston, TX 77082.



Carbon dioxide valorization through microbial electrosynthesis (MES) is promising due to its potential for mild operating conditions and stable long-term performance. Previous MES studies have typically shown poor organic production rates using direct electron transfer mechanisms, prompting the use of electrochemically generated H<sub>2</sub>. Still, CO is a more favorable electron donor than H<sub>2</sub> as it provides more thermodynamic reducing power for conversion of CO<sub>2</sub> into valuable products. Here, we incorporated highly selective cobalt phthalocyanine catalysts into new planar 2D and porous 3D MES cathodes to produce syngas rather than H<sub>2</sub> and boost the overall bioconversion rates of CO<sub>2</sub> into value-added products (i.e. acetate and ethanol). The 2D planar cathodes required a larger potential to maintain similar current densities as the 3D porous cathodes and showed a slow decline in CO production and increase in H<sub>2</sub> production after 250 h. In comparison, the 3D porous electrodes allowed for more stable CO and H<sub>2</sub> generation that also led to higher maximum acetate and ethanol titers. Demonstration of these new cathode materials shows significant progress towards more stable and effective MES operations and delivers useful insight on syngas mediated electron transfer and utilization in bioelectrochemical systems.

**Status:** published work in Resources, Conservation and Recycling 2022, **184**, 106395

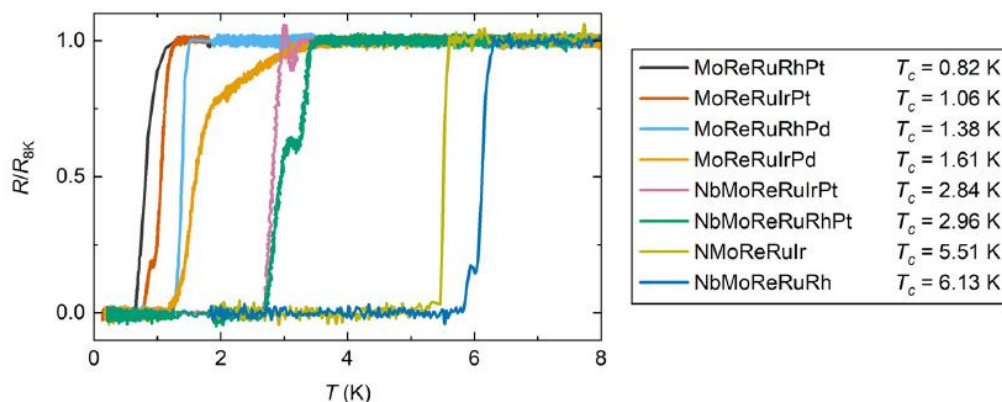


## Department of Chemistry

## Phase stability and possible superconductivity of new 4d and 5d transition metal high-entropy alloys

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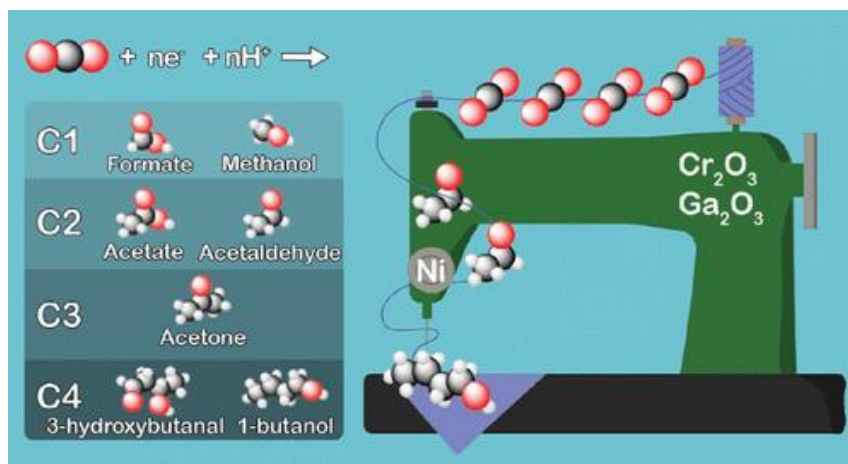
We report the synthesis of new equimolar high-entropy alloys formed from five or six 4d/5d transition metals that are each from a different Group of the Periodic Table. These include MoReRuRhPt and MoReRuIrPt, which appear to crystallize as single hexagonal close-packed phases and so are isostructural and isoelectronic to the high-pressure phase of the well-known high-entropy alloy CrMnFeCoNi. Other compositions crystallize as mixed phases, which we rationalize using the atomic size difference,  $\delta$ , and the electronegativity difference,  $\Delta\chi$ , of the constituent elements. Finally, we find signs of superconductivity in eight of these new systems.

**Status:** published work in Journal of Solid State Chemistry 2023, **321**, 123881

## Direct Synthesis of 1-Butanol with High Faradaic Efficiency from CO<sub>2</sub> Utilizing Cascade Catalysis at a Ni-Enhanced (Cr<sub>2</sub>O<sub>3</sub>)<sub>3</sub>Ga<sub>2</sub>O<sub>3</sub> Electrocatalyst

Steve P. Cronin, Stephanie Dulovic, Josef A. Lawrence, Kai A. Filsinger, Alma Paola Hernandez-Gonzalez, Rebecca Evans, Joseph W. Stiles, Jalah Morris, István Pelczer, and Andrew B. Bocarsly

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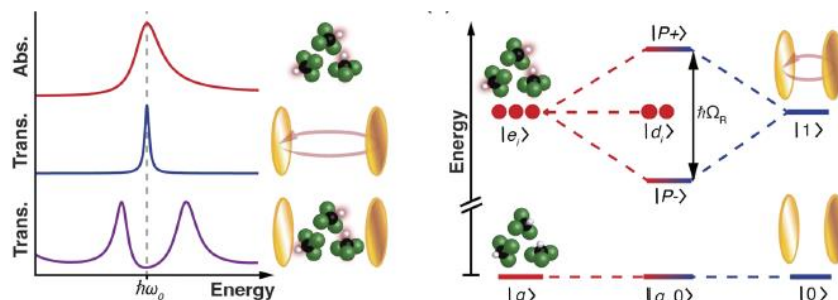
Electrochemical transformation of CO<sub>2</sub> into energy dense liquid fuels provides a viable solution to challenges regarding climate change and nonrenewable resource dependence. Here, we report on the modification of a Cr-Ga oxide electrocatalyst through the introduction of nickel to generate a catalyst that generates 1-butanol at unprecedented faradaic efficiencies ( $\xi = 42\%$ ). This faradaic efficiency occurs at  $-1.48$  V vs Ag/AgCl, with 1-butanol production commencing at an overpotential of 320 mV. At this potential, minor products include formate, methanol, acetic acid, acetone, and 3-hydroxybutanal. At  $-1.0$  and  $-1.4$  V, 3-hydroxybutanal becomes the primary product. This is in contrast to the nickel-free (Cr<sub>2</sub>O<sub>3</sub>)<sub>3</sub>(Ga<sub>2</sub>O<sub>3</sub>) system, where neither 3-hydroxybutanal nor 1-butanol was detected. Mechanistic studies show that formate is the initial CO<sub>2</sub> reduction product and identify acetaldehyde as the key intermediate. Nickel is found responsible for the coupling and reduction of acetaldehyde to generate the higher molecular weight carbon products observed. To the best of our knowledge, this is the first electrocatalyst to generate 1-butanol with high faradaic efficiency.

**Status:** published work in J. Am. Chem. Soc. 2023, **145**, 6762–6772

## Ultrafast dynamics of CN radical reactions with chloroform solvent under vibrational strong coupling

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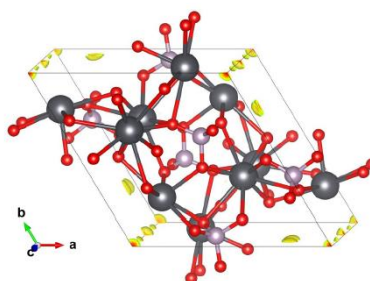
Polariton chemistry may provide a new means to control molecular reactivity, permitting remote, reversible modification of reaction energetics, kinetics, and product yields. A considerable body of experimental and theoretical work has already demonstrated that strong coupling between a molecular vibrational mode and the confined electromagnetic field of an optical cavity can alter chemical reactivity without external illumination. However, the mechanisms underlying cavity-altered chemistry remain unclear in large part. Here, we experimentally investigate photolysis-induced reactions of cyanide radicals with strongly-coupled chloroform ( $\text{CHCl}_3$ ) solvent molecules and examine the intracavity rates of photofragment recombination, solvent complexation, and hydrogen abstraction. We use a microfluidic optical cavity fitted with dichroic mirrors to facilitate vibrational strong coupling (VSC) of the C–H stretching mode of  $\text{CHCl}_3$ . Ultrafast transient absorption experiments performed with cavities tuned on- and off-resonance reveal that VSC of the  $\text{CHCl}_3$  C–H stretching transition does not significantly modify any measured rate constants, including those associated with the hydrogen abstraction reaction. This work represents the first experimental study of an elementary bimolecular reaction under VSC. We discuss how the conspicuous absence of cavity-altered effects in this system may provide insights into the mechanisms of modified ground state reactivity under VSC and help bridge the divide between experimental results and theoretical predictions in vibrational polariton chemistry.

**Status:** published work in J. Chem. Phys. 2023, **159**, 164302

## Pb<sub>9</sub>Cu(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>: Phonon bands, localized flat-band magnetism, models, & chemical analysis

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<sup>1</sup>Donostia International Physics Center (DIPC), Donostia-San Sebastian, Spain; <sup>2</sup>Department of Chemistry, Princeton University, Princeton, NJ, USA; <sup>3</sup>Department of Physics, Princeton University, Princeton, NJ, USA; <sup>4</sup>Max Planck Institute for Chemical Physics of Solids, Dresden, Germany; <sup>5</sup>Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon, USA; <sup>6</sup>IKERBASQUE, Basque Foundation for Science, Bilbao, Spain.



Doped lead apatite (LK-99) has been proposed as a candidate ambient temperature and pressure superconductor. However, these claims are largely unsubstantiated. To this end, our synthesis and subsequent analysis of an LK-99 sample reveals a multiphase material that does not exhibit high-temperature superconductivity. We study the structure of this phase with single-crystal x-ray diffraction (SXRD) and find a structure consistent with doped Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>. However, the material is transparent, which rules out a superconducting nature. From *ab initio* defect formation energy calculations, we find that the material likely hosts OH<sup>−</sup> anions, rather than divalent O<sub>2</sub><sup>−</sup> anions, within the hexagonal channels and that Cu substitution is highly thermodynamically disfavored. Together, these calculations suggest it is doubtful that Cu enters the structure in meaningful concentrations. We perform *ab initio* calculations of the topology, quantum geometry, and Wannier function localization in the Cu-dominated flat bands of four separate doped structures. In all cases, we find they are atomically localized by irreps, Wilson loops, and the Fubini-Study metric. It is unlikely that such bands can support strong superfluidity, and instead are susceptible to ferromagnetism at low temperatures. In sum, Pb<sub>9</sub>Cu(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> could more likely be a magnet, rather than an ambient temperature and pressure superconductor.

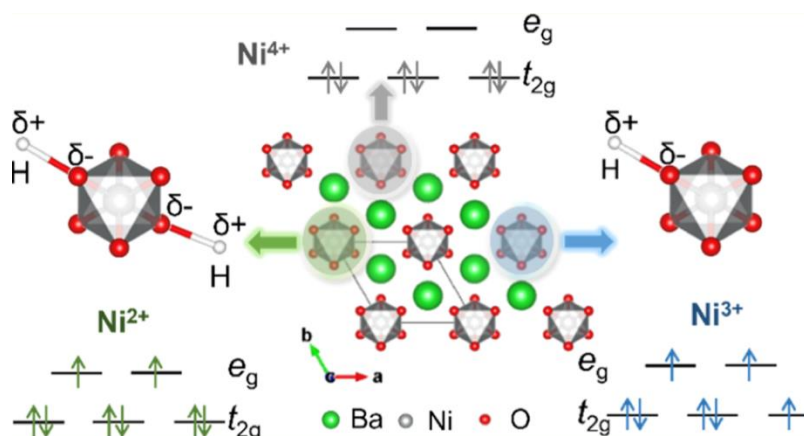
**Status:** published work in Phys. Rev. B 2023, **108**, 235127



## Hidden Hydroxides in KOH-Grown BaNiO<sub>3</sub> Crystals: A Potential Link to Their Catalytic Behavior

Lun Jin,<sup>1</sup> Haozhe Wang,<sup>1</sup> Xianghan Xu,<sup>1</sup> Danrui Ni,<sup>1</sup> Chen Yang,<sup>1</sup> Yu-Chieh Ku,<sup>2</sup> Cheng-En Liu,<sup>2</sup> Chang-Yang Kuo,<sup>2</sup> Chun-Fu Chang,<sup>3</sup> Raimundas Sereika,<sup>4</sup> Wenli Bi,<sup>4</sup> Weiwei Xie,<sup>5</sup> and Robert J. Cava<sup>1</sup>

<sup>1</sup>Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States; <sup>2</sup>Department of Electrophysics, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan; <sup>3</sup>Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany; <sup>4</sup>Department of Physics, University of Alabama, Birmingham, Alabama 35294, United States; <sup>5</sup>Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States.



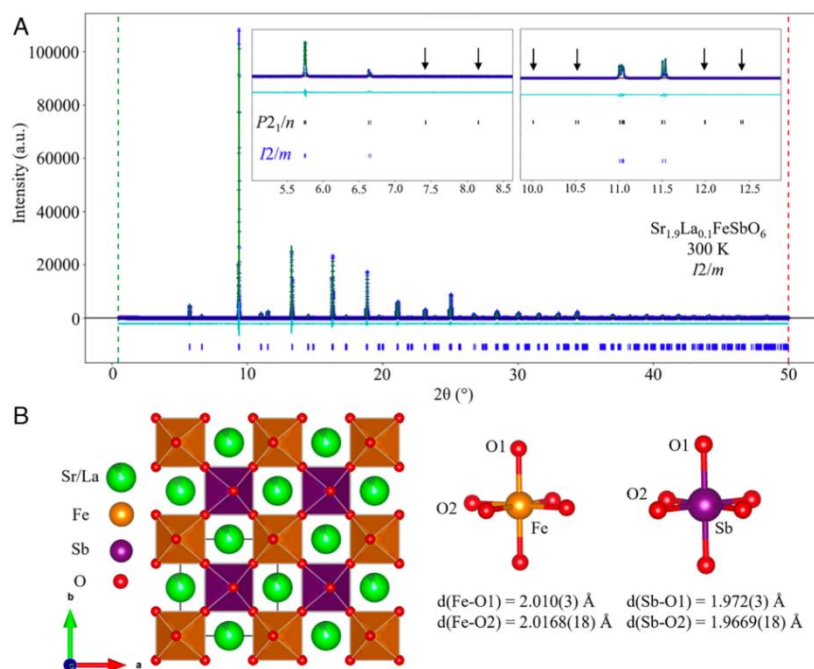
The hexagonal perovskite BaNiO<sub>3</sub>, prepared via nonceramic approaches, is known to act as a good catalyst for the oxygen evolution reaction (OER) in alkaline media. Here, we report our observation that BaNiO<sub>3</sub> synthesized via KOH flux growth and high-pressure ceramic synthesis with high O<sub>2</sub> pressure have different magnetic properties. We show that this is because the KOH flux-grown crystals made in open air are actually a hydroxide-containing form of BaNiO<sub>3</sub> that can be “dried” upon annealing in an O<sub>2</sub> flow. This work not only unveils a previously unknown aspect of the BaNiO<sub>3</sub> OER catalyst and offers some insights into the underlying mechanism, but also suggests that hydroxide ions may be present in other hexagonal perovskite oxides prepared in wet conditions.

**Status:** published work in Chem. Mater. 2023, **35**, 9434–9443

## Electron doping of a double-perovskite flat-band system

Lun Jin,<sup>1</sup> Nicodemos Varnava,<sup>2,3</sup> Danrui Ni,<sup>1</sup> Xin Gui,<sup>1</sup> Xianghan Xu,<sup>1</sup> Yuanfeng Xu,<sup>4</sup> Andrei Bernevig,<sup>3,4,5</sup> and Robert J. Cava.<sup>1</sup>

<sup>1</sup>Department of Chemistry, Princeton University, Princeton, NJ 08544; <sup>2</sup>Department of Physics & Astronomy, Rutgers University, Piscataway, NJ 08854; <sup>3</sup>Donostia International Physics Center, 20018 Donostia- San Sebastian, Spain; <sup>4</sup>Department of Physics, Princeton University, Princeton, NJ 08544; and <sup>5</sup>IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain



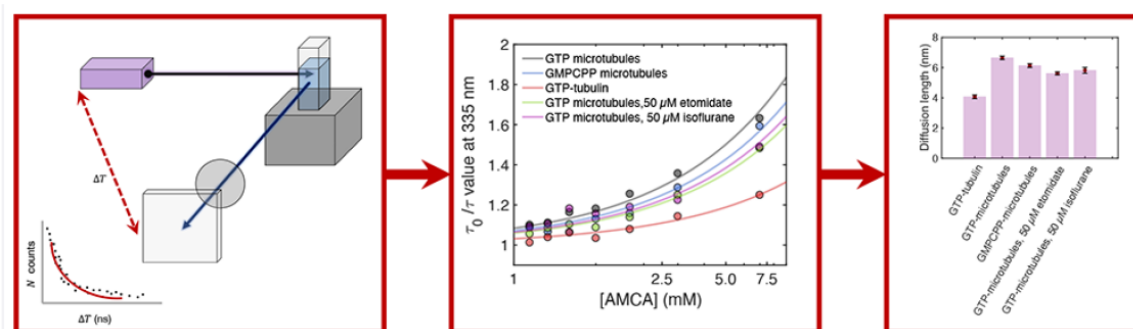
Electronic structure calculations indicate that the  $\text{Sr}_2\text{FeSbO}_6$  double perovskite has a flat-band set just above the Fermi level that includes contributions from ordinary subbands with weak kinetic electron hopping plus a flat subband that can be attributed to the lattice geometry and orbital interference. To place the Fermi energy in that flat band, electron-doped samples with formulas  $\text{Sr}_{2-x}\text{La}_x\text{FeSbO}_6$  ( $0 \leq x \leq 0.3$ ) were synthesized, and their magnetism and ambient temperature crystal structures were determined by high-resolution synchrotron X-ray powder diffraction. All materials appear to display an antiferromagnetic-like maximum in the magnetic susceptibility, but the dominant spin coupling evolves from antiferromagnetic to ferromagnetic on electron doping. Which of the three subbands or combinations is responsible for the behavior has not been determined.

**Status:** published work in PNAS 2023, **120**, e2218997120

## Electronic Energy Migration in Microtubules

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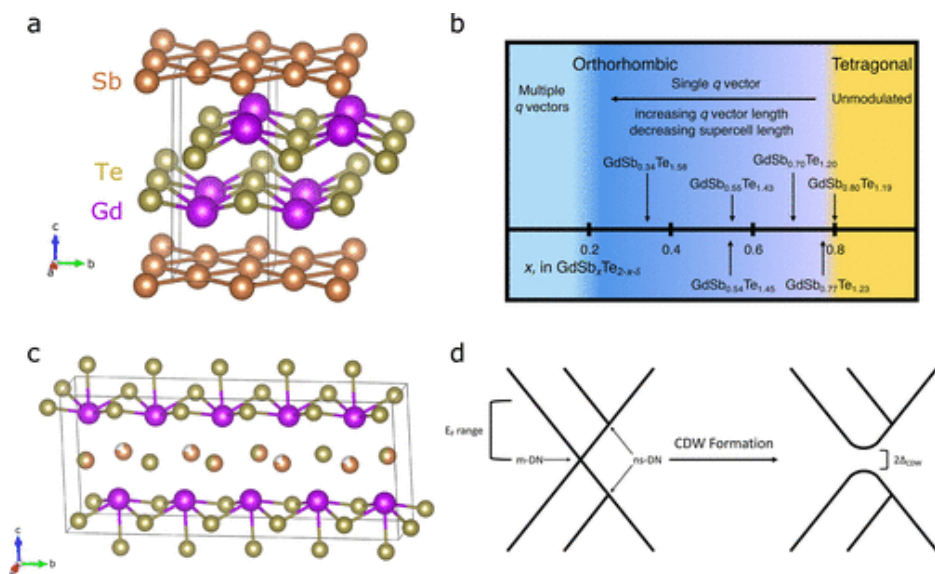
The repeating arrangement of tubulin dimers confers great mechanical strength to microtubules, which are used as scaffolds for intracellular macromolecular transport in cells and exploited in biohybrid devices. The crystalline order in a microtubule, with lattice constants short enough to allow energy transfer between amino acid chromophores, is similar to synthetic structures designed for light harvesting. After photoexcitation, can these amino acid chromophores transfer excitation energy along the microtubule like light-harvesting system? Here, we use tryptophan autofluorescence lifetimes to probe energy hopping between aromatic residues in tubulin and microtubules. By studying how the quencher concentration alters tryptophan autofluorescence lifetimes, we demonstrate that electronic energy can diffuse over 6.6 nm in microtubules. We discover that while diffusion lengths are influenced by tubulin polymerization state, they are not significantly altered by the average number of protofilaments. We also demonstrate that the presence of the anesthetics etomidate and isoflurane reduce exciton diffusion. Energy transport as explained by conventional Förster theory does not sufficiently explain our observations. Our studies indicate that microtubules are, unexpectedly, effective light harvesters.

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# Ultrafast Dynamics of the Topological Semimetal $\text{GdSb}_x\text{Te}_{2-x-\delta}$ in the Presence and Absence of a Charge Density Wave

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Time-resolved dynamics in charge-density-wave materials have revealed interesting out-of-equilibrium electronic responses. However, these are typically only performed in a single material possessing a CDW. Here, we report on the ultrafast dynamics of the  $\text{GdSb}_x\text{Te}_{2-x-\delta}$  series of materials where EF can be tuned, resulting in a change from an undistorted tetragonal phase to a CDW with a wavevector that depends on  $x$ . Using mid-infrared, near-infrared, and visible excitation, we find the dynamics are sensitive to both EF and the presence of the CDW. Specifically, as the Sb content of the compounds increases, transient spectral features shift to higher probe energies. In addition, we observe an enhanced lifetime and change in the sign of the transient signal upon removing the CDW with high Sb concentrations. Finally, we reveal fluence- and temperature-dependent photoinduced responses of the differential reflectivity, which provide evidence of transient charge density wave suppression in related telluride materials. Taken together our results provide a blueprint for future ultrafast studies of CDW systems.

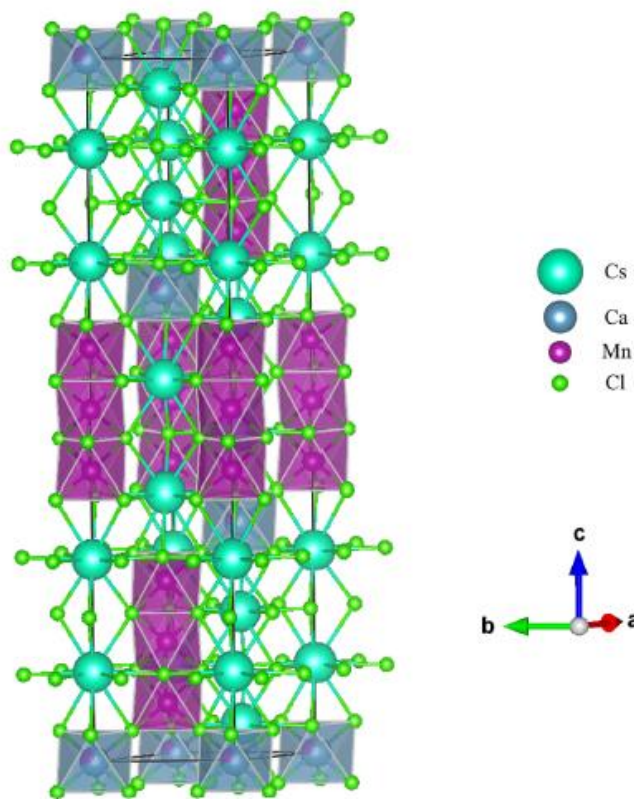
**Status:** published work in J. Phys. Chem. C 2023, **127**, 577–584

## The 12-layer trimer-based hexagonal perovskite $\text{Cs}_4\text{Ca}_{0.7}\text{Mn}_{3.3}\text{Cl}_{12}$

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We describe the crystal structure and basic magnetic properties of  $\text{Cs}_4\text{Ca}_{0.7}\text{Mn}_{3.3}\text{Cl}_{12}$ , a previously unreported twelve layer (12L-) hexagonal (R-3m) chloride perovskite. Its crystal structure features face sharing  $\text{MnCl}_6$  octahedra that form  $\text{Mn}_3\text{Cl}_{12}$  trimers. The trimers, which form a triangular array, are separated by corner sharing to layers of disordered single  $\text{Ca}(\text{Mn})\text{Cl}_6$  octahedra. The decreased intratrimer Mn–Mn distance yields stronger magnetic coupling within trimers than between trimers. The dominant magnetic interactions are antiferromagnetic ( $\theta_{\text{CW}} = -105$  K), the effective magnetic moment per  $\text{Mn}^{2+}$  is  $6.5 \mu_B$ , and potential signatures of magnetic frustration are observed. Behavior consistent with short- and long-range magnetic order is exhibited at approximately 37 and 0.7 K, respectively.

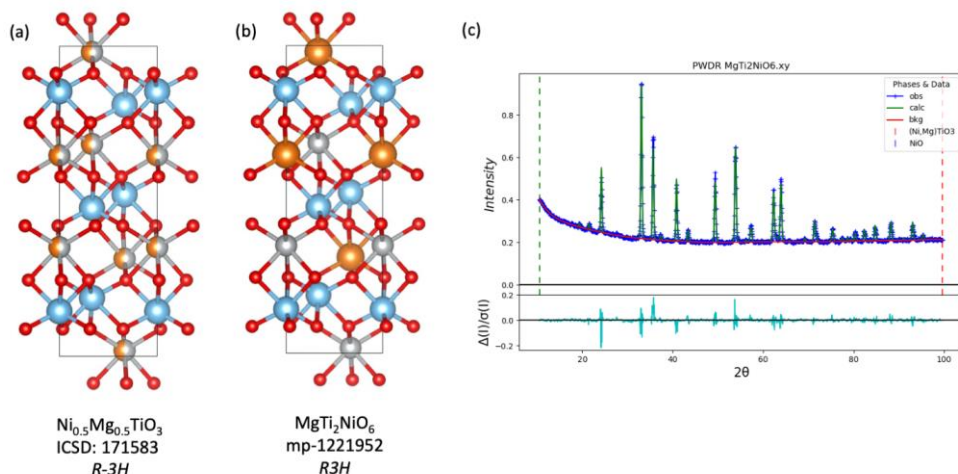
**Status:** published work in Journal of Solid State Chemistry 2023, **324**, 124095



# Challenges in high-throughput inorganic material prediction and autonomous synthesis

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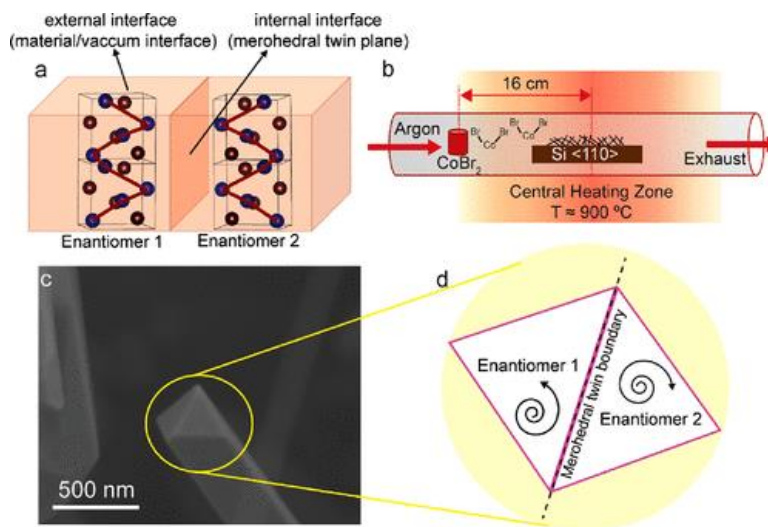
Materials discovery lays the foundation for many technological advancements. Predicting and discovering new materials are not simple tasks. We here outline some basic principles of solid-state chemistry, which might help to advance both, and discuss pitfalls and challenges in materials discovery. We 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: (i) automated Rietveld analysis of powder x-ray diffraction data is not yet reliable. Future improvement of such, and the development of a reliable artificial intelligence-based tool for Rietveld fitting, would be very helpful. (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 known alloys or solid solutions. This error might be related to the difficulty of modeling disorder in a computationally economical way, and needs to be addressed both by computational and experimental material scientists. We highlight important issues in materials discovery, computational chemistry, and autonomous interpretation of x-ray diffraction.

**Status:** work posted on ChemRxiv.org: doi.org/10.26434/chemrxiv-2024-5p9j4

## Atomically Sharp Internal Interface in a Chiral Weyl Semimetal Nanowire

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Internal interfaces in Weyl semimetals (WSMs) are predicted to host distinct topological features that are different from the commonly studied external interfaces (crystal-to-vacuum boundaries). However, the lack of atomically sharp and crystallographically oriented internal interfaces in WSMs makes it difficult to experimentally investigate topological states buried inside the material. Here, we study a unique internal interface known as merohedral twin boundary in chemically synthesized single-crystal nanowires (NWs) of CoSi, a chiral WSM of space group  $P2_13$  (No. 198). Scanning transmission electron microscopy reveals that this internal interface is a (001) twin plane which connects two enantiomeric counterparts at an atomically sharp interface with inversion twinning. Ab initio calculations show localized internal Fermi arcs at the (001) twin plane that can be clearly distinguished from both external Fermi arcs and bulk states. These merohedrally twinned CoSi NWs provide an ideal platform to explore topological properties associated with internal interfaces in WSMs.

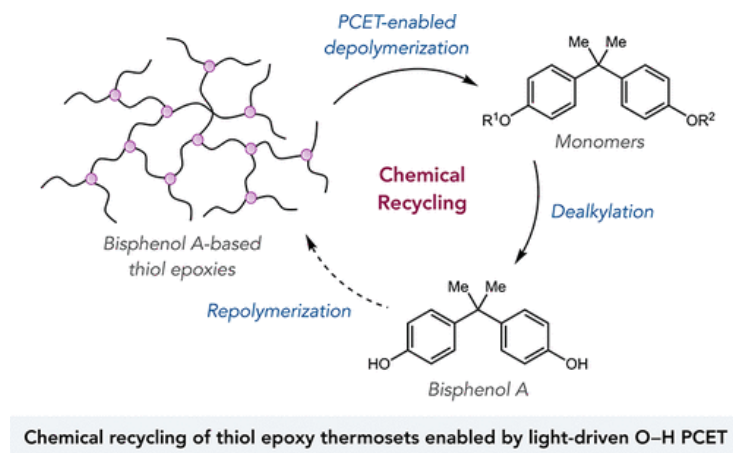
**Status:** published work in Nano Lett. 2023, **23**, 2695–2702

# Chemical Recycling of Thiol Epoxy Thermosets via Light-Driven C–C Bond Cleavage

Suong T. Nguyen,<sup>1</sup> Lydia R. Fries,<sup>1</sup> James H. Cox,<sup>1</sup> Yuting Ma,<sup>2</sup> Brett P. Fors,<sup>2</sup> Robert R. Knowles<sup>1</sup>

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Epoxy thermosets are high-volume materials that play a central role in a wide range of engineering applications; however, technologies to recycle these polymers remain rare. Here, we present a catalytic, light-driven method that enables chemical recycling of industrially relevant thiol epoxy thermosets to their original monomer at ambient temperature. This strategy relies on the proton-coupled electron transfer (PCET) activation of hydroxy groups within the polymer network to generate key alkoxy radicals that promote the fragmentation of the polymer through C–C bond  $\beta$ -scission. The method fully depolymerizes insoluble thiol epoxy thermosets into well-defined mixtures of small-molecule products, which can collectively be converted into the original monomer via a one-step dealkylation process. Notably, this process is selective and efficient even in the presence of other commodity plastics and additives commonly found in commercial applications. These results constitute an important step toward making epoxy thermosets recyclable and more generally exemplify the potential of PCET to offer a more sustainable end-of-life for a diverse array of commercial plastics.

**Status:** published work in J. Am. Chem. Soc. 2023, **145**, 11151–11160

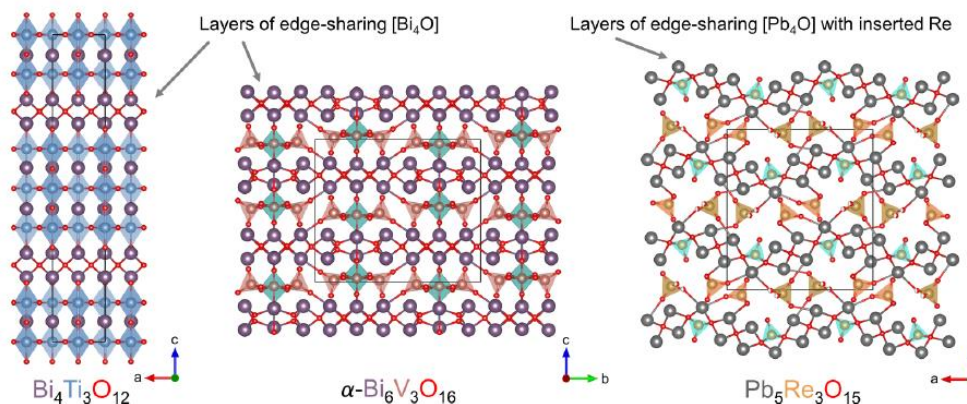
## Quasi-one-dimensional $\text{Pb}_5\text{Re}_3\text{O}_{15}$ : A 5d realization of the Heisenberg antiferromagnetic spin-1/2 chain

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Quasi-one-dimensional (1D) magnetic compounds connect the exact solutions of low-dimensional magnetic geometries, which promise quantum spin liquid behavior and exotic quasiparticles, with real-world materials, in which competing magnetic interactions affect their implementation in quantum information science. Here, the structural determination and quasi-1D magnetic behavior of a previously unreported compound,  $\text{Pb}_5\text{Re}_3\text{O}_{15}$ , is presented. Like the anisotropic triangular  $\text{A}_3\text{ReO}_5\text{Cl}_2$  ( $\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$ ) materials,  $\text{Pb}_5\text{Re}_3\text{O}_{15}$  contains  $[\text{ReO}_5]$  square pyramids inserted into anion-centered quasi-two-dimensional layers and hosts spin-1/2 moments on the  $\text{Re}^{6+}$  ions.  $\text{Pb}_5\text{Re}_3\text{O}_{15}$ , however, has a more ideal quasi-1D geometry than the  $\text{A}_3\text{ReO}_5\text{Cl}_2$  materials, with larger interchain distances and interlayer spacing. Quasi-1D magnetic behavior in  $\text{Pb}_5\text{Re}_3\text{O}_{15}$  is confirmed by fitting the temperature-dependent magnetic susceptibility with the Bonner-Fisher model for a spin-1/2 antiferromagnetically coupled chain, yielding an intrachain coupling constant of  $|J|/k_B = 54.5\text{K}$ .  $\text{Pb}_5\text{Re}_3\text{O}_{15}$  is highly insulating at room temperature, and heat capacity data below 10 K reveal a linear-T contribution that suggests the presence of low-temperature spinon excitations. With a lack of three-dimensional ordering down to at least 0.6 K,  $\text{Pb}_5\text{Re}_3\text{O}_{15}$  is proposed as a model system for studying the quantum magnetism of quasi-1D Heisenberg chains in a real-world 5d<sup>1</sup> antiferromagnetic material.

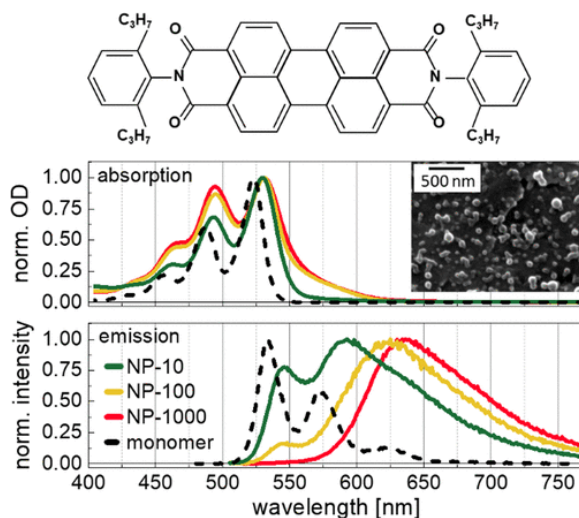
**Status:** published work in Phys. Rev. Materials 2023, **7**, 114408

# Comparison of Frenkel and Excimer Exciton Diffusion in Perylene Bisimide Nanoparticles

Chris Rehhagen,<sup>1</sup> Shahnawaz Rafiq,<sup>2</sup> Kyra N. Schwarz,<sup>2</sup> Gregory D. Scholes,<sup>2</sup> Stefan Lochbrunner<sup>1</sup>

<sup>1</sup>*Institute for Physics and Department Life, Light and Matter, University of Rostock, 18051 Rostock, Germany;*

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Exciton migration is an important process for light harvesting with organic systems and often the bottleneck. Especially the formation of trap states hinders the mobility considerably. Although excimer excitons are often referred to as traps, their mobility has been demonstrated while their nature is still unclear. Here, we compare the mobility of singlet and excimer excitons in nanoparticles consisting of the same type of perylene bisimide molecules. By changing the preparation conditions, nanoparticles with different intermolecular coupling strengths are prepared. Femtosecond transient absorption spectroscopy reveals the formation of excimer excitons from Frenkel excitons. The mobility of both exciton types is determined by evaluating exciton–exciton annihilation processes. In the lower coupling regime, singlet mobility is observed, whereas for stronger coupling the dynamics is dominated by a 10-fold increased excimer mobility. The excimer mobility can thus even be higher than the singlet mobility and is affected by the intermolecular electronic coupling.

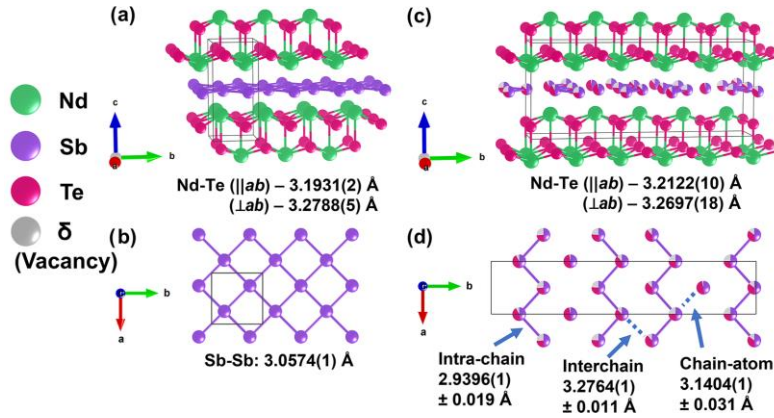
**Status:** published work in J. Phys. Chem. Lett. 2023, **14**, 4490–4496



# Charge density wave-templated spin cycloid in topological semimetal $\text{NdSb}_x\text{Te}_{2-x-\delta}$

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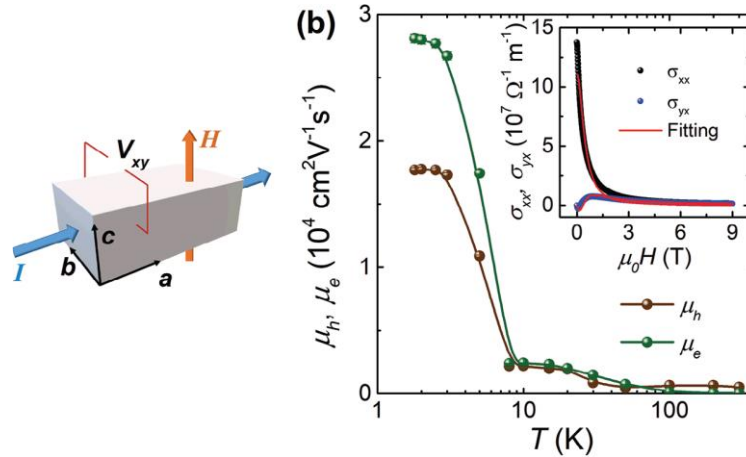
Magnetic topological semimetals present open questions regarding the interplay of crystal symmetry, magnetism, band topology, and electron correlations.  $\text{LnSb}_x\text{Te}_{2-x-\delta}$  is a family of square-net-derived topological semimetals that allow compositional control of band filling. Previously studied Gd and Ce members containing a CDW have shown complex magnetic phase diagrams, but to this date no magnetic structures have been solved within the CDW regime of this family of compounds. Here, we report on the interplay of the CDW with magnetism in  $\text{NdSb}_x\text{Te}_{2-x-\delta}$  by comparing the undistorted square net member  $\text{NdSb}_{0.94}\text{Te}_{0.92}$  with the CDW-distorted phase  $\text{NdSb}_{0.48}\text{Te}_{1.37}$ , via single-crystal x-ray diffraction, magnetometry, heat capacity, and neutron powder diffraction.  $\text{NdSb}_{0.94}\text{Te}_{0.92}$  is a collinear antiferromagnet with  $T_N \sim 2.7 \text{ K}$ , where spins align antiparallel to each other, but parallel to the square net of the nuclear structure.  $\text{NdSb}_{0.48}\text{Te}_{1.37}$  exhibits a nearly fivefold-modulated CDW ( $q_{\text{CDW}} = 0.18$ ).  $\text{NdSb}_{0.48}\text{Te}_{1.37}$  displays more complex magnetism with  $T_N = 2.3 \text{ K}$ , additional metamagnetic transitions, and an elliptical cycloid magnetic structure with  $q_{\text{mag}} = -0.41b^*$ . The magnitudes of  $q_{\text{CDW}}$  and  $q_{\text{mag}}$  exhibit an integer relationship,  $1 + 2q_{\text{mag}} = q_{\text{CDW}}$ , implying a coupling between the CDW and magnetic structure. Given that the CDW is localized within the nonmagnetic distorted square net, we propose that conduction electrons “template” the spin modulation via the Ruderman-Kittel-Kasuya-Yosida interaction.

**Status:** published work in Phys. Rev. Materials 2023, **7**, 044203

## Anisotropic and High-Mobility Electronic Transport in a Quasi 2D Antiferromagnet NdSb<sub>2</sub>

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<sup>1</sup>Department of Chemistry, Princeton University, Princeton, NJ 08544, USA; <sup>2</sup>Princeton Materials Institute, Princeton University, Princeton, NJ 08544, USA; <sup>3</sup>Department of Physics, Boston College, Chestnut Hill, MA 02467, USA; <sup>4</sup>CHESS, Cornell University, Ithaca, NY 14853, USA



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<sub>2</sub> is an ideal example. Even with a relatively small interlayer distance, this material can be exfoliated down to few layers. NdSb<sub>2</sub> 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.

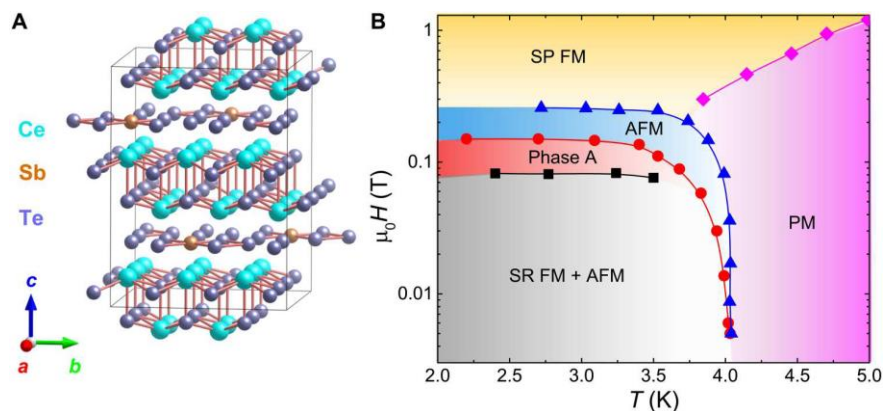
**Status:** published work in Advanced Functional Materials, 2023, 2308733

## Colossal magnetoresistance in the multiple wave vector charge density wave regime of an antiferromagnetic Dirac semimetal

Ratnadwip Singha,<sup>1</sup> Kirstine J. Dalgaard,<sup>1</sup> Dmitry Marchenko,<sup>2</sup> Maxim Krivenkov,<sup>2</sup> Emile D. L. Rienks,<sup>2</sup> Milena Jovanovic,<sup>1</sup> Samuel M. L. Teicher,<sup>3</sup> Jiayi Hu,<sup>4</sup> Tyger H. Salters,<sup>1</sup> Jingjing Lin,<sup>4</sup> Andrei Varykhalov,<sup>2</sup> N. Phuan Ong,<sup>4</sup> Leslie M. Schoop<sup>1</sup>

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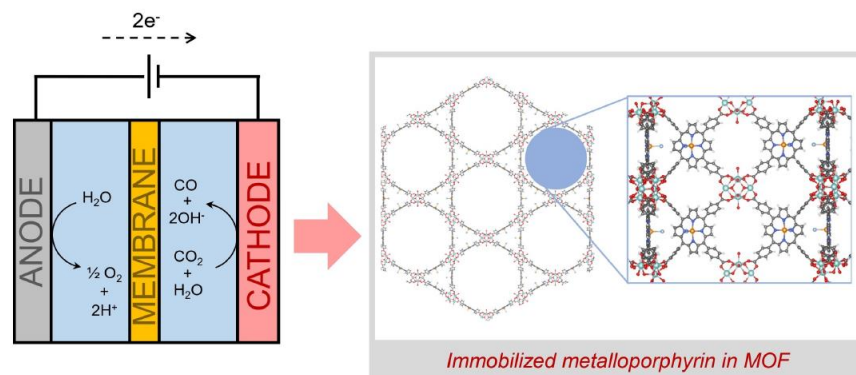
Colossal negative magnetoresistance is a well-known phenomenon, notably observed in hole-doped ferromagnetic manganites. It remains a major research topic due to its potential in technological applications. In contrast, topological semimetals show large but positive magnetoresistance, originated from the high-mobility charge carriers. Here, we show that in the highly electron-doped region, the Dirac semimetal CeSbTe demonstrates similar properties as the manganites. CeSb<sub>0.11</sub>Te<sub>1.90</sub> hosts multiple charge density wave modulation vectors and has a complex magnetic phase diagram. We confirm that this compound is an antiferromagnetic Dirac semimetal. Despite having a metallic Fermi surface, the electronic transport properties are semiconductor-like and deviate from known theoretical models. An external magnetic field induces a semiconductor metal-like transition, which results in a colossal negative magnetoresistance. Moreover, signatures of the coupling between the charge density wave and a spin modulation are observed in resistivity. This spin modulation also produces a giant anomalous Hall response.

**Status:** published work in Science Advances, 2023, **9**, eadh0145

## Mechanistic Elucidations of Highly Dispersed Metalloporphyrin Metal-Organic Framework Catalysts for CO<sub>2</sub> Electroreduction

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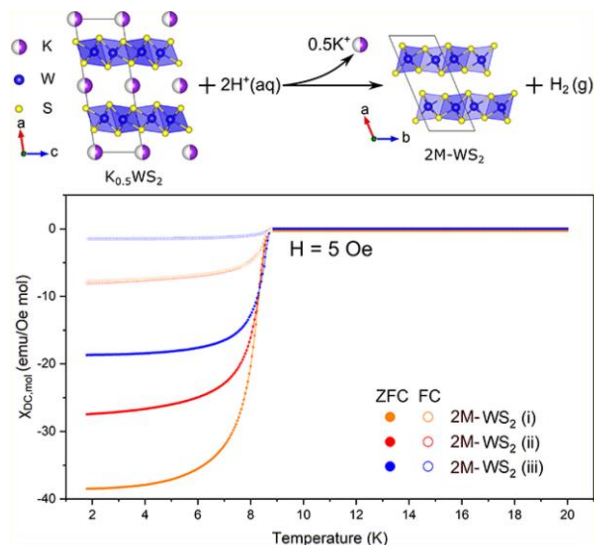
Immobilization of porphyrin complexes into crystalline metal–organic frameworks (MOFs) enables high exposure of porphyrin active sites for CO<sub>2</sub> electroreduction. Herein, well-dispersed iron-porphyrin-based MOF (PCN-222(Fe)) on carbon-based electrodes revealed optimal turnover frequencies for CO<sub>2</sub> electroreduction to CO at 1 wt.% catalyst loading, beyond which the intrinsic catalyst activity declined due to CO<sub>2</sub> mass transport limitations. In situ Raman suggested that PCN-222(Fe) maintained its structure under electrochemical bias, permitting mechanistic investigations. These revealed a stepwise electron transfer-proton transfer mechanism for CO<sub>2</sub> electroreduction on PCN-222(Fe) electrodes, which followed a shift from a rate-limiting electron transfer to CO<sub>2</sub> mass transfer as the potential increased from -0.6 V to -1.0 V vs. RHE. Our results demonstrate how intrinsic catalytic investigations and in situ spectroscopy are needed to elucidate CO<sub>2</sub> electroreduction mechanisms on PCN-222(Fe) MOFs.

**Status:** published work in *Angewandte Chemie*, 2023, **62**, e202218208

## Acid-Assisted Soft Chemical Route for Preparing High-Quality Superconducting 2M-WS<sub>2</sub>

X. Song,<sup>1</sup> B. Hoff,<sup>1</sup> R. Singha,<sup>1</sup> J. W. Stiles,<sup>1</sup> G. Skorupskii,<sup>1</sup> J. F. Khoury,<sup>1</sup> G. Cheng,<sup>2</sup> F. Kamm,<sup>3</sup> A. J. Uzan,<sup>4</sup> S. Dulovic,<sup>1</sup> S. Wu,<sup>4</sup> F. Pielnhofer,<sup>3</sup> Nan Yao,<sup>2</sup> and Leslie M. Schoop<sup>1</sup>

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2M-WS<sub>2</sub> is a metastable, superconducting polymorph of the transition metal dichalcogenide (TMD) WS<sub>2</sub>, comprised of layers of face-sharing distorted WS<sub>6</sub> octahedra. It is predicted to host non-Abelian quantum states, promising for topological computing. Due to its thermodynamic instability, 2M-WS<sub>2</sub> cannot be synthesized using solid-state synthesis. Rather, it requires a top-down approach in which K<sup>+</sup> is deintercalated from K<sub>x</sub>WS<sub>2</sub>; so far, this process has been completed using a strong oxidizer, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in dilute H<sub>2</sub>SO<sub>4</sub>. A disadvantage of such synthesis is that the harsh reaction condition may cause the crystal quality to suffer. In this study, we found that the K-deintercalation process from K<sub>x</sub>WS<sub>2</sub> is spontaneous, and a non-oxidative acidic reaction environment is sufficient to facilitate the oxidation of K<sub>x</sub>WS<sub>2</sub> to 2M-WS<sub>2</sub> while reducing H<sup>+</sup> to H<sub>2</sub>. By analyzing the superconducting transition in the heat capacity, we found that 2M-WS<sub>2</sub> made using less aggressive methods has higher superconducting volume fractions. We describe how to access the superconducting 2M phase of WS<sub>2</sub> as high-quality crystals.

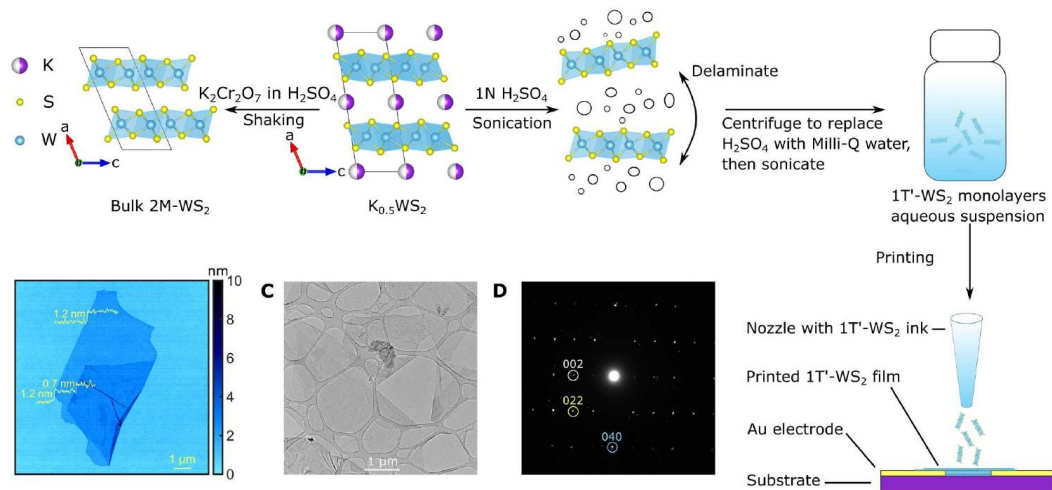
**Status:** published work in Chemistry of Materials 2023, **35**, 5487



# Synthesis of an aqueous, air-stable, superconducting 1T'-WS<sub>2</sub> monolayer ink

Xiaoyu Song,<sup>1</sup> Ratnadwip Singha,<sup>1</sup> Guangming Cheng,<sup>2</sup> Yao-Wen Yeh,<sup>3</sup> Franziska Kamm,<sup>4</sup> Jason F. Khoury,<sup>1</sup> Brianna L. Hoff,<sup>1</sup> Joseph W. Stiles,<sup>1</sup> Florian Pielnhofer,<sup>4</sup> Philip E. Batson,<sup>3</sup> Nan Yao,<sup>2</sup> Leslie M. Schoop<sup>1</sup>

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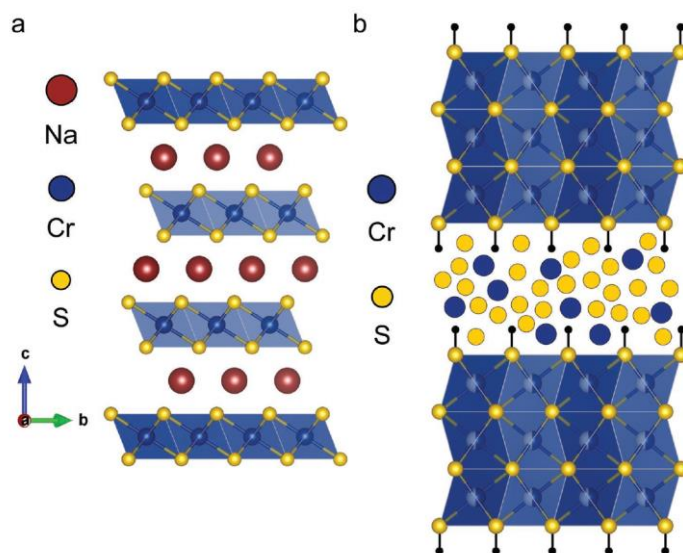
Liquid-phase chemical exfoliation can achieve industry-scale production of two-dimensional (2D) materials for a wide range of applications. However, many 2D materials with potential applications in quantum technologies often fail to leave the laboratory setting because of their air sensitivity and depreciation of physical performance after chemical processing. We report a simple chemical exfoliation method to create a stable, aqueous, surfactant-free, superconducting ink containing phase-pure 1T'-WS<sub>2</sub> monolayers that are isostructural to the air-sensitive topological insulator 1T'-WTe<sub>2</sub>. The printed film is metallic at room temperature and superconducting below 7.3 kelvin, shows strong anisotropic unconventional superconducting behavior with an in-plane and out-of-plane upper critical magnetic field of 30.1 and 5.3 tesla, and is stable at ambient conditions for at least 30 days. Our results show that chemical processing can make nontrivial 2D materials that were formerly only studied in laboratories commercially accessible.

**Status:** published work in Science Advances 2023, **9**, eadd6167

# Unlocking High Capacity and Fast Na<sup>+</sup> Diffusion of H<sub>x</sub>CrS<sub>2</sub> by Proton-Exchange Pretreatment

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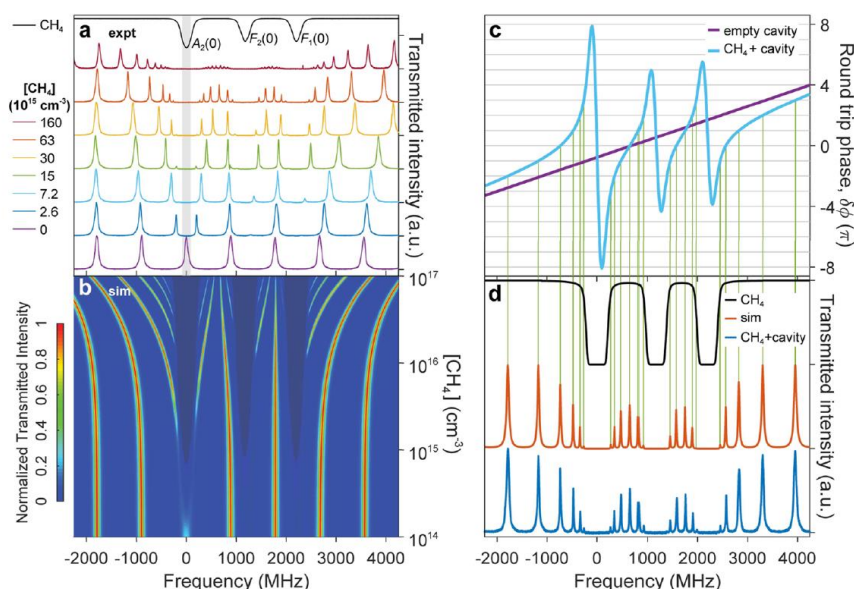
This study presents a new material, “H<sub>x</sub>CrS<sub>2</sub>” (denotes approximate composition) formed by proton-exchange of NaCrS<sub>2</sub> which has a measured capacity of 728 mAh g<sup>-1</sup> with significant improvements to capacity retention, sustaining over 700 mAh g<sup>-1</sup> during cycling experiments. This is the highest reported capacity for a transition metal sulfide electrode and outperforms the most promising proposed sodium anodes to date. H<sub>x</sub>CrS<sub>2</sub> exhibits a biphasic structure featuring alternating crystalline and amorphous lamella on the scale of a few nanometers. This unique structural motif enables reversible access to Cr redox in the material resulting in higher capacities than seen in the parent structure which features only S redox. Pretreatment by proton-exchange offers a route to materials such as H<sub>x</sub>CrS<sub>2</sub> which provide fast diffusion and high capacities for sodium-ion batteries.

**Status:** published work in Advanced Materials 2023, **35**, 2209811

## A versatile platform for gas-phase molecular polaritonics

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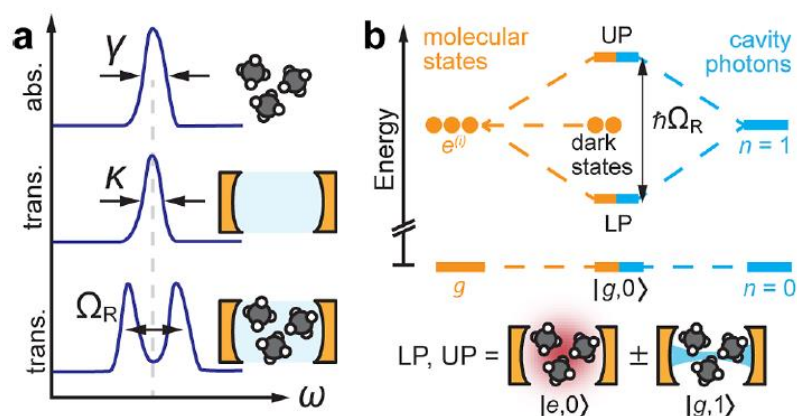
Cavity coupling of gas-phase molecules will enable studies of benchmark chemical processes under strong light–matter interactions with a high level of experimental control and no solvent effects. We recently demonstrated the formation of gas-phase molecular polaritons by strongly coupling bright  $\nu_3$ ,  $J = 3 \rightarrow 4$  rovibrational transitions of methane ( $\text{CH}_4$ ) to a Fabry–Pérot optical cavity mode inside a cryogenic buffer gas cell. Here, we further explore the flexible capabilities of this infrastructure. We show that we can greatly increase the collective coupling strength of the molecular ensemble to the cavity by increasing the intracavity  $\text{CH}_4$  number density. We explore polariton formation for cavity geometries of varying length, finesse, and mirror radius of curvature. We also report a proof-of-principle demonstration of rovibrational gas-phase polariton formation at room temperature. This experimental flexibility affords a great degree of control over the properties of molecular polaritons and opens up a wider range of simple molecular processes to future interrogation under strong cavity-coupling. We anticipate that ongoing work in gas-phase polaritonics will facilitate convergence between experimental results and theoretical models of cavity-altered chemistry and physics.

**Status:** published work in J. Chem. Phys. 2023, **159**, 164202

# Rovibrational Polaritons in Gas-Phase Methane

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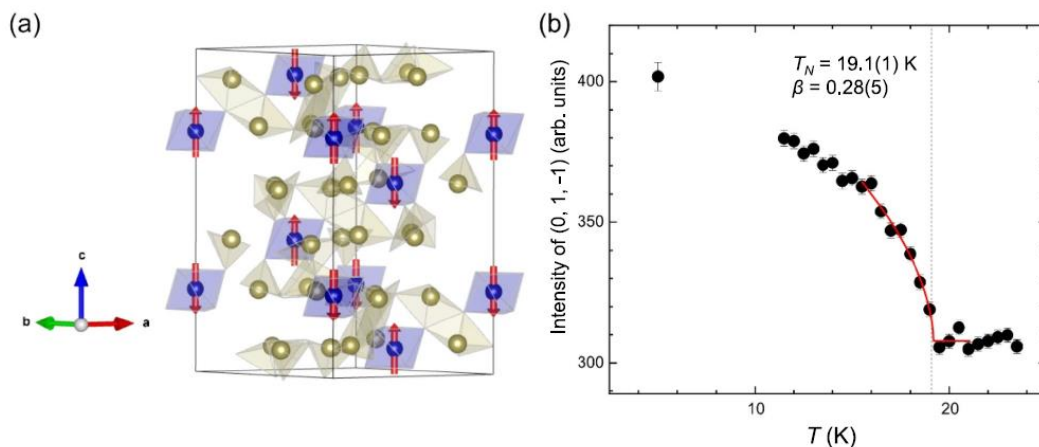
Polaritonic states arise when a bright optical transition of a molecular ensemble is resonantly matched to an optical cavity mode frequency. Here, we lay the groundwork to study the behavior of polaritons in clean, isolated systems by establishing a new platform for vibrational strong coupling in gas-phase molecules. We access the strong coupling regime in an intracavity cryogenic buffer gas cell optimized for the preparation of simultaneously cold and dense ensembles and report a proof-of-principle demonstration in gas-phase methane. We strongly cavity-couple individual rovibrational transitions and probe a range of coupling strengths and detunings. We reproduce our findings with classical cavity transmission simulations in the presence of strong intracavity absorbers. This infrastructure will provide a new testbed for benchmark studies of cavity-altered chemistry.

**Status:** published work in J. Am. Chem. Soc. 2023, **145**, 5982

# Large off-diagonal magnetoelectricity in a triangular $\text{Co}^{2+}$ -based collinear antiferromagnet

Xianghan Xu,<sup>1</sup> Yiqing Hao,<sup>2</sup> Shiyu Peng,<sup>3</sup> Qiang Zhang,<sup>2</sup> Danrui Ni,<sup>1</sup> Chen Yang,<sup>1</sup> Xi Dai,<sup>3</sup> Huibo Cao,<sup>2</sup> and R. J. Cava<sup>1</sup>

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Magnetic toroidicity is an uncommon type of magnetic structure in solid-state materials. Here, we experimentally demonstrate that collinear spins in a material with  $R\bar{3}$  lattice symmetry can host a significant magnetic toroidicity, even parallel to the ordered spins. Taking advantage of a single crystal sample of  $\text{CoTe}_6\text{O}_{13}$  with an  $R\bar{3}$  space group and a  $\text{Co}^{2+}$  triangular sublattice, temperature-dependent magnetic, thermodynamic, and neutron diffraction results reveal A-type antiferromagnetic order below 19.5 K, with magnetic point group  $\bar{3}'$  and  $\mathbf{k} = (0,0,0)$ . Our symmetry analysis suggests that the missing-mirror symmetry in the lattice could lead to the local spin canting for a toroidal moment along the  $c$  axis. Experimentally, we observe a large off-diagonal magnetoelectric coefficient of 41.2 ps/m that evidences the magnetic toroidicity. In addition, the paramagnetic state exhibits a large effective moment per  $\text{Co}^{2+}$ , indicating that the magnetic moment in  $\text{CoTe}_6\text{O}_{13}$  has a significant orbital contribution.  $\text{CoTe}_6\text{O}_{13}$  embodies an excellent opportunity for the study of next-generation functional magnetoelectric materials.

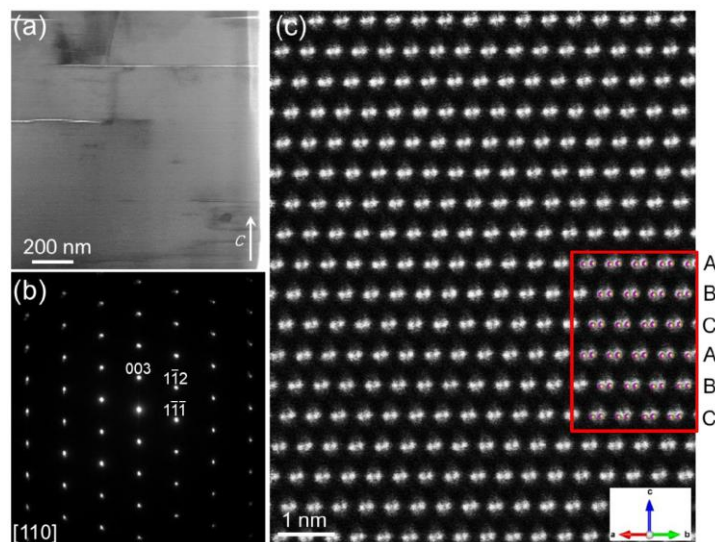
**Status:** published work in Nature Comm. 2023, **14**, 8034



## Spin disorder in a stacking polytype of a layered magnet

Xianghan Xu,<sup>1</sup> Guangming Cheng,<sup>2</sup> Danrui Ni,<sup>1</sup> Xin Gui,<sup>3</sup> Weiwei Xie,<sup>4</sup> Nan Yao,<sup>2</sup> and R. J. Cava<sup>1</sup>

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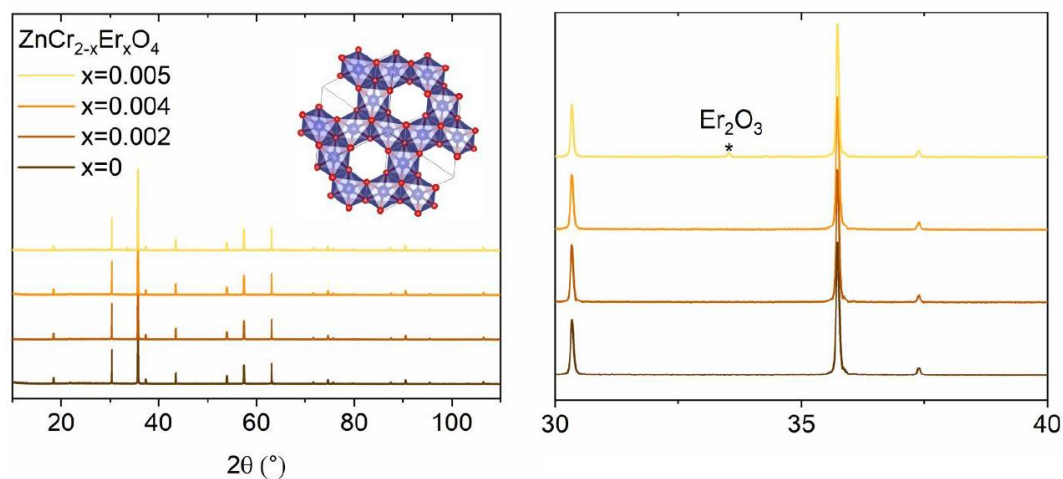
Strongly correlated ground states and exotic quasiparticle excitations in low-dimensional systems are central research topics in the solid-state research community. The present work develops a new layered material and explores the physical properties. Single crystals of 3R-Na<sub>2</sub>MnTeO<sub>6</sub> were synthesized via a flux method. Single crystal x-ray diffraction and transmission electron microscopy reveal a crystal structure with ABC-type stacking and an R-3 space group, which establishes this material as a stacking polytype to previously reported 2H-Na<sub>2</sub>MnTeO<sub>6</sub>. Magnetic and heat capacity measurements demonstrate dominant antiferromagnetic interactions, the absence of long-range magnetic order down to 0.5 K, and field-dependent short range magnetic correlations. A structural transition at ~ 23 K observed in dielectric measurements may be related to displacements of the Na positions. Our results demonstrate that 3R-Na<sub>2</sub>MnTeO<sub>6</sub> displays low-dimensional magnetism, disordered structure and spins, and the system displays a rich structure variety.

**Status:** published work in Phys. Rev. Materials 2023, **7**, 024407

## The Er doping of $\text{ZnCr}_2\text{O}_4$

Chen Yang,<sup>1,2</sup> Danrui Ni,<sup>1</sup> Nan Yao,<sup>3</sup> and Robert J. Cava<sup>1</sup>

<sup>1</sup>Department of Chemistry, Princeton University, Princeton, NJ, USA; <sup>2</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ, USA; <sup>3</sup>Princeton Materials Institute, Princeton University, Princeton, NJ, USA.



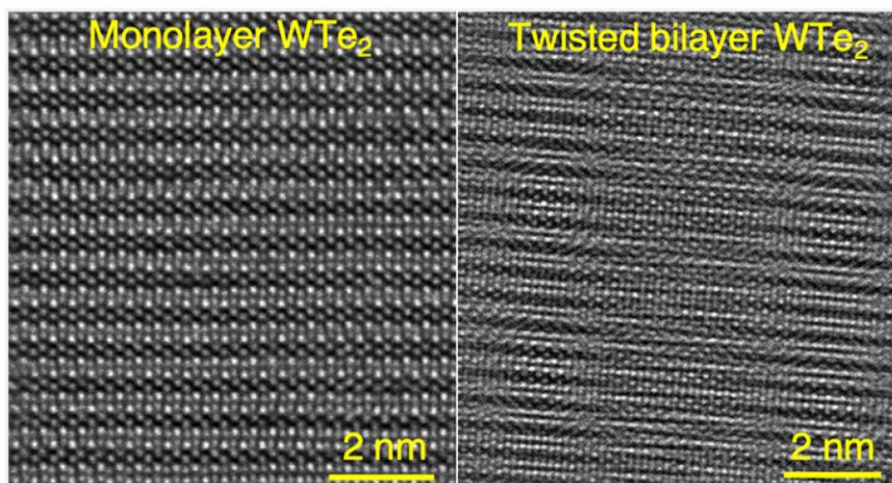
Magnetic  $\text{Er}^{3+}$  is doped into the well-studied frustrated normal spinel  $\text{ZnCr}_2\text{O}_4$ . Various spectroscopies are employed to prove that  $\text{Er}^{3+}$  successfully enters the spinel to form  $\text{ZnCr}_{2-x}\text{Er}_x\text{O}_4$  for  $x$  less than 0.005. The low levels of  $\text{Er}^{3+}$  doping possible nonetheless have a significant effect on the frustrated magnetism and the ordering that is seen near 12 K in the undoped material.

**Status:** work posted on arXiv.org: 2312.04376, 2023

## Atomic Resolution Imaging of Highly Air-Sensitive Monolayer and Twisted-Bilayer WTe<sub>2</sub>

Fang Yuan,<sup>1</sup> Yanyu Jia,<sup>2</sup> Guangming Cheng,<sup>3</sup> Ratnadwip Singha,<sup>1</sup> Shiming Lei,<sup>1</sup> Nan Yao,<sup>3</sup> Sanfeng Wu,<sup>2</sup> and Leslie M. Schoop<sup>1</sup>

<sup>1</sup>Department of Chemistry, Princeton University, Princeton, New Jersey, United States; <sup>2</sup>Department of Physics, Princeton University, Princeton, New Jersey, United States; <sup>3</sup>Princeton Materials Institute, Princeton University, Princeton, New Jersey, United States.



Bulk Td-WTe<sub>2</sub> is a semimetal, while its monolayer counterpart is a two-dimensional (2D) topological insulator. Recently, electronic transport resembling a Luttinger liquid state was found in twisted-bilayer WTe<sub>2</sub> (tWTe<sub>2</sub>) with a twist angle of  $\sim 5^\circ$ . Despite the strong interest in 2D WTe<sub>2</sub> systems, little experimental information is available about their intrinsic microstructure, leaving obstacles in modeling their physical properties. The monolayer, and consequently tWTe<sub>2</sub>, are highly air-sensitive, and therefore, probing their atomic structures is difficult. In this study, we develop a robust method for atomic-resolution visualization of monolayers and tWTe<sub>2</sub> obtained through mechanical exfoliation and fabrication. We confirm the high crystalline quality of mechanically exfoliated WTe<sub>2</sub> samples and observe that tWTe<sub>2</sub> with twist angles of  $\sim 5^\circ$  and  $\sim 2^\circ$  retains its pristine moiré structure without substantial deformations or reconstructions. The results provide a structural foundation for future electronic modeling of monolayer and tWTe<sub>2</sub>.

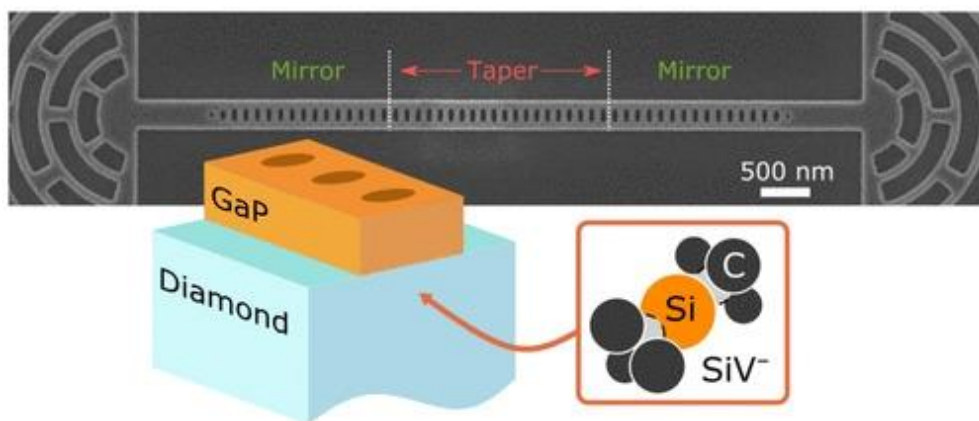
**Status:** published work in Nano Letters 2023, **23**, 6868-6874

## **Department of Electrical and Computer Engineering**

## Hybrid Integration of GaP Photonic Crystal Cavities with Silicon-Vacancy Centers in Diamond by Stamp-Transfer

Srivatsa Chakravarthi,<sup>1</sup> Nicholas S. Yama,<sup>2</sup> Alex Abulnaga,<sup>3</sup> Ding Huang,<sup>3</sup> Christian Pederson,<sup>1</sup> Karine Hestroffer,<sup>4</sup> Fariba Hatami,<sup>4</sup> Nathalie P. de Leon,<sup>3</sup> and Kai-Mei C. Fu<sup>1,5</sup>

<sup>1</sup>Physics Department, University of Washington, Seattle, Washington 98105, USA, <sup>2</sup>Electrical and Computer Engineering Department, University of Washington, Seattle, Washington 98105, USA; <sup>3</sup>Electrical and Computer Engineering Department, Princeton University, Princeton, New Jersey 08544, USA; <sup>4</sup>Department of Physics, Humboldt-Universität zu Berlin, Newtonstrasse, Berlin, 10117, Germany; <sup>5</sup>Electrical and Computer Engineering Department, University of Washington, Seattle, Washington 98105, USA; Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA



Optically addressable solid-state defects are emerging as some of the most promising qubit platforms for quantum networks. Maximizing photon-defect interaction by nanophotonic cavity coupling is key to network efficiency. We demonstrate fabrication of gallium phosphide 1-D photonic crystal waveguide cavities on a silicon oxide carrier and subsequent integration with implanted silicon-vacancy (SiV) centers in diamond using a stamp-transfer technique. The stamping process avoids diamond etching and allows fine-tuning of the cavities prior to integration. After transfer to diamond, we measure cavity quality factors ( $Q$ ) of up to 8900 and perform resonant excitation of single SiV centers coupled to these cavities. For a cavity with a  $Q$  of 4100, we observe a 3-fold lifetime reduction on-resonance, corresponding to a maximum potential cooperativity of  $C = 2$ . These results indicate promise for high photon-defect interaction in a platform which avoids fabrication of the quantum defect host crystal.

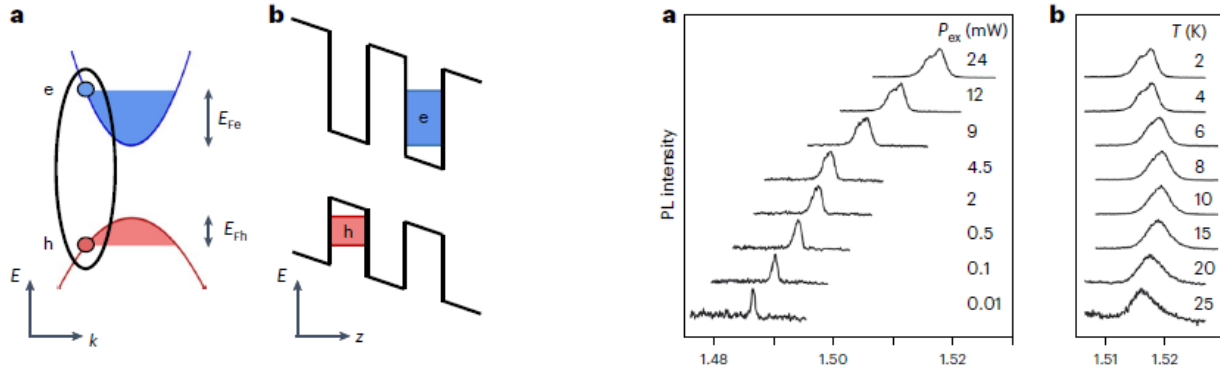
**Status:** published work in Nano Lett. 2023, **23**, 3708–3715



## Fermi edge singularity in neutral electron–hole system

D. J. Choksy,<sup>1</sup> E. A. Szwed,<sup>1</sup> L. V. Butov,<sup>1</sup> K. W. Baldwin,<sup>2</sup> and L. N. Pfeiffer<sup>2</sup>

<sup>1</sup>Department of Physics, University of California at San Diego, La Jolla, CA, USA. <sup>2</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ, USA.



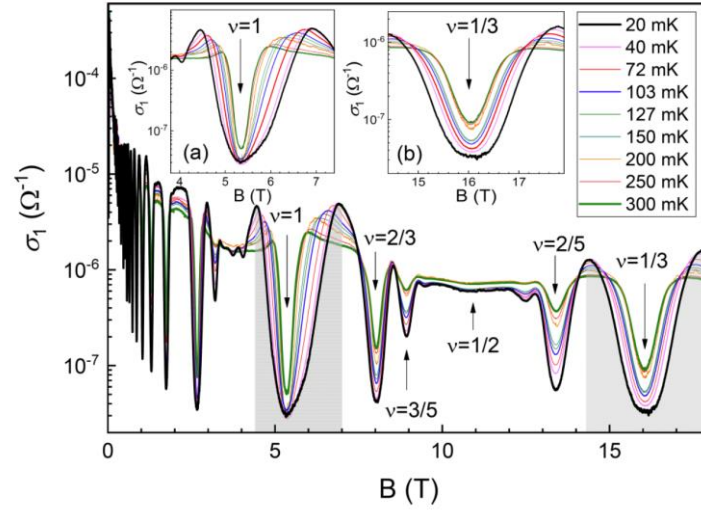
In neutral dense electron–hole systems at low temperatures, theory predicted Cooper-pair-like excitons exist at the Fermi energy and form a Bardeen–Cooper–Schrieffer-like condensate. Optical excitations create electron–hole systems with the density controlled via the excitation power. However, the intense optical excitations required to achieve high densities cause substantial heating that prevents the realization of simultaneously dense and cold electron–hole systems in conventional semiconductors. Here we show that the separation of electron and hole layers enables the realization of a simultaneously dense and cold electron–hole system. We find a strong enhancement of photoluminescence intensity at the Fermi energy of the neutral dense ultracold electron–hole system that demonstrates the emergence of an excitonic Fermi edge singularity due to the formation of Cooper-pair-like excitons at the Fermi energy. Our measurements also show a crossover from the hydrogen-like excitons to the Cooper-pair-like excitons with increasing density, consistent with the theoretical prediction of a smooth transition.

**Status:** published work in Nature Physics 2023, **19**, 1275–1279

## Coexistence of two hole phases in high-quality p-GaAs/AlGaAs in the vicinity of Landau-level filling factors $\nu = 1$ and $\nu = (1/3)$

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<sup>1</sup>Ioffe Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia; <sup>2</sup>National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA; <sup>3</sup>Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, USA; <sup>4</sup>Department of Physics, University of Oslo, Blindern, 0316 Oslo, Norway.



We focused on the transverse AC magnetoconductance of a high-mobility p-GaAs/AlGaAs quantum well ( $p = 1.2 \times 10^{11} \text{cm}^{-2}$ ) in the vicinity of two values of the Landau-level filling factor  $\nu$ :  $\nu = 1$  (integer quantum Hall effect) and  $\nu = 1/3$  (fractional quantum Hall effect). The complex transverse AC conductance  $\sigma_{xx}^{\text{AC}}(\omega)$  was found from simultaneous measurements of attenuation and velocity of surface acoustic waves propagating along the interface between a piezoelectric crystal and the two-dimensional hole system under investigation. We analyzed both the real and imaginary parts of the hole conductance and compared the similarities and differences between the results for filling factor 1 and filling factor  $1/3$ . Both to the left and to the right of these values maxima of a specific shape, “wings,” arose in the  $\sigma(\nu)$  dependences at those two  $\nu$ . Analysis of the results of our acoustic measurements at different temperatures and surface acoustic wave frequencies allowed us to attribute these wings to the formation of collective localized states, namely, the domains of a pinned Wigner crystal, i.e., a Wigner solid. While the Wigner solid has been observed in 2D hole systems previously, we were able to detect it at the highest hole density and, therefore, the lowest hole-hole interaction reported.

**Status:** published work in Phys. Rev. B 2023, **107**, 085301

## Thin-Film Organic Heteroepitaxy

Jordan T. Dull,<sup>1</sup> Xu He,<sup>1</sup> Jonathan Viereck,<sup>2</sup> Qianxiang Ai,<sup>3</sup> Ritika Ramprasad,<sup>1</sup> Maria Clara Otani,<sup>1</sup> Jeni Sorli,<sup>4</sup> Jason W. Brandt,<sup>5</sup> Brad P. Carrow,<sup>5</sup> Arthur D. Tinoco,<sup>6</sup> Yueh-Lin Loo,<sup>4</sup> Chad Risko,<sup>3</sup> Sylvie Rangan,<sup>2</sup> Antoine Kahn,<sup>1</sup> and Barry P. Rand<sup>1,7</sup>

<sup>1</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ 08544, USA;

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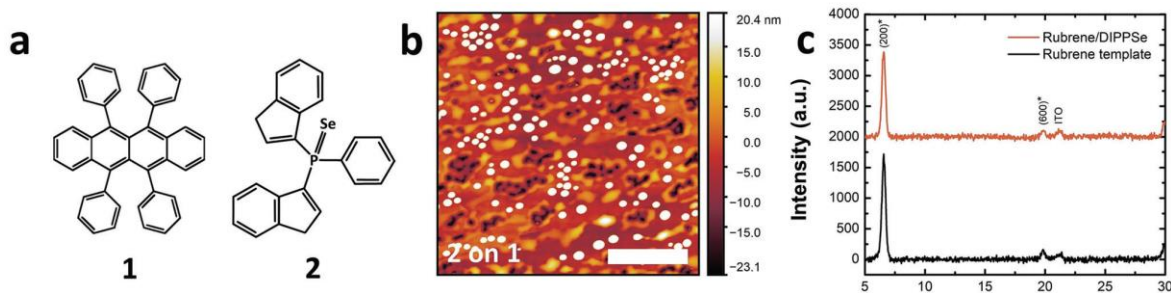
NJ 08854, USA <sup>3</sup>Department of Chemistry and Center for Applied Energy Research, University of Kentucky,

Lexington, KY 40506, USA; <sup>4</sup>Department of Chemical and Biological Engineering, Princeton University, Princeton,

NJ 08544, USA; <sup>5</sup>Department of Chemistry, Princeton University, Princeton, NJ 08544, USA; <sup>6</sup>Department of

Chemistry, University of Puerto Rico-Río Piedras Campus, San Juan, PR 00925, USA; <sup>7</sup>Andlinger Center for

Energy and the Environment, Princeton University, Princeton, NJ 08544, USA.



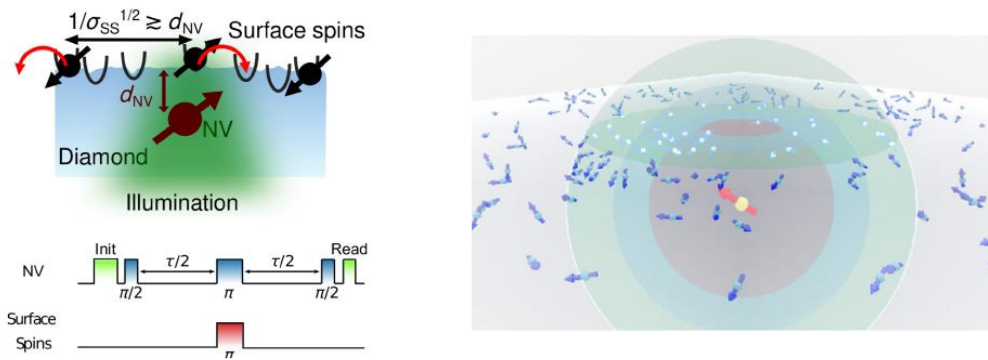
Incorporating crystalline organic semiconductors into electronic devices requires understanding of heteroepitaxy given the ubiquity of heterojunctions in these devices. However, while rules for commensurate epitaxy of covalent or ionic inorganic material systems are known to be dictated by lattice matching constraints, rules for heteroepitaxy of molecular systems are still being written. Here, it is found that lattice matching alone is insufficient to achieve heteroepitaxy in molecular systems, owing to weak intermolecular forces that describe molecular crystals. It is found that, in addition, the lattice matched plane also must be the lowest energy surface of the adcrystal to achieve one-to-one commensurate molecular heteroepitaxy over a large area. Ultraviolet photoelectron spectroscopy demonstrates the lattice matched interface to be of higher electronic quality than a disordered interface of the same materials.

**Status:** published work in *Advanced Materials* 2023, **35**, 2302871

# Probing Spin Dynamics on Diamond Surfaces Using a Single Quantum Sensor

Bo L. Dwyer,<sup>1</sup> Lila V.H. Rodgers,<sup>2</sup> E. K. Urbach,<sup>1</sup> D. Bluvstein,<sup>1</sup> S. Sangtawesin,<sup>3</sup> H. Zhou,<sup>1</sup> Y. Nassab,<sup>2</sup> M. Fitzpatrick,<sup>2</sup> Zh. Yuan,<sup>2</sup> K. De Greve,<sup>1</sup> E. L. Peterson,<sup>1</sup> H. Knowles,<sup>1</sup> T. Sumarac,<sup>1</sup> Jyh-Pin Chou,<sup>4</sup> A. Gali,<sup>5,6</sup> V.V. Dobrovitski,<sup>7</sup> M. D. Lukin,<sup>1</sup> and N. P. de Leon<sup>2</sup>

<sup>1</sup>Department of Physics, Harvard University, Cambridge, MA, USA; <sup>2</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ, USA; <sup>3</sup>School of Physics and Center of Excellence in Advanced Functional Materials, Suranaree University of Technology, Nakhon Ratchasima, Thailand; <sup>4</sup>Department of Physics, National Changhua University of Education, Changhua, Taiwan; <sup>5</sup>Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Budapest, Hungary; <sup>6</sup>Department of Atomic Physics, Institute of Physics, Budapest University of Technology and Economics, Budapest, Hungary; <sup>7</sup>QuTech and Kavli Institute of Nanoscience, Delft University of Technology, Delft, Netherlands.



Understanding the dynamics of a quantum bit's environment is essential for the realization of practical systems for quantum information processing and metrology. We use single nitrogen-vacancy (NV) centers in diamond to study the dynamics of a disordered spin ensemble at the diamond surface. When the average surface spin spacing exceeds the NV center depth, we find that the surface spin contribution to the NV center free induction decay can be described by a stretched exponential with variable power  $n$ . We show that these observations are consistent with a model in which the spatial positions of the surface spins are fixed for each measurement. In particular, we observe a depth-dependent critical time associated with a dynamical transition from Gaussian ( $n = 2$ ) decay to  $n = 2/3$ , and show that this transition arises from the competition between the small decay contributions of many distant spins and strong coupling to a few proximal spins at the surface. These observations demonstrate the potential of a local sensor for understanding complex systems pathways for controlling spin qubits at the surface.

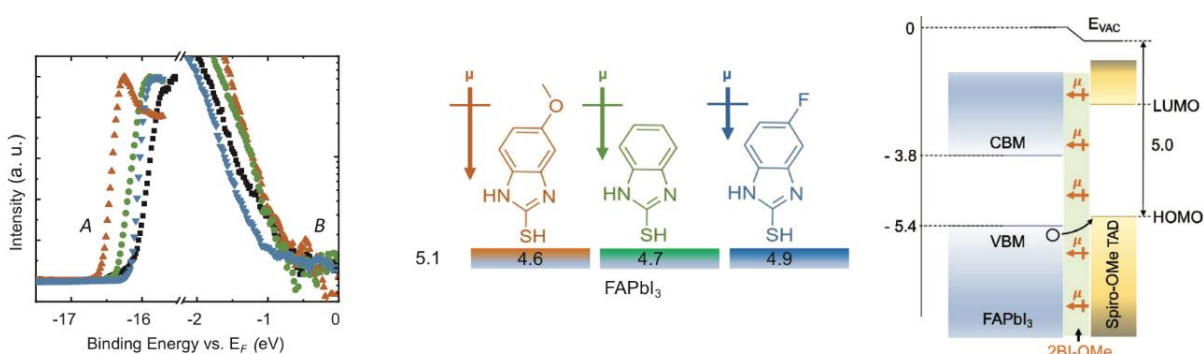
**Status:** published work in PRX Quantum, 2022, **3**, 040328

# Triiodide Attacks the Organic Cation in Hybrid Lead Halide Perovskites: Mechanism and Suppression

Junnan Hu,<sup>1</sup> Zhaojian Xu,<sup>1</sup> Tucker L. Murrey,<sup>1</sup> István Pelczar,<sup>2</sup> Antoine Kahn,<sup>1</sup> Jeffrey Schwartz,<sup>2</sup> and Barry P. Rand<sup>3</sup>

<sup>1</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ 08544, USA;

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Molecular I<sub>2</sub> can be produced from iodide-based lead perovskites under thermal stress; triiodide, I<sub>3</sub><sup>-</sup>, is formed from this I<sub>2</sub> and I<sup>-</sup>. Triiodide attacks protic cation MA<sup>+</sup> or FA<sup>+</sup>-based lead halide perovskites (MA<sup>+</sup>, methylammonium; FA<sup>+</sup>, formamidinium) as explicated through solution-based nuclear magnetic resonance (NMR) studies: triiodide has strong hydrogen-bonding affinity for MA<sup>+</sup> or FA<sup>+</sup>, which leads to their deprotonation and perovskite decomposition. Triiodide is a catalyst for this decomposition that can be obviated through perovskite surface treatment with thiol reducing agents. In contrast to methods using thiol incorporation into perovskite precursor solutions, no penetration of the thiol into the bulk perovskite is observed, yet its surface application stabilizes the perovskite against triiodide-mediated thermal stress. Thiol applied to the interface between FAPbI<sub>3</sub> and Spiro-OMeTAD (“Spiro”) prevents oxidized iodine species penetration into Spiro and thus preserves its hole-transport efficacy. Surface-applied thiol affects the perovskite work function; it ameliorates hole injection into the Spiro overlayer, thus improving device performance. It helps to increase interfacial adhesion (“wetting”): fewer voids are observed at the Spiro/perovskite interface if thiols are applied. Perovskite solar cells (PSCs) incorporating interfacial thiol treatment maintain over 80% of their initial power conversion efficiency (PCE) after 300 h of 85 °C thermal stress.

**Status:** published work in Adv. Mater. 2023, **35**, 2303373



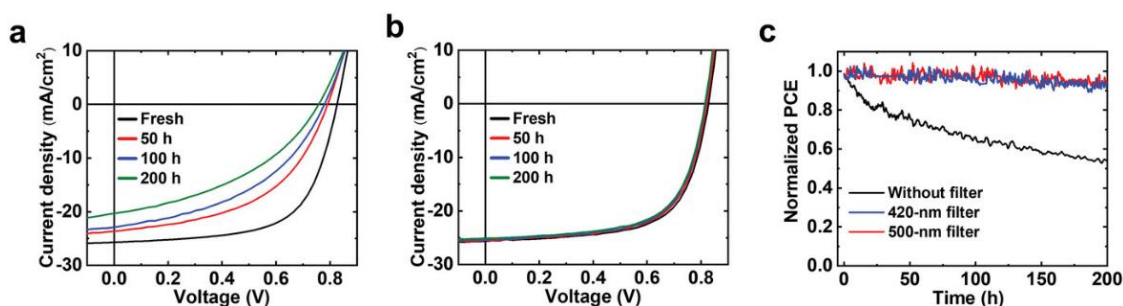
# Photochemical Decomposition of Y-Series Non-Fullerene Acceptors Is Responsible for Degradation of High-Efficiency Organic Solar Cells

Tianran Liu,<sup>1</sup> Quinn C. Burlingame,<sup>2</sup> Marko R. Ivancevic,<sup>3</sup> Xiao Liu,<sup>1</sup> Junnan Hu,<sup>1</sup> Barry P. Rand,<sup>1,2</sup> Yueh-Lin Loo.<sup>3</sup>

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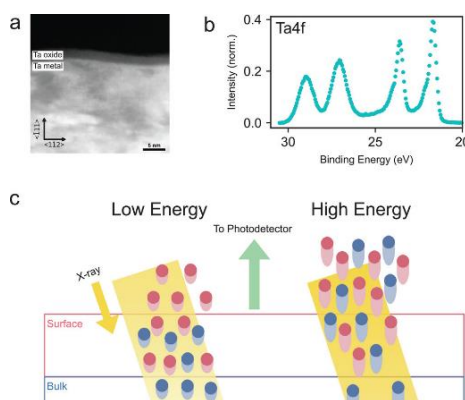
Organic photovoltaic cells that employ Y-series non-fullerene acceptors (NFAs) have recently achieved impressive power-conversion efficiencies (>18%). To fulfill their commercial promise, it is important to quantify their operational lifetimes and understand their degradation mechanisms. In this work, the spectral-dependent photostability of films and solar cells comprising several Y-series acceptors and the donor polymer PM6 is investigated systematically. By applying longpass filters during aging, it is shown that UV/near-UV photons are responsible for the photochemical decomposition of Y-series acceptors; this degradation is the primary driver of early solar cell performance losses. Using mass spectrometry, the vinylene linkage between the core and electron-accepting moieties of Y-series acceptors is identified as the weak point susceptible to cleavage under UV-illumination. Employing a series of device characterization, along with numerical simulations, the efficiency losses in organic photovoltaic cells are attributed to the formation of traps, which reduces charge extraction efficiency and facilitates non-radiative recombination as the Y-series acceptors degrade. This study provides new insights for molecular degradation of organic photovoltaic absorber materials and highlights the importance of future molecular design and strategies for improved solar cell stability.

**Status:** published work in Adv. Energy Mater. 2023, **13**, 2300046

## Chemical Profiles of the Oxides on Tantalum in State of the Art Superconducting Circuits

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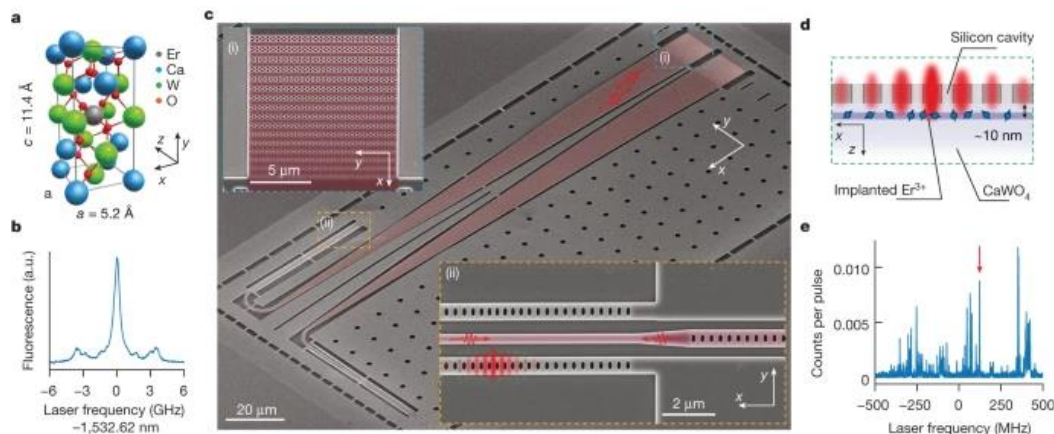
Over the past decades, superconducting qubits have emerged as one of the leading hardware platforms for realizing a quantum processor. Consequently, researchers have made significant effort to understand the loss channels that limit the coherence times of superconducting qubits. A major source of loss has been attributed to two level systems that are present at the material interfaces. It is recently shown that replacing the metal in the capacitor of a transmon with tantalum yields record relaxation and coherence times for superconducting qubits, motivating a detailed study of the tantalum surface. In this work, the chemical profile of the surface of tantalum films grown on c-plane sapphire using variable energy X-ray photoelectron spectroscopy (VEXPS) is studied. The different oxidation states of tantalum that are present in the native oxide resulting from exposure to air are identified, and their distribution through the depth of the film is measured. Furthermore, it is shown how the volume and depth distribution of these tantalum oxidation states can be altered by various chemical treatments. Correlating these measurements with detailed measurements of quantum devices may elucidate the underlying microscopic sources of loss.

**Status:** published work in Adv. Sci. 2023, **10**, 2300921

# Indistinguishable telecom band photons from a single Er ion in the solid state

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Atomic defects in the solid state are a key component of quantum repeater networks for long-distance quantum communication<sup>1</sup>. Recently, there has been significant interest in rare earth ions, in particular Er<sup>3+</sup> for its telecom band optical transition that allows long-distance transmission in optical fibres. However, the development of repeater nodes based on rare earth ions has been hampered by optical spectral diffusion, precluding indistinguishable single-photon generation. Here, we implant Er<sup>3+</sup> into CaWO<sub>4</sub>, a material that combines a non-polar site symmetry, low decoherence from nuclear spins and is free of background rare earth ions, to realize significantly reduced optical spectral diffusion. For shallow implanted ions coupled to nanophotonic cavities with large Purcell factor, we observe single-scan optical linewidths of 150 kHz and long-term spectral diffusion of 63 kHz, both close to the Purcell-enhanced radiative linewidth of 21 kHz. This enables the observation of Hong–Ou–Mandel interference between successively emitted photons with a visibility of  $V = 80(4)\%$ , measured after a 36 km delay line. We also observe spin relaxation times  $T_{1,s} = 3.7 \text{ s}$  and  $T_{2,s} > 200 \text{ μs}$ , with the latter limited by paramagnetic impurities in the crystal instead of nuclear spins. This represents a notable step towards the construction of telecom band quantum repeater networks with single Er<sup>3+</sup> ions.

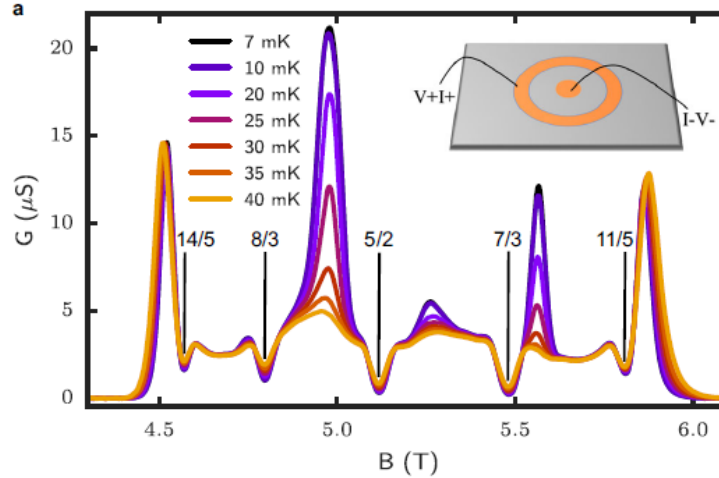
**Status:** published work in Nature 2023, **620**, 977–981

## Large composite fermion effective mass at filling factor 5/2

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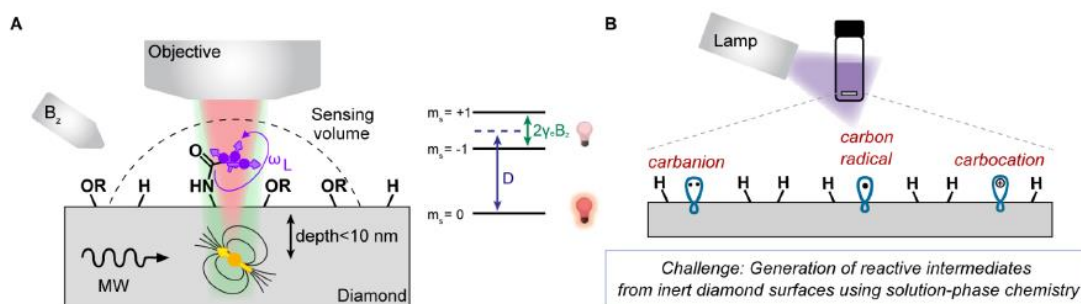


The 5/2 fractional quantum Hall effect in the second Landau level of extremely clean two-dimensional electron gases has attracted much attention due to its topological order predicted to host quasiparticles that obey non-Abelian quantum statistics and could serve as a basis for fault-tolerant quantum computations. While previous works have established the Fermi liquid (FL) nature of its putative composite fermion (CF) normal phase, little is known regarding its thermodynamics properties and as a result its effective mass is entirely unknown. Here, we report on time-resolved specific heat measurements at filling factor 5/2, and we examine the ratio of specific heat to temperature as a function of temperature. Combining these specific heat data with existing longitudinal thermopower data measuring the entropy in the clean limit we find that, unless a phase transition/crossover gives rise to large specific heat anomaly, both datasets point towards a large effective mass in the FL phase of CFs at 5/2. We estimate the effective-to-bare mass ratio  $m^*/m_e$  to be ranging from  $\sim 2$  to 4, which is two to three times larger than previously measured values in the first Landau level.

**Status:** published work in Nature Communications 2023, **14**, 7250

# Diamond Surface Functionalization via Visible Light-Driven C–H Activation for Nanoscale Quantum Sensing

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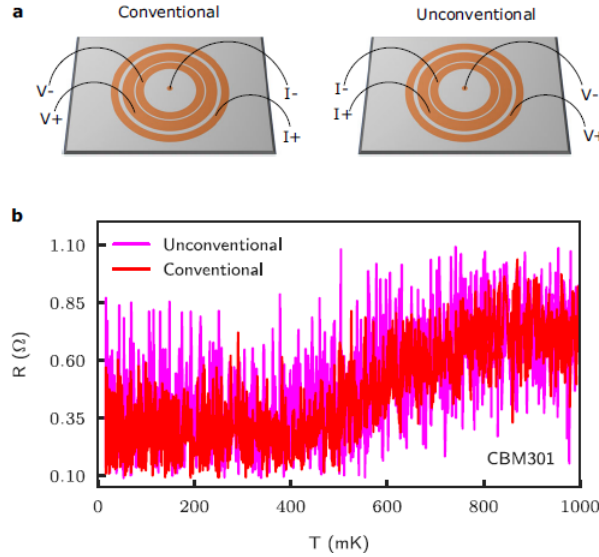
Nitrogen-vacancy (NV) centers in diamond are a promising platform for nanoscale nuclear magnetic resonance (NMR) sensing. Despite significant progress towards using NV centers to detect nuclear spins down to the single spin level, NV-based spectroscopy of individual, intact, arbitrary target molecules remains elusive. The inert nature of diamond typically requires harsh functionalization techniques, limiting the scope of functional groups that can be attached to the surface. Solution-phase chemical methods can be more readily generalized to install diverse functional groups. In this work, we report a versatile strategy to directly functionalize C–H bonds on single-crystal diamond surfaces under ambient conditions. Hydrogen atom abstraction from surface C–H bonds generates carbon-centered radicals that can form C–F, C–Cl, C–S, and C–N bonds at the surface. We verify covalent bond formation using lab and synchrotron-based surface analysis. As a proof of principle, we use shallow ensembles of NV centers to detect nuclear spins from functional groups attached to the surface. Our approach opens the door to deploying NV centers as a broad tool for chemical sensing and single-molecule spectroscopy.

**Status:** work posted on arXiv.org: 2309.07354, 2023

## Anomalous electronic transport in high-mobility Corbino rings

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We report low-temperature electronic transport measurements performed in two multi-terminal Corbino samples formed in GaAs/Al-GaAs two-dimensional electron gases (2DEG) with both ultra-high electron mobility ( $\gtrsim 20 \times 10^6 \text{ cm}^2/\text{Vs}$ ) and with distinct electron density of  $1.7$  and  $3.6 \times 10^{11} \text{ cm}^{-2}$ . In both Corbino samples, a non-monotonic behavior is observed in the temperature dependence of the resistance below 1 K. Surprisingly, a sharp decrease in resistance is observed with increasing temperature in the sample with lower electron density, whereas an opposite behavior is observed in the sample with higher density. To investigate further, transport measurements were performed in large van der Pauw samples having identical heterostructures, and as expected they exhibit resistivity that is monotonic with temperature. Finally, we discuss the results in terms of various lengthscales leading to ballistic and hydrodynamic electronic transport, as well as a possible Gurzhi effect.

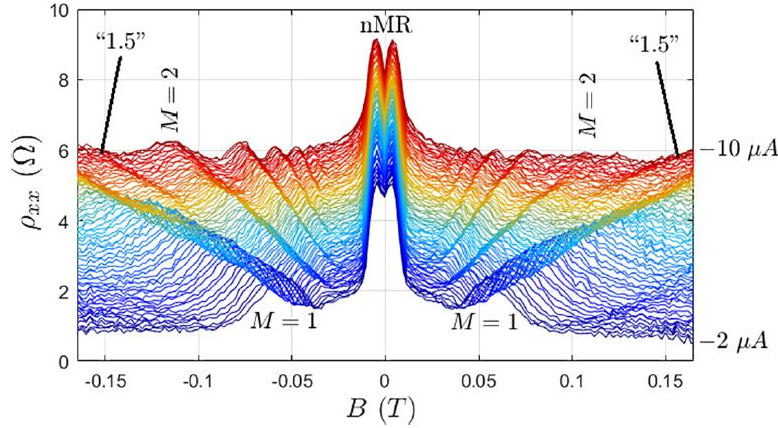
**Status:** published work in Nature Comm. 2023, **14**, 3906



# Nonlinear transport phenomena and current-induced hydrodynamics in ultrahigh mobility two-dimensional electron gas

Z. T. Wang,<sup>1</sup> M. Hilke,<sup>1</sup> N. Fong,<sup>2</sup> D. G. Austing,<sup>1,2</sup> S. A. Studenikin,<sup>2</sup> K. W. West,<sup>3</sup> and L. N. Pfeiffer<sup>3</sup>

<sup>1</sup>Department of Physics, McGill University, Montréal, Quebec H3A 2T8, Canada; <sup>2</sup>Emerging Technology Division, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; <sup>3</sup>Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, USA



We report on nonlinear transport phenomena at high filling factor and DC current-induced electronic hydrodynamics in an ultrahigh mobility ( $\mu = 20 \times 10^6 \text{ cm}^2/\text{Vs}$ ) two-dimensional electron gas in a narrow (15 –  $\mu\text{m}$  wide) GaAs/AlGaAs Hall bar for DC current densities reaching 0.67 A/m. The various phenomena and the boundaries between the phenomena are captured together in a two-dimensional differential resistivity map as a function of magnetic field (up to 250 mT) and DC current. This map, which resembles a phase diagram, demarcate distinct regions dominated by Shubnikov-de Haas (SdH) oscillations around zero DC current; negative magnetoresistance and a double-peak feature (both ballistic in origin) around zero field; and Hall field-induced resistance oscillations (HIROs) radiating out from the origin. We show that increasing the DC current suppresses the electron-electron scattering length that drives a growing hydrodynamic contribution to both the differential longitudinal and transverse (Hall) resistivities. We also find a significant difference between the quantum lifetime extracted from SdH oscillations, and the quantum lifetime extracted from HIROs. In addition, we observe an unexpected HIRO-like feature close to midway between the first-order and the second-order HIRO maxima at high DC current.

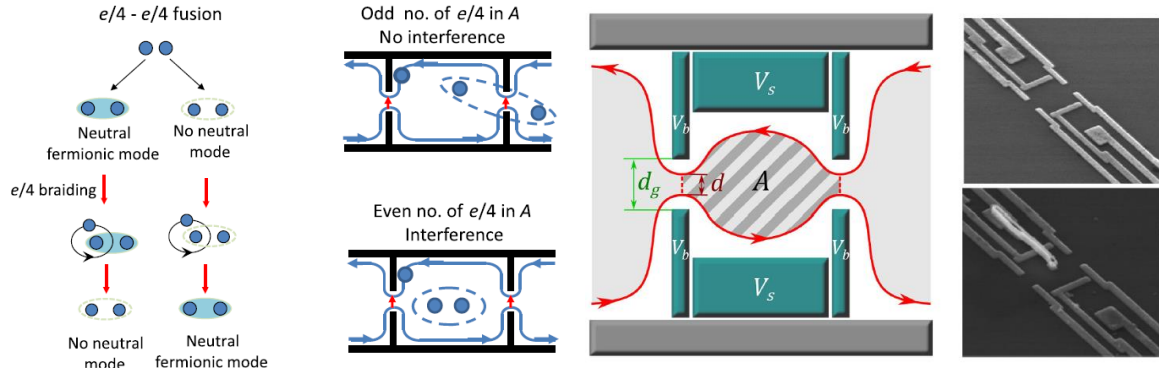
**Status:** published work in Phys. Rev. B 2023, **107**, 195406

# Interference Measurements of Non-Abelian $e/4$ & Abelian $e/2$ Quasiparticle Braiding

R. L. Willett,<sup>1</sup> K. Shtengel,<sup>2</sup> C. Nayak,<sup>3,4</sup> L. N. Pfeiffer,<sup>5</sup> Y. J. Chung,<sup>5</sup> M. L. Peabody,<sup>1</sup> K.W. Baldwin,<sup>5</sup> and K.W. West<sup>5</sup>

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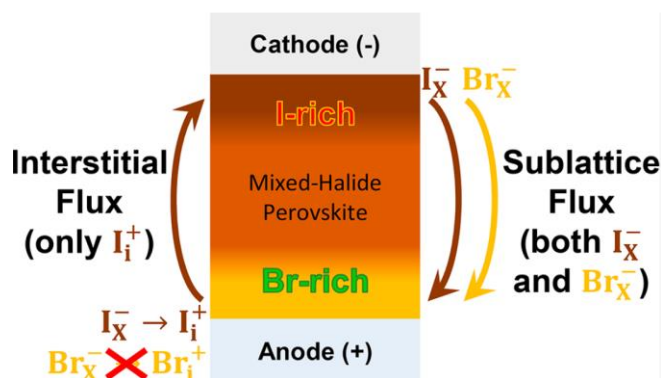
The quantum Hall states at filling factors  $\nu = 5/2$  and  $7/2$  are expected to have Abelian charge- $e/2$  quasiparticles and non-Abelian charge- $e/4$  quasiparticles. The non-Abelian statistics of the latter is predicted to display a striking interferometric signature, the even-odd effect. By measuring resistance oscillations as a function of the magnetic field in Fabry-Perot interferometers using new high-purity heterostructures, we for the first time report experimental evidence for the non-Abelian nature of excitations at  $\nu = 7/2$ . At both  $\nu = 5/2$  and  $7/2$ , we also examine, for the first time, the fermion parity. The phase of observed  $e/4$  oscillations is reproducible and stable over long times (hours) near both filling factors, indicating stability of the fermion parity. At both fractions, when phase fluctuations are observed, they are predominantly  $\pi$  phase flips, consistent with either fermion parity change or change in the number of the enclosed  $e/4$  quasiparticles. We also examine lower-frequency oscillations attributable to Abelian interference processes in both states. Taken together, these results constitute new evidence for the non-Abelian nature of  $e/4$  quasiparticles; the observed lifetime of their combined fermion parity further strengthens the case for their utility for topological quantum computation.

**Status:** published work in Phys. Rev. X 2023, **13**, 011028

## Halogen Redox Shuttle Explains Voltage-Induced Halide Redistribution in Mixed-Halide Perovskite Devices

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<sup>1</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ, USA; <sup>2</sup>National Renewable Energy Laboratory, Golden, CO, USA; <sup>3</sup>Renewable and Sustainable Energy Institute and Department of Physics, University of Colorado Boulder, Boulder, CO, USA; <sup>4</sup>Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA



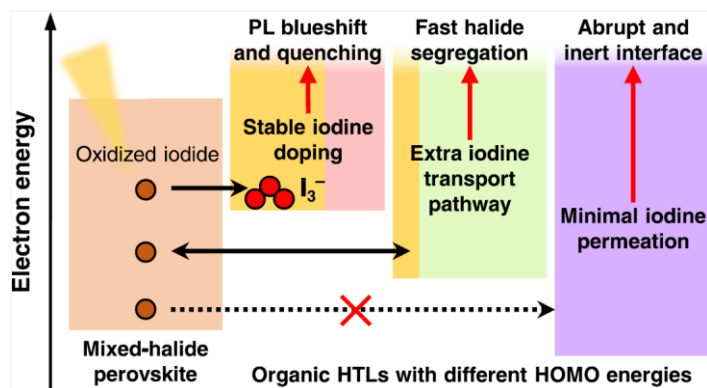
Voltage-induced halide segregation greatly limits the optoelectronic applications of mixed-halide perovskite devices, but a mechanistic explanation behind this phenomenon remains unclear. In this work, we use electron microscopy and elemental mapping to directly measure the halide redistribution in mixed-halide perovskite solar cells with quasi-ion-impermeable contact layers under different bias polarities to find iodide and bromide accumulation at the cathode and anode, respectively. This is consistent with a mechanism based on preferential iodide oxidation at the anode, leading to unbalanced  $I_i^+$ ,  $I_X^-$ , and  $Br_X^-$  fluxes. Importantly, switching the anode from “inert” Au to “active” Ag prevents segregation because Ag oxidation precludes the oxidation of lattice iodide, which suggests employing redox-active additives as a general strategy to suppress halide segregation. Overall, these results show that halide perovskite devices operate as solid-state electrochemical cells when threshold voltages are exceeded, providing fresh insight to understand the impacts of voltage bias on halide perovskite devices.

**Status:** published work in ACS Energy Lett. 2023, **8**, 513

## Origins of Photoluminescence Instabilities at Halide Perovskite/Organic Hole Transport Layer Interfaces

Zhaojian Xu,<sup>1</sup> Daniel D. Astridge,<sup>2</sup> Ross A. Kerner,<sup>3</sup> Xinjue Zhong,<sup>1</sup> Junnan Hu,<sup>1</sup> Jisu Hong,<sup>1</sup> Jesse A. Wisch,<sup>1</sup> Kai Zhu,<sup>3</sup> Joseph J. Berry,<sup>3,4</sup> Antoine Kahn,<sup>1</sup> Alan Sellinger,<sup>2</sup> and Barry P. Rand<sup>1,5</sup>

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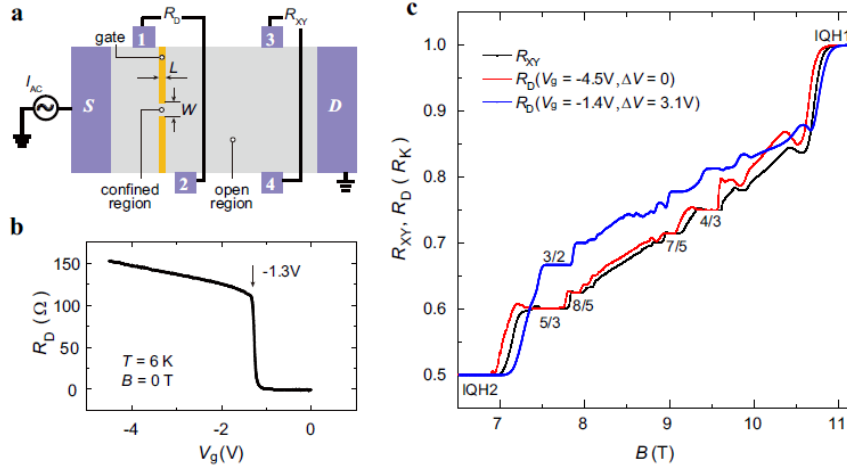
Metal halide perovskites are promising for optoelectronic device applications; however, their poor stability under solar illumination remains a primary concern. While the intrinsic photostability of isolated neat perovskite samples has been widely discussed, it is important to explore how charge transport layers-employed in most devices-impact photostability. Herein, we study the effect of organic hole transport layers (HTLs) on light-induced halide segregation and photoluminescence (PL) quenching at perovskite/organic HTL interfaces. By employing a series of organic HTLs, we demonstrate that the HTL's highest occupied molecular orbital energy dictates behavior; furthermore, we reveal the key role of halogen loss from the perovskite and subsequent permeation into organic HTLs, where it acts as a PL quencher at the interface and introduces additional mass transport pathways to facilitate halide phase separation. In doing so, we both reveal the microscopic mechanism of non-radiative recombination at perovskite/organic HTL interfaces and detail the chemical rationale for closely matching the perovskite/organic HTL energetics to maximize solar cell efficiency and stability.

**Status:** published work in J. Am. Chem. Soc. 2023, **145**, 11846

# Anomalous quantized plateaus in two-dimensional electron gas with gate confinement

Jiaojie Yan,<sup>1</sup> Yijia Wu,<sup>1</sup> Shuai Yuan,<sup>1</sup> Xiao Liu,<sup>1</sup> L. N. Pfeiffer,<sup>2</sup> K. W. West,<sup>2</sup> Yang Liu,<sup>1</sup> Hailong Fu,<sup>3</sup> X. C. Xie,<sup>1,4</sup> and Xi Lin<sup>1,4,5</sup>

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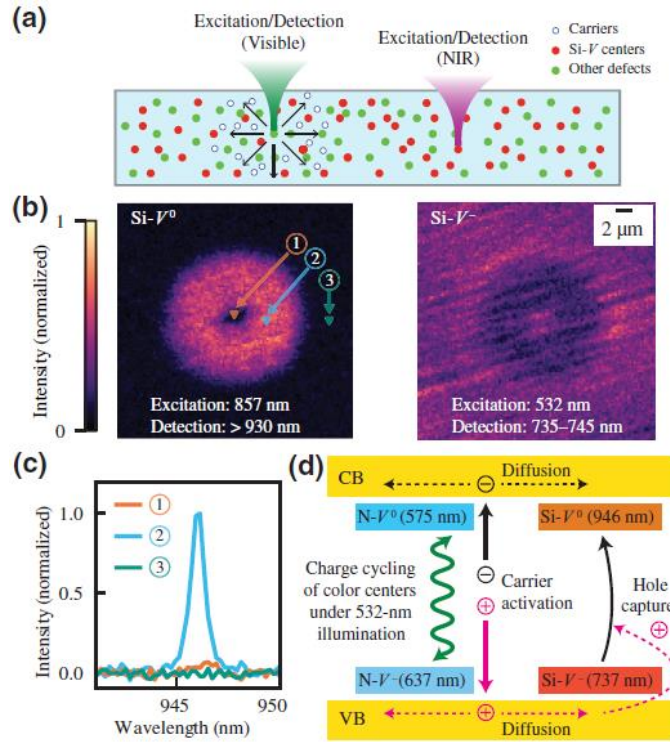
Quantum information can be coded by the topologically protected edges of fractional quantum Hall (FQH) states. Investigation on FQH edges in the hope of searching and utilizing non-Abelian statistics has been a focused challenge for years. Manipulating the edges, e.g. to bring edges close to each other or to separate edges spatially, is a common and essential step for such studies. The FQH edge structures in a confined region are typically presupposed to be the same as that in the open region in analysis of experimental results, but whether they remain unchanged with extra confinement is obscure. In this work, we present a series of unexpected plateaus in a confined single-layer two-dimensional electron gas (2DEG), which are quantized at anomalous fractions such as  $9/4$ ,  $17/11$ ,  $16/13$  and the reported  $3/2$ . We explain all the plateaus by assuming surprisingly larger filling factors in the confined region. Our findings enrich the understanding of edge states in the confined region and in the applications of gate manipulation, which is crucial for the experiments with quantum point contact and interferometer.

**Status:** published work in Nature Comm. 2023, **14**, 1758

# Neutral Silicon-Vacancy Centers in Diamond via Photoactivated Itinerant Carriers

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<sup>1</sup>Department of Electrical and Computer Engineering, Princeton University, USA; <sup>2</sup>Element Six, Harwell, UK



Neutral silicon-vacancy (Si-V<sup>0</sup>) centers in diamond are promising candidates for quantum network applications because of their exceptional optical properties and spin coherence. However, the stabilization of Si-V<sup>0</sup> centers requires careful Fermi-level engineering of the diamond host material, making further technological development challenging. Here, we show that Si-V<sup>0</sup> centers can be efficiently stabilized by photoactivated itinerant carriers. Even in this nonequilibrium configuration, the resulting Si-V<sup>0</sup> centers are stable enough to allow for resonant optical excitation and optically detected magnetic resonance. Our results pave the way for on-demand generation of Si-V<sup>0</sup> centers as well as other emerging quantum defects in diamond.

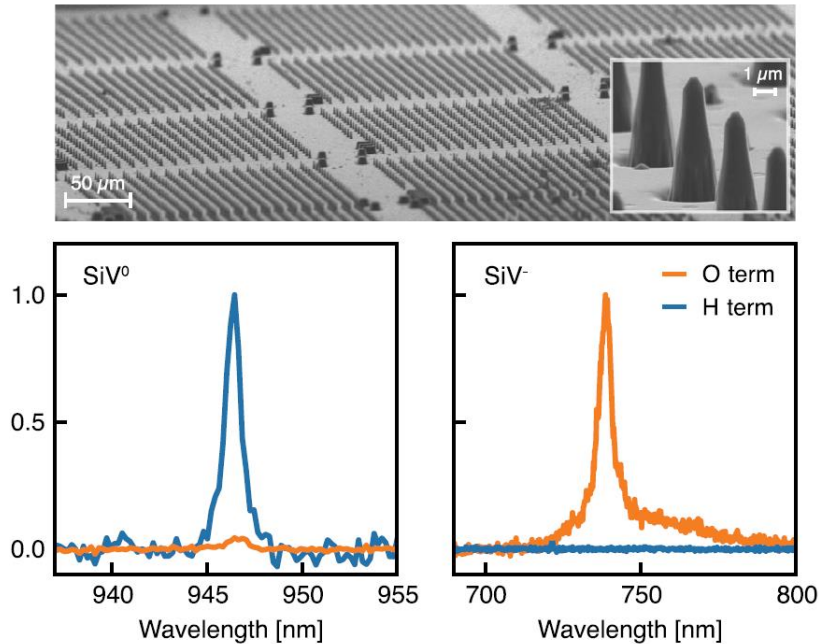
**Status:** published work in Phys. Rev. Applied 2023, **19**, 034022



# Neutral Silicon Vacancy Centers in Undoped Diamond via Surface Control

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Neutral silicon vacancy centers (SiV<sup>0</sup>) in diamond are promising candidates for quantum applications; however, stabilizing SiV<sup>0</sup> requires high-purity, boron-doped diamond, which is not a readily available material. Here, we demonstrate an alternative approach via chemical control of the diamond surface. We use low-damage chemical processing and annealing in a hydrogen environment to realize reversible and highly stable charge state tuning in undoped diamond. The resulting SiV<sup>0</sup> centers display optically detected magnetic resonance and bulklike optical properties. Controlling the charge state tuning via surface termination offers a route for scalable technologies based on SiV<sup>0</sup> centers, as well as charge state engineering of other defects.

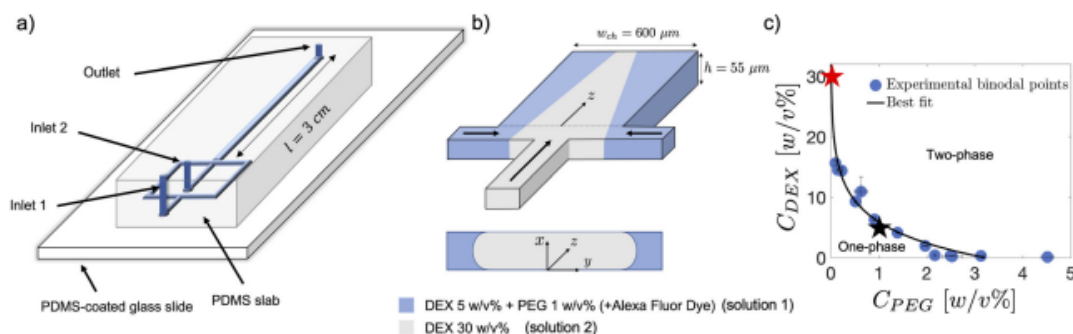
**Status:** published work in Phys. Rev. Lett. 2023, **130**, 166902

## **Department of Mechanical and Aerospace Engineering**

## Flows of a nonequilibrated aqueous two-phase system in a microchannel

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Liquid–liquid phase separation is a rich and dynamic process, which recently has gained new interest, especially in biology and for material synthesis. In this work, we experimentally show that co-flow of a nonequilibrated aqueous two-phase system within a planar flow-focusing microfluidic device results in a three-dimensional flow, as the two nonequilibrated solutions move downstream along the length of the microchannel. After the system reaches steady-state, invasion fronts from the outer stream are formed along the top and bottom walls of the microfluidic device. The invasion fronts advance towards the center of the channel, until they merge. We first show by tuning the concentration of polymer species within the system that the formation of these fronts is due to liquid–liquid phase separation. Moreover, the rate of invasion from the outer stream increases with increasing polymer concentrations in the streams. We hypothesize the invasion front formation and growth is driven by Marangoni flow induced by the polymer concentration gradient along the width of the channel, as the system is undergoing phase separation. In addition, we show how at various downstream positions the system reaches its steady-state configuration once the two fluid streams flow side-by-side in the channel.

**Status:** published work in Soft Matter 2023, **19**, 3551

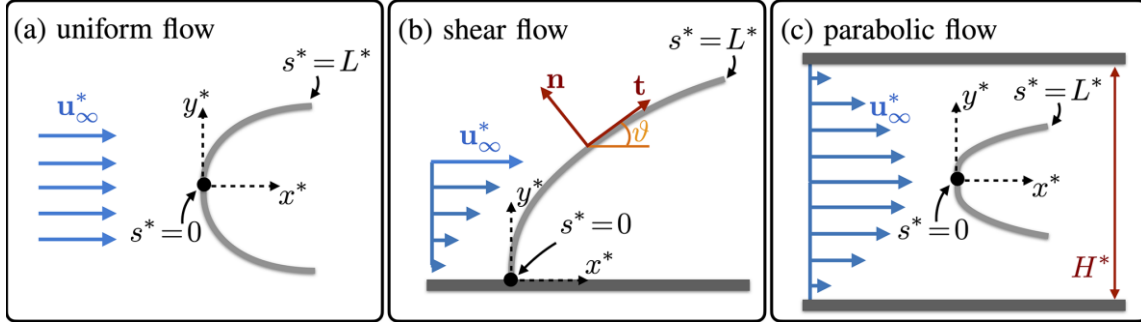
## Shape of a tethered filament in various low-Reynolds-number flows

Christina Kurzthaler,<sup>1,2</sup> Rodolfo Brandão,<sup>2,3</sup> Ory Schnitzer,<sup>3</sup> and Howard A. Stone<sup>2</sup>

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We consider the steady-state deformation of an elastic filament in various unidirectional, low-Reynolds-number flows, with the filament either clamped at one end, perpendicular to the flow, or tethered at its center and deforming symmetrically about a plane parallel to the flow. We employ a slender-body model to describe the filament shape as a function of the background flow and a nondimensional compliance  $\eta$  characterizing the ratio of viscous to elastic forces. For  $\eta \ll 1$ , we describe the small deformation of the filament by means of a regular perturbation expansion. For  $\eta \gg 1$ , the filament strongly bends such that it is nearly parallel to the flow except close to the tether point; we analyze this singular limit using boundary-layer theory, finding that the radius of curvature near the tether point, as well as the distance of the parallel segment from the tether point, scale like  $\eta^{-1/2}$  for flow profiles that do not vanish at the tether point, and like  $\eta^{-1/3}$  for flow profiles that vanish linearly away from the tether point. We also use a Wentzel-Kramers-Brillouin approach to derive a leading-order approximation for the exponentially small slope of the filament away from the tether point. We compare numerical solutions of the model over a wide range of  $\eta$  values with closed-form predictions obtained in both asymptotic limits, focusing on particular uniform, shear and parabolic flow profiles relevant to experiments.

**Status:** published work in Phys. Rev. Fluids 2023, **8**, 014101

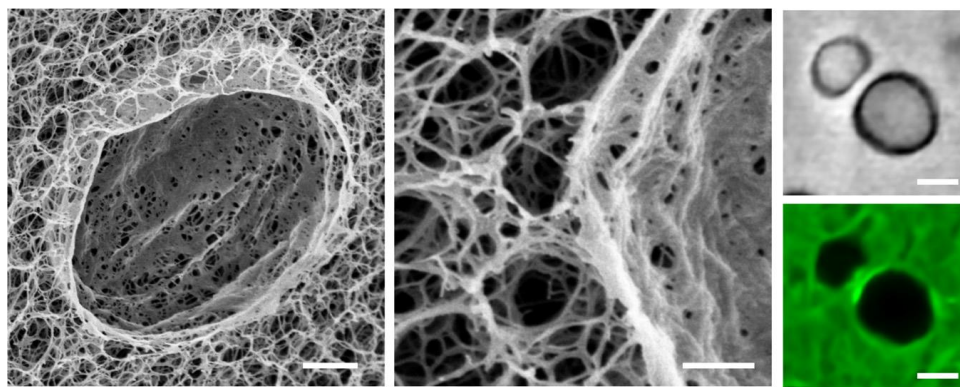
## Liquid–liquid phase separation within fibrillar networks

Jason X. Liu,<sup>1,2</sup> Mikko P. Haataja,<sup>1,2</sup> Andrej Košmrlj,<sup>1,2</sup> Sujit S. Datta,<sup>3</sup> Craig B. Arnold,<sup>1,2</sup> Rodney D. Priestley,<sup>2,3</sup>

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<sup>3</sup>*Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA.*



Complex fibrillar networks mediate liquid–liquid phase separation of biomolecular condensates within the cell. Mechanical interactions between these condensates and the surrounding networks are increasingly implicated in the physiology of the condensates and yet, the physical principles underlying phase separation within intracellular media remain poorly understood. Here, we elucidate the dynamics and mechanics of liquid–liquid phase separation within fibrillar networks by condensing oil droplets within biopolymer gels. We find that condensates constrained within the network pore space grow in abrupt temporal bursts. The subsequent restructuring of condensates and concomitant network deformation is contingent on the fracture of network fibrils, which is determined by a competition between condensate capillarity and network strength. As a synthetic analog to intracellular phase separation, these results further our understanding of the mechanical interactions between biomolecular condensates and fibrillar networks in the cell.

**Status:** published work in Nature Communications 2023, **14**, 6085

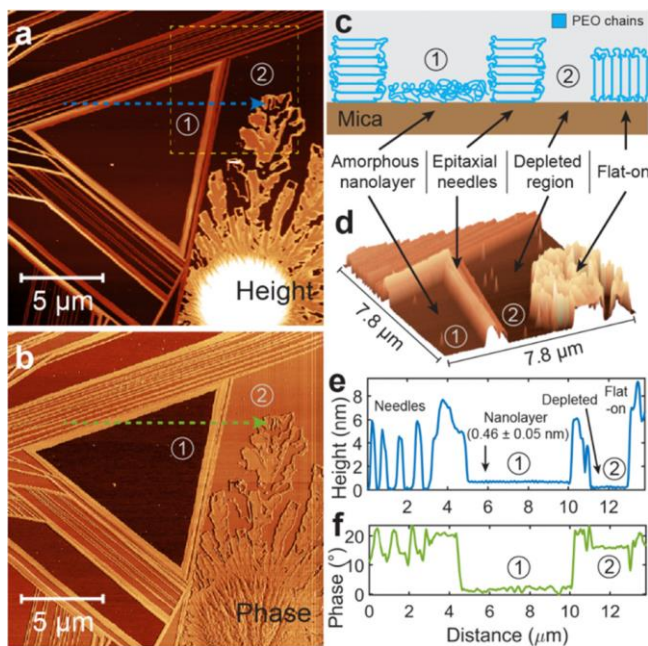
## Anisotropic material depletion in epitaxial polymer crystallization

Jason X. Liu,<sup>1,2</sup> Yang Xia,<sup>1</sup> Yucheng Wang,<sup>3</sup> Mikko P. Haataja,<sup>1,2</sup> Craig B. Arnold,<sup>1,2</sup> Rodney D. Priestley,<sup>2,3</sup>

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The physical properties of a semicrystalline polymer thin film are intimately related to the morphology of its crystalline domains. While the mechanisms underlying crystallization of flat-on oriented polymer crystals are well known, similar mechanisms remain elusive for edge-on oriented thin films due to the propensity of substantially thin films to adopt flat-on orientations. Here, we employ an epitaxial polymer–substrate relationship to enforce edge-on crystallization in thin films. Using matrix-assisted pulsed laser evaporation (MAPLE), we deposit films in which crystal nucleation is spatially separated from subsequent epitaxial crystallization. These experiments, together with phase-field simulations, demonstrate a highly anisotropic and localized material depletion during edge-on crystallization. These results provide deeper insight into the physics of polymer crystallization under confinement and introduce a processing motif in the crystallization of ultrathin structured films.

**Status:** published work in *Soft Matter* 2023, **19**, 7691–7695



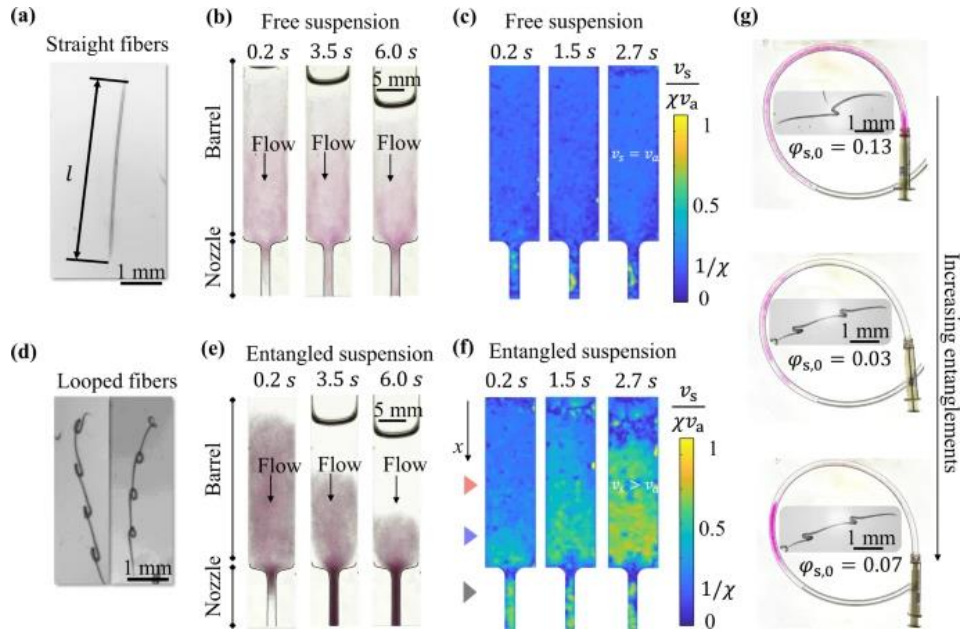
# Controlling extrudate volume fraction through poroelastic extrusion of entangled looped fibers

Zehao Pan,<sup>1</sup> Janine K. Nunes,<sup>1</sup> Camille Duprat,<sup>1,3</sup> Ho Cheung Shum,<sup>2</sup> Howard A. Stone<sup>1</sup>

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<sup>3</sup>LadHyX, CNRS, Ecole polytechnique, Institut polytechnique de Paris, 91120 Palaiseau, France.



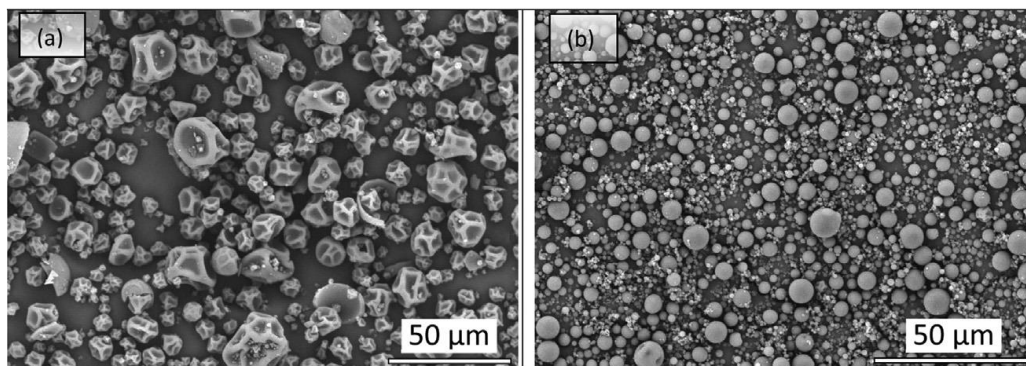
When a suspension of spherical or near-spherical particles passes through a constriction the particle volume fraction either remains the same or decreases. In contrast to these particulate suspensions, here we observe that an entangled fiber suspension increases its volume fraction up to 14-fold after passing through a constriction. We attribute this response to the entanglements among the fibers that allows the network to move faster than the liquid. By changing the fiber geometry, we find that the entanglements originate from interlocking shapes or high fiber flexibility. A quantitative poroelastic model is used to explain the increase in velocity and extrudate volume fraction. These results provide a new strategy to use fiber volume fraction, flexibility, and shape to tune soft material properties, e.g., suspension concentration and porosity, during delivery, as occurs in healthcare, three-dimensional printing, and material repair.

**Status:** published work in Nature Communications 2023, **14**, 1242

## Rapid Room-Temperature Aerosol Dehydration Versus Spray Drying: A Novel Paradigm in Biopharmaceutical Drying Technologies

Sadegh Poozesh,<sup>1</sup> Maksim Mezhericher,<sup>2</sup> Zehao Pan,<sup>2</sup> Uzair Chaudhary,<sup>1</sup> Prakash Manikwar,<sup>1</sup> Howard A. Stone.<sup>2</sup>

<sup>1</sup>*Dosage Form Design and Development, BioPharmaceuticals Development, R&D, AstraZeneca, Gaithersburg, MD, USA;* <sup>2</sup>*Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, USA*



To ensure the high quality of biopharmaceutical products, it is imperative to implement specialized unit operations that effectively safeguard the structural integrity of large molecules. While lyophilization has long been a reliable process, spray drying has recently garnered attention for its particle engineering capabilities for the pulmonary route of administration. However, maintaining the integrity of biologics during spray drying remains a challenge. To address this issue, we explored a novel dehydration system based on aerosol-assisted room-temperature drying of biological formulations called Rapid Room-Temperature Aerosol Dehydration. We compared the quality attributes of the bulk powder of biopharmaceutical products manufactured using this drying technology with that of traditional spray drying. For all the fragment antigen-binding formulations tested, in terms of protein degradation and aerosol performance, we were able to achieve a better product quality using this drying technology compared to the spray drying technique. We also highlight areas for improvement in future prototypes and prospective commercial versions of the system. Overall, the offered dehydration system holds potential for improving the quality and diversity of biopharmaceutical products and may pave the way for more efficient and effective production methods in the biopharma industry.

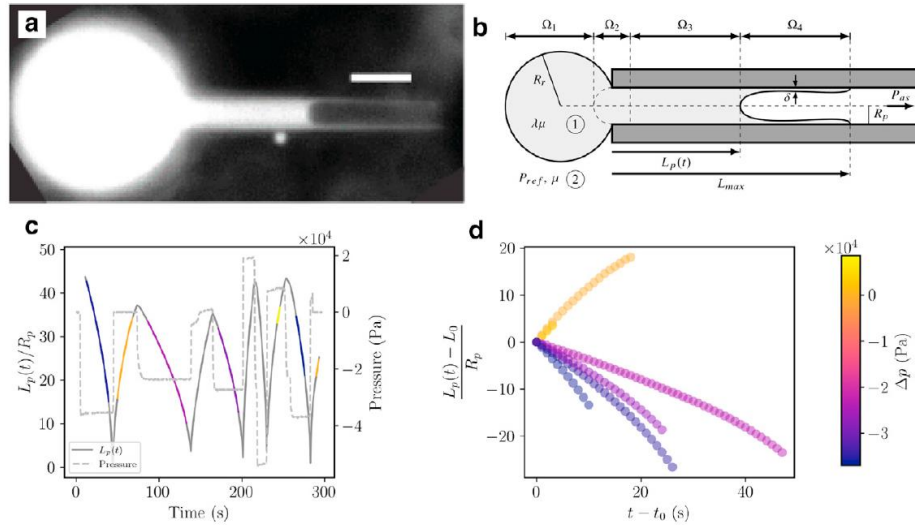
**Status:** published work in Journal of Pharmaceutical Sciences 2023

# A calibration-free model of micropipette aspiration for measuring properties of protein condensates

James V. Roggeveen,<sup>1</sup> Huan Wang,<sup>2</sup> Zheng Shi,<sup>2</sup> Howard A. Stone.<sup>1</sup>

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<sup>2</sup>Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey, USA



There is growing evidence that biological condensates, which are also referred to as membraneless organelles, and liquid-liquid phase separation play critical roles regulating many important cellular processes. Understanding the roles these condensates play in biology is predicated on understanding the material properties of these complex substances. Recently, micropipette aspiration (MPA) has been proposed as a tool to assay the viscosity and surface tension of condensates. This tool allows the measurement of both material properties in one relatively simple experiment. The model describing the dynamics of MPA for objects with an external membrane does not correctly capture the hydrodynamics of unbounded fluids, leading to a calibration parameter several orders of magnitude larger than predicted. In this work we derive a new model for MPA of biological condensates that does not require any calibration and is consistent with the hydrodynamics of the MPA geometry. We validate the predictions of this model by conducting MPA experiments on a standard silicone oil of known material properties and are able to predict the viscosity and surface tension using MPA. Finally, we reanalyze with this new model the MPA data presented in previous works.

**Status:** published work in Biophysical Journal 2024, **123**, 1–11

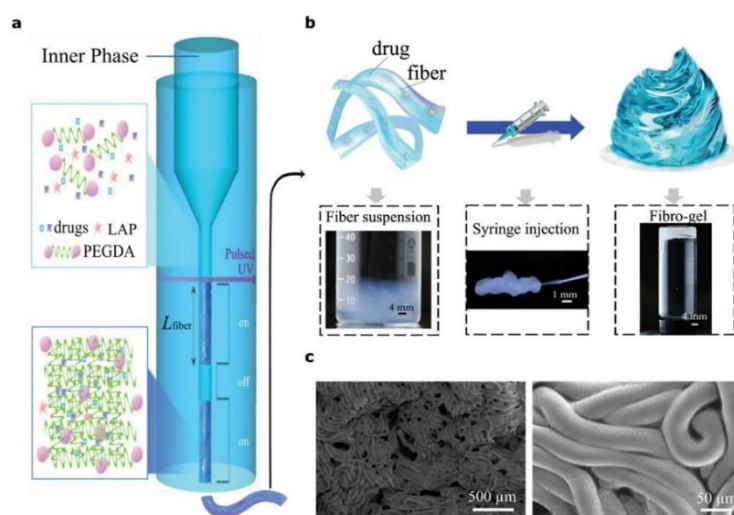
# Fibro-Gel: An All-Aqueous Hydrogel Consisting of Microfibers with Tunable Release Profile and its Application in Wound Healing

Yanting Shen,<sup>1</sup> Yuan Liu,<sup>1</sup> Janine K. Nunes,<sup>2</sup> Chenmin Wang,<sup>3</sup> Miao Xu,<sup>1</sup> Michael K.T. To,<sup>3</sup> Howard A. Stone,<sup>2</sup> Ho Cheung Shum.<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China;

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Injectable hydrogels are valuable tools in tissue engineering and regenerative medicine due to their unique advantages of injectability with minimal invasiveness and usability for irregularly shaped sites. However, it remains challenging to achieve scalable manufacturing together with matching physicochemical properties and on-demand drug release for a high level of control over biophysical and biomedical cues to direct endogenous cells. Here, the use of an injectable fibro-gel is demonstrated, a water-filled network of entangled hydrogel microfibers, whose physicochemical properties and drug release profiles can be tailored to overcome these shortcomings. The potential use of the fibro-gel for advancing tissue regeneration is explored with a mice excision skin model. Preliminary in vivo tests indicate that the fibro-gel promotes wound healing and new healthy tissue regeneration at a faster rate than a commercial gel. Moreover, it is demonstrated that the release of distinct drugs at different rates can further accelerate wound healing. This fibro-gel offers a promising approach in biomedical fields such as therapeutic delivery, medical dressings, and 3D tissue scaffolds for tissue engineering.

**Status:** published work in Adv. Mater. 2023, **35**, 2211637



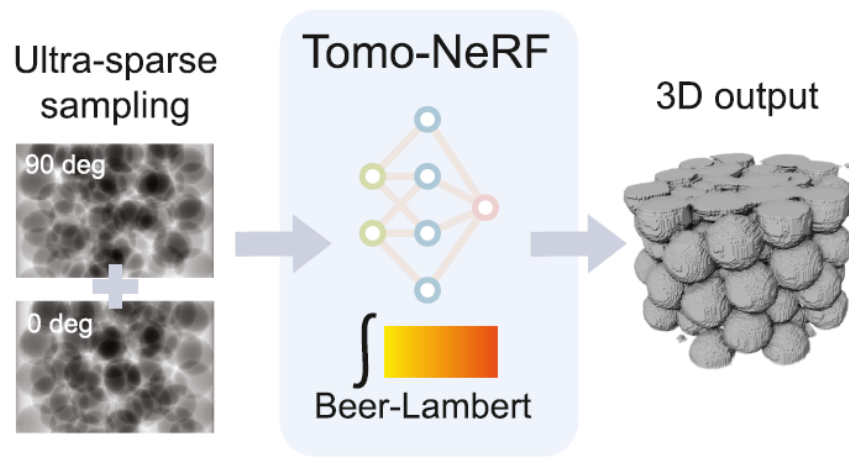


# Ultrasparse View X-ray Computed Tomography for 4D Imaging

Yanjie Zheng<sup>1</sup> and Kelsey B. Hatzell<sup>1,2</sup>

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<sup>2</sup>Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08540, USA.



X-ray computed tomography (CT) is a noninvasive, nondestructive approach to imaging materials, material systems, and engineered components in two and three dimensions. Acquisition of three-dimensional (3D) images requires the collection of hundreds or thousands of through-thickness X-ray radiographic images from different angles. Such 3D data acquisition strategies commonly involve suboptimal temporal sampling for in situ and operando studies (4D imaging). Herein, we introduce a sparse-view imaging approach, Tomo-NeRF, which is capable of reconstructing high-fidelity 3D images from <10 two-dimensional radiographic images. Experimental 2D and 3D X-ray images were used to test the reconstruction capability in two-view, four-view, and six-view scenarios. Tomo-NeRF is capable of reconstructing 3D images with a structural similarity of 0.9971–0.9975 and a voxel-wise accuracy of 81.83–89.59% from 2D experimentally obtained images. The reconstruction accuracy for the experimentally obtained images is less than the synthetic structures. Experimentally obtained images demonstrate a similarity of 0.9973–0.9984 and a voxel wise accuracy of 84.31–95.77%.

**Status:** published work in ACS Applied Materials & Interfaces 2023, **15**, 35024

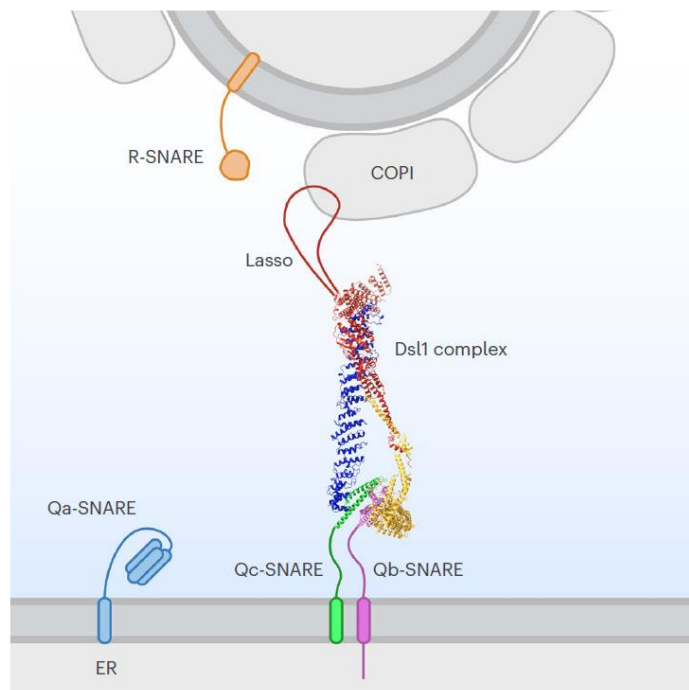


## **Department of Molecular Biology**

## 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

*Department of Molecular Biology, Princeton University, Princeton, NJ, USA*



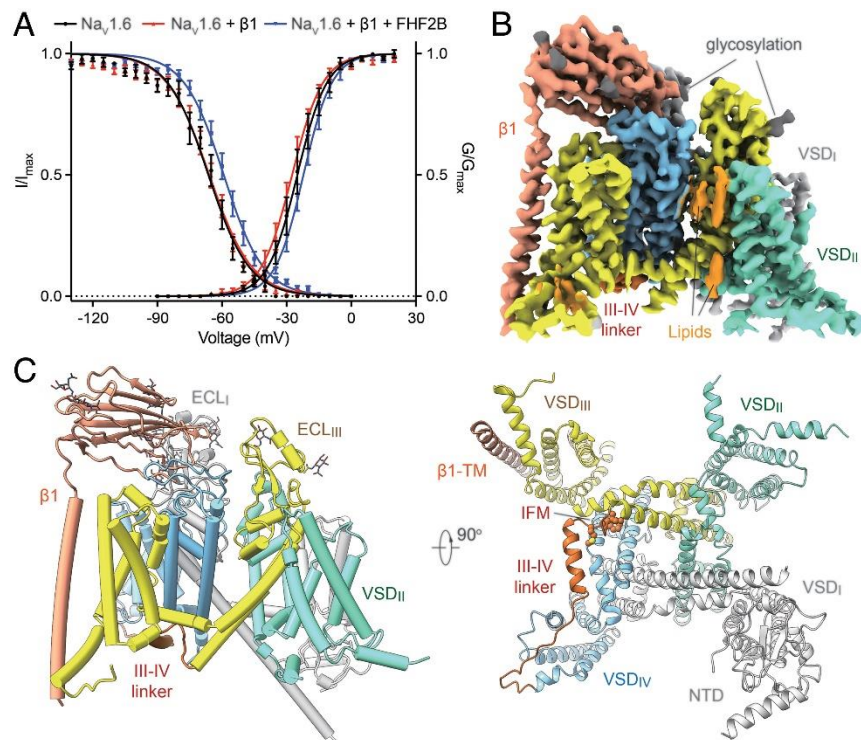
Most membrane fusion reactions in eukaryotic cells are mediated by multisubunit tethering complexes (MTCs) and SNARE proteins. MTCs are much larger than SNAREs and are thought to mediate the initial attachment of two membranes. Complementary SNAREs then form membrane-bridging complexes whose assembly 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 and Molecular Biology 2024.

## Cryo-EM structure of human voltage-gated sodium channel Na<sub>v</sub>1.6

Xiao Fan,<sup>1</sup> Jian Huang,<sup>1</sup> Xueqin Jin,<sup>2</sup> and Nieng Yan.<sup>1,2</sup>

<sup>1</sup>Department of Molecular Biology, Princeton University, Princeton, NJ 08544, USA; <sup>2</sup>State Key Laboratory of Membrane Biology, Beijing Frontier Research Center for Biological Structures, Tsinghua-Peking Joint Center for Life Sciences, School of Life Sciences, Tsinghua University, Beijing 100084, China.



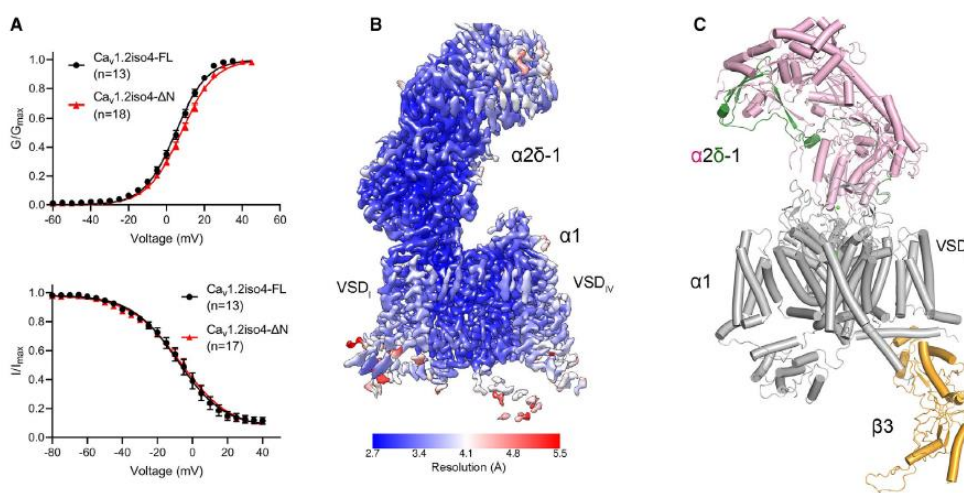
Voltage-gated sodium channel Na<sub>v</sub>1.6 plays a crucial role in neuronal firing in the central nervous system (CNS). Aberrant function of Na<sub>v</sub>1.6 may lead to epilepsy and other neurological disorders. Specific inhibitors of Na<sub>v</sub>1.6 thus have therapeutic potentials. Here we present the cryo-EM structure of human Na<sub>v</sub>1.6 in the presence of auxiliary subunits  $\beta$ 1 and fibroblast growth factor homologous factor 2B (FHF2B) at an overall resolution of 3.1 Å. The overall structure represents an inactivated state with closed pore domain (PD) and all “up” voltage-sensing domains. A conserved carbohydrate–aromatic interaction involving Trp302 and Asn326, together with the  $\beta$ 1 subunit, stabilizes the extracellular loop in repeat I. Apart from regular lipids that are resolved in the EM map, an unprecedented Y-shaped density that belongs to an unidentified molecule binds to the PD, revealing a potential site for developing Na<sub>v</sub>1.6-specific blockers. Structural mapping of disease-related Na<sub>v</sub>1.6 mutations provides insights into their pathogenic mechanism.

**Status:** published work in PNAS 2023, **120**, e2220578120

# Structural basis for human Ca<sub>v</sub>1.2 inhibition by multiple drugs and the neurotoxin calciseptine

Shuai Gao,<sup>1,2</sup> Xia Yao,<sup>1,2</sup> Jiaofeng Chen,<sup>3</sup> Gaoxingyu Huang,<sup>4</sup> Xiao Fan,<sup>2</sup> Lingfeng Xue,<sup>5</sup> Zhangqiang Li,<sup>3</sup> Tong Wu,<sup>3</sup> Yupeng Zheng,<sup>6</sup> Jian Huang,<sup>2</sup> Xueqin Jin,<sup>3</sup> Yan Wang,<sup>7</sup> Zhifei Wang,<sup>7</sup> Yong Yu,<sup>7</sup> Lei Liu,<sup>6</sup> Xiaojing Pan,<sup>3,8</sup> Chen Song,<sup>5</sup> Nieng Yan<sup>2,3,8</sup>

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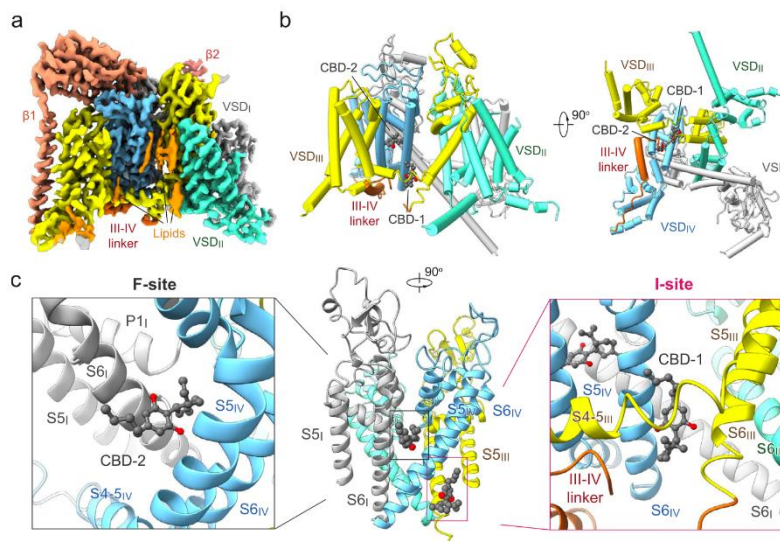
Ca<sub>v</sub>1.2 channels play crucial roles in various neuronal and physiological processes. Here, we present cryo-EM structures of human Ca<sub>v</sub>1.2, both in its apo form and in complex with several drugs, as well as the peptide neurotoxin calciseptine. Most structures, apo or bound to calciseptine, amlodipine, or a combination of amiodarone and sofosbuvir, exhibit a consistent inactivated conformation with a sealed gate, three up voltage-sensing domains (VSDs), and a down VSD<sub>II</sub>. Calciseptine sits on the shoulder of the pore domain, away from the permeation path. In contrast, when pinaverium bromide, an antispasmodic drug, is inserted into a cavity reminiscent of the IFM-binding site in Nav channels, a series of structural changes occur, including upward movement of VSD<sub>II</sub> coupled with dilation of the selectivity filter and its surrounding segments in repeat III. Meanwhile, S4-S5<sub>III</sub> merges with S5<sub>III</sub> to become a single helix, resulting in a widened but still non-conductive intracellular gate

**Status:** published work in Cell 2023, **186**, 5363–5374

## Cannabidiol inhibits $\text{Na}_v$ channels through two distinct binding sites

Jian Huang,<sup>1,4</sup> Xiao Fan,<sup>1,4</sup> Xueqin Jin,<sup>2</sup> Sooyeon Jo,<sup>3</sup> Hanxiong Bear Zhang,<sup>3</sup> Akie Fujita,<sup>3</sup> Bruce P. Bean,<sup>3</sup> and Nieng Yan,<sup>1,2</sup>

<sup>1</sup>Department of Molecular Biology, Princeton University, Princeton, NJ 08544, USA. <sup>2</sup>Beijing Frontier Research Center for Biological Structures, State Key Laboratory of Membrane Biology, Tsinghua-Peking Joint Center for Life Sciences, School of Life Sciences, Tsinghua University, Beijing 100084, China. <sup>3</sup>Department of Neurobiology, Harvard Medical School, Boston, MA 02115, USA.



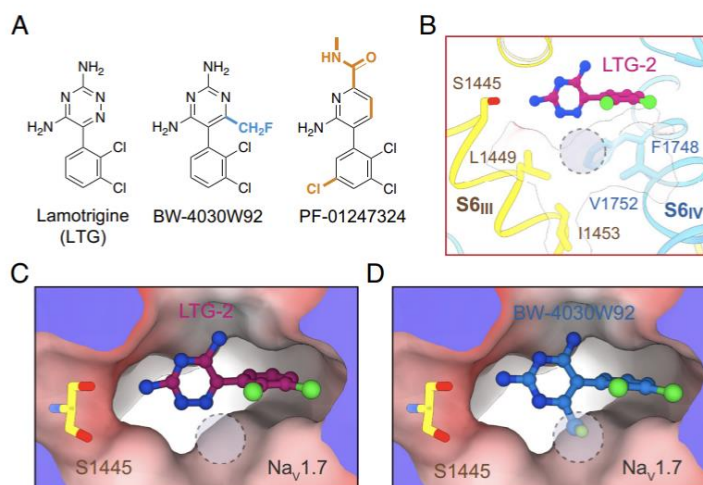
Abstract Cannabidiol (CBD), a major non-psychoactive phytocannabinoid in cannabis, is an effective treatment for some forms of epilepsy and pain. At high concentrations, CBD interacts with a huge variety of proteins, but which targets are most relevant for clinical actions is still unclear. Here we show that CBD interacts with  $\text{Na}_v1.7$  channels at sub-micromolar concentrations in a state-dependent manner. Electrophysiological experiments show that CBD binds to the inactivated state of  $\text{Na}_v1.7$  channels with a dissociation constant of about 50 nM. The cryo-EM structure of CBD bound to  $\text{Na}_v1.7$  channels reveals two distinct binding sites. One is in the IV-I fenestration near the upper pore. The other binding site is directly next to the inactivated “wedged” position of the Ile/Phe/Met (IFM) motif on the short linker between repeats III and IV, which mediates fast inactivation. Consistent with producing a direct stabilization of the inactivated state, mutating residues in this binding site greatly reduced state-dependent binding of CBD. The identification of this binding site may enable design of compounds with improved properties compared to CBD itself.

**Status:** published work in Nature Communications 2023, **14**, 3613

## Dual-pocket inhibition of Na<sub>v</sub> channels by the antiepileptic drug lamotrigine

Jian Huang,<sup>1</sup> Xiao Fan,<sup>1</sup> Xueqin Jin,<sup>2</sup> Liming Teng,<sup>2</sup> and Nieng Yan<sup>1,2</sup>

<sup>1</sup>Department of Molecular Biology, Princeton University, Princeton, NJ 08544, USA. <sup>2</sup>Beijing Frontier Research Center for Biological Structures, State Key Laboratory of Membrane Biology, Tsinghua-Peking Joint Center for Life Sciences, School of Life Sciences, Tsinghua University, Beijing 100084, China.



Voltage-gated sodium (Na<sub>v</sub>) channels govern membrane excitability, thus setting the foundation for various physiological and neuronal processes. Nav channels serve as the primary targets for several classes of widely used and investigational drugs, including local anesthetics, antiepileptic drugs, antiarrhythmics, and analgesics. In this study, we present cryogenic electron microscopy (cryo-EM) structures of human Na<sub>v</sub>1.7 bound to two clinical drugs, riluzole (RLZ) and lamotrigine (LTG), at resolutions of 2.9 Å and 2.7 Å, respectively. A 3D EM reconstruction of ligand-free Na<sub>v</sub>1.7 was also obtained at 2.1 Å resolution. RLZ resides in the central cavity of the pore domain and is coordinated by residues from repeats III and IV. Whereas one LTG molecule also binds to the central cavity, the other is found beneath the intracellular gate, known as site BIG. Therefore, LTG, similar to lacosamide and cannabidiol, blocks Nav channels via a dual-pocket mechanism. These structures, complemented with docking and mutational analyses, also explain the structure–activity relationships of the LTG-related linear 6,6 series that have been developed for improved efficacy and subtype specificity on different Na<sub>v</sub> channels. Our findings reveal the molecular basis for these drugs' mechanism of action and will aid the development of novel antiepileptic and pain-relieving drugs.

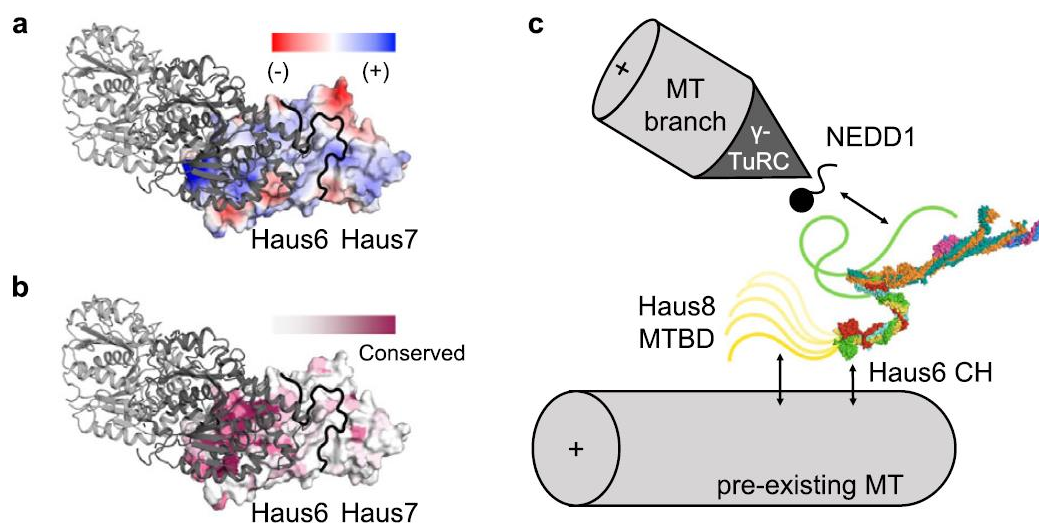
**Status:** published work in PNAS 2023, **120**, e2309773120



## Integrated model of the vertebrate augmin complex

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Accurate segregation of chromosomes is required to maintain genome integrity during cell division. This feat is accomplished by the microtubule-based spindle. To build a spindle rapidly and with high fidelity, cells take advantage of branching microtubule nucleation, which rapidly amplifies microtubules during cell division. Branching microtubule nucleation relies on the heterooctameric augmin complex, but lack of structure information about augmin has hindered understanding how it promotes branching. In this work, we combine cryo-electron microscopy, protein structural prediction, and visualization of fused bulky tags via negative stain electron microscopy to identify the location and orientation of each subunit within the augmin structure. Evolutionary analysis shows that augmin's structure is highly conserved across eukaryotes, and that augmin contains a previously unidentified microtubule binding site. Thus, our findings provide insight into the mechanism of branching microtubule nucleation.

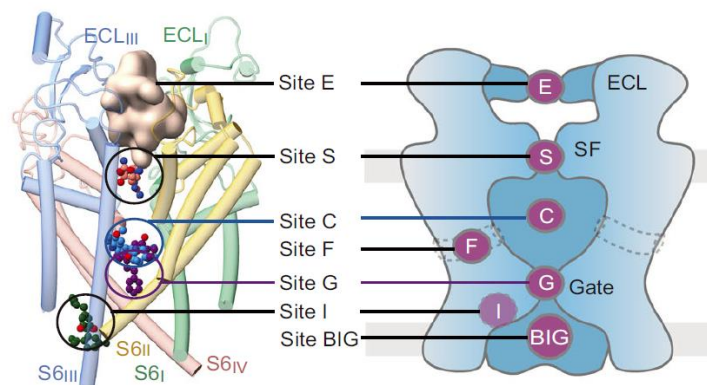
**Status:** published work in Nature Comm. 2023, **14**, 2072

## Structural mapping of Na<sub>v</sub>1.7 antagonists

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Voltage-gated sodium (Na<sub>v</sub>) channels are targeted by a number of widely used and investigational drugs for the treatment of epilepsy, arrhythmia, pain, and other disorders. Despite recent advances in structural elucidation of Na<sub>v</sub> channels, the binding mode of most Na<sub>v</sub>-targeting drugs remains unknown. Here we report high-resolution cryo-EM structures of human Na<sub>v</sub>1.7 treated with drugs and lead compounds with representative chemical backbones at resolutions of 2.6-3.2 Å. A binding site beneath the intracellular gate (site BIG) accommodates carbamazepine, bupivacaine, and lacosamide. Unexpectedly, a second molecule of lacosamide plugs into the selectivity filter from the central cavity. Fenestrations are popular sites for various state-dependent drugs. We show that vinpocetine, a synthetic derivative of a vinca alkaloid, and hardwickiic acid, a natural product with antinociceptive effect, bind to the III-IV fenestration, while vixotrigine, an analgesic candidate, penetrates the IV-I fenestration of the pore domain. Our results permit building a 3D structural map for known drug-binding sites on Na<sub>v</sub> channels summarized from the present and previous structures.

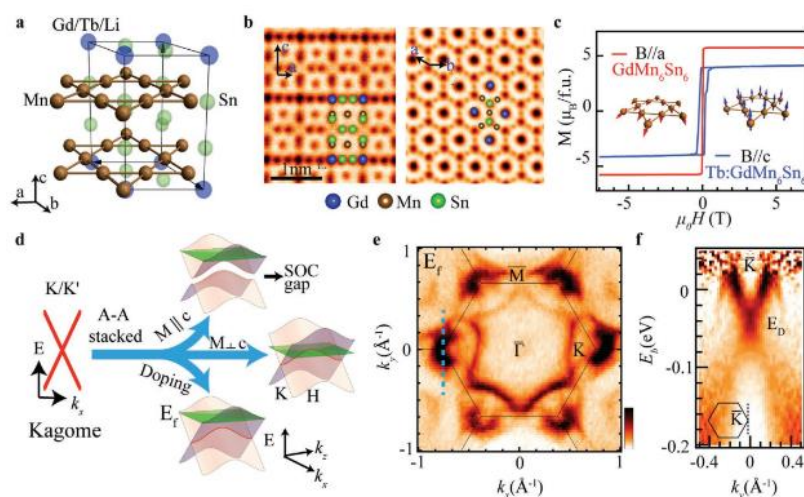
**Status:** published work in Nature Comm. 2023, **14**, 3224

## Department of Physics

## Visualization of Tunable Weyl Line in A–A Stacking Kagome Magnets

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USA

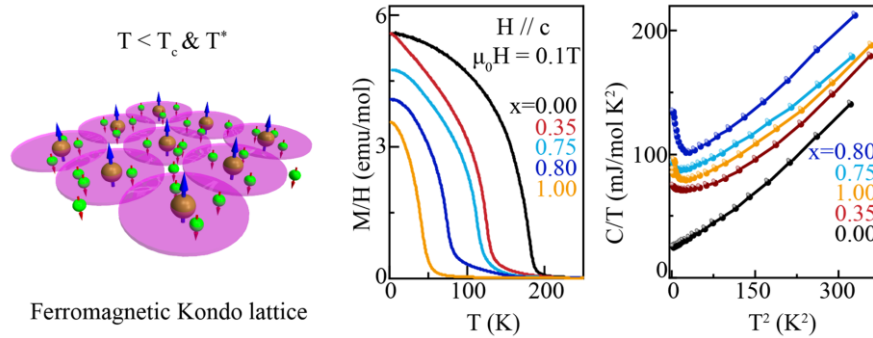
Kagome magnets provide a fascinating platform for a plethora of topological quantum phenomena, in which the delicate interplay between frustrated crystal structure, magnetization, and spin–orbit coupling can engender highly tunable topological states. Here, utilizing angle-resolved photoemission spectroscopy, the Weyl lines are directly visualized with strong out-of-plane dispersion in the A–A stacked Kagome magnet GdMn<sub>6</sub>Sn<sub>6</sub>. Remarkably, the Weyl lines exhibit a strong magnetization-direction-tunable SOC gap and binding energy tunability after substituting Gd with Tb and Li, respectively. These results illustrate the magnetization direction and valence counting as efficient tuning knobs for realizing and controlling distinct 3D topological phases.

**Status:** published work in Adv. Mater. 2023, **35**, 2205927

# Observation of Kondo lattice and Kondo-enhanced anomalous Hall effect in an itinerant ferromagnet

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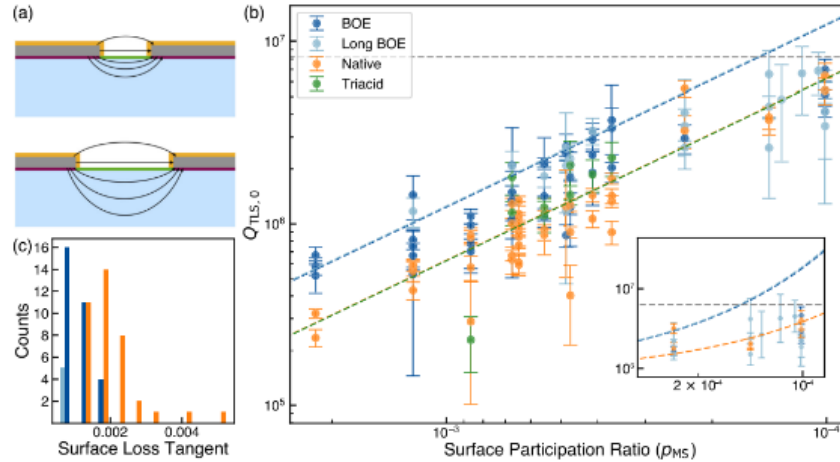
The interplay between Kondo screening and magnetic interactions is central to comprehending the intricate phases in heavy-fermion compounds. However, the role of the itinerant magnetic order has been largely uncharted in the context of heavy-fermion systems. Here we demonstrate the coexistence of the coherent Kondo screening and d-orbital ferromagnetism in material system  $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{As}_2$ , through comprehensive thermodynamic and electrical transport measurements. Remarkably, by changing the ratio of Ce/La, we observe a substantial enhancement of the anomalous Hall effect (AHE) in the Kondo lattice regime. The value of the Hall conductivity quantitatively matches with the first-principle calculation that optimized with our ARPES results and can be attributed to the large Berry curvature (BC) density engendered by the topological nodal rings composed of the Ce-4f and Co-3d orbitals at  $E_f$ . Our findings point to a new platform for topological responses in a novel Kondo lattice environment.

**Status:** work posted on arXiv.org: 2302.12113

## Disentangling Losses in Tantalum Superconducting Circuits

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<sup>1</sup>Department of Physics, Princeton University, Princeton, NJ, USA; <sup>2</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ, USA; <sup>3</sup>Department of Chemistry, Princeton University, Princeton, NJ, USA; <sup>4</sup>Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY, USA.



Superconducting qubits are a leading system for realizing large-scale quantum processors, but overall gate fidelities suffer from coherence times limited by microwave dielectric loss. Recently discovered tantalum-based qubits exhibit record lifetimes exceeding 0.3 ms. Here, we perform systematic, detailed measurements of superconducting tantalum resonators in order to disentangle sources of loss that limit state-of-the-art tantalum devices. By studying the dependence of loss on temperature, microwave photon number, and device geometry, we quantify materials-related losses and observe that the losses are dominated by several types of saturable two-level systems (TLSs). With four different surface conditions, we quantitatively extract the linear absorption associated with different surface TLS sources. Finally, we quantify the impact of the chemical processing at single photon powers, the relevant conditions for qubit device performance. In this regime, we measure resonators with internal quality factors ranging from 5 to  $15 \times 10^6$ , comparable to the best qubits reported. In these devices, the surface and bulk TLS contributions to loss are comparable, showing that systematic improvements in materials on both fronts are necessary to improve qubit coherence further.

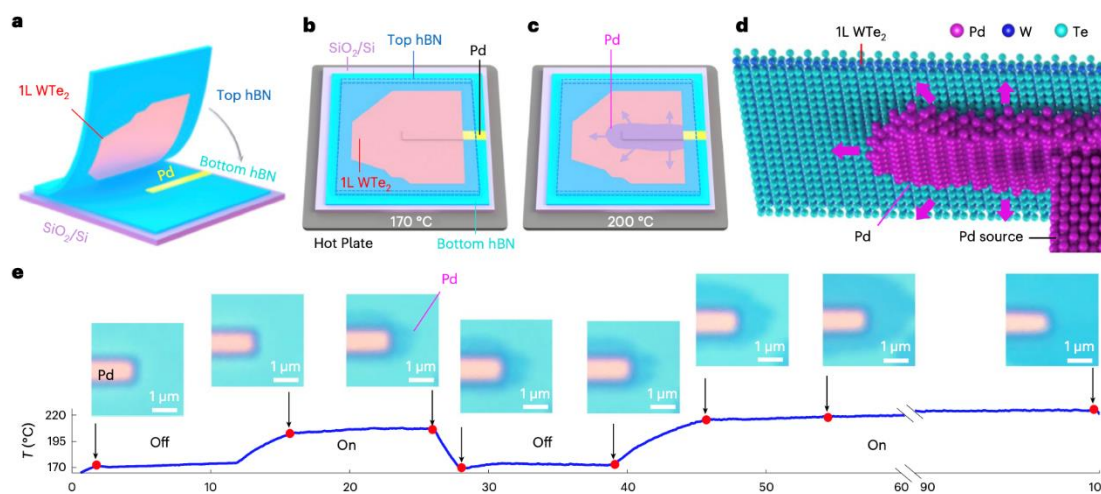
**Status:** published work in Phys. Rev. X 2023, **13**, 041005



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

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

<sup>1</sup>Department of Physics, Princeton University, Princeton, NJ, USA. <sup>2</sup>Department of Chemistry, Princeton University, Princeton, NJ, USA. <sup>3</sup>Princeton Materials Institute, Princeton University, Princeton, NJ, USA. <sup>4</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ, USA. <sup>5</sup>Research Center for Electronic and Optical Materials, National Institute for Materials Science, Tsukuba, Japan. <sup>6</sup>Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, Japan.



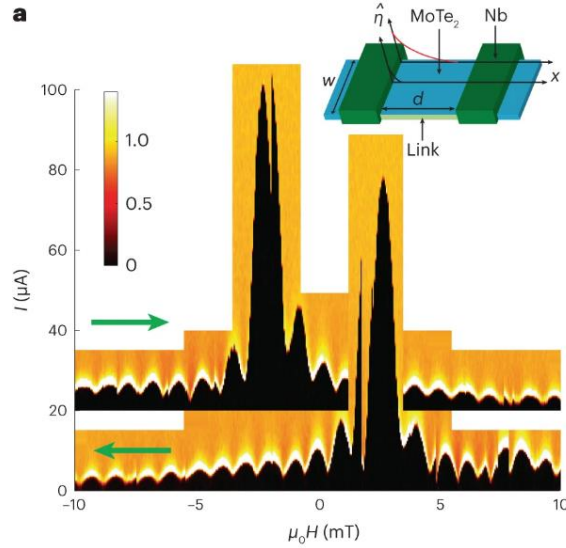
Conventional vapour deposition or epitaxial growth of two-dimensional (2D) materials and heterostructures is conducted in a large chamber in which masses transport from the source to the substrate. Here we report a chamber-free, on-chip approach for growing 2D crystalline structures directly in a nanoscale 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<sub>7</sub>WTe<sub>2</sub>, 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 in Nature Synthesis 2023

# Edge supercurrent reveals competition between condensates in a Weyl superconductor

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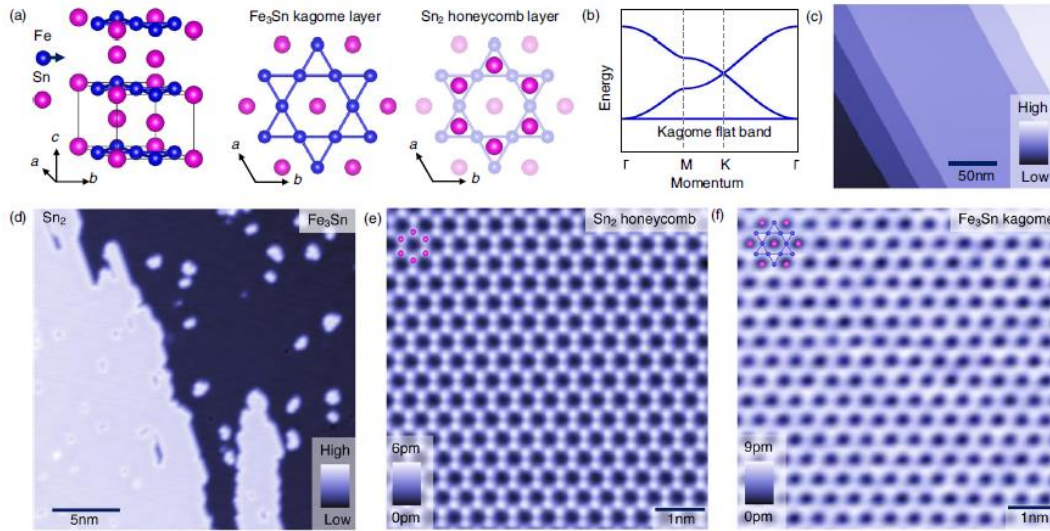
In topological materials, the edge states are readily distinguished from the bulk states. The situation where a topological semimetal becomes superconducting so that Cooper pairs occupy both the bulk and the edge states is not well understood. In particular, we do not know if we can force their pairing symmetries to be different. Here we show that, when supercurrent is injected into the superconducting Weyl semimetal MoTe<sub>2</sub> from Nb contacts, the invasive s-wave pairing potential from Nb is incompatible with the intrinsic Cooper pair condensate in MoTe<sub>2</sub>. 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<sub>2</sub>. 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

# Imaging real-space flat band localization in kagome magnet FeSn

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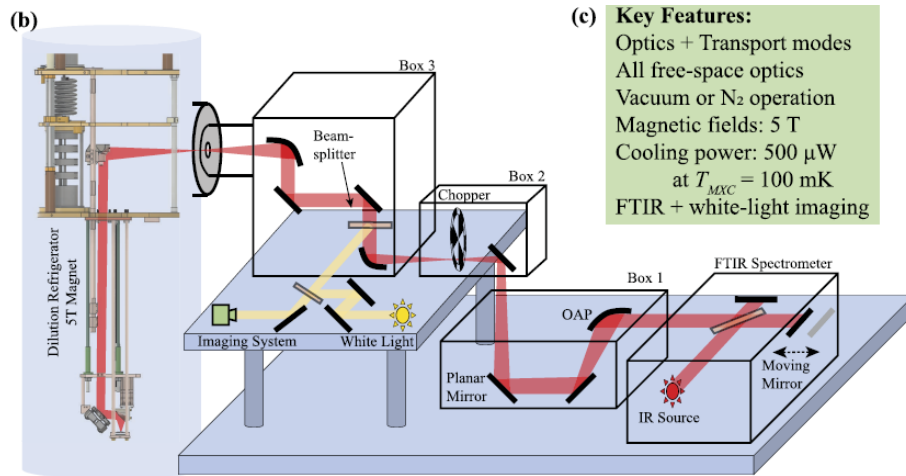
Kagome lattices host flat bands due to their frustrated lattice geometry, which leads to destructive quantum interference of electron wave functions. Here, we report imaging of the kagome flat band localization in real-space using scanning tunneling microscopy. We identify both the Fe<sub>3</sub>Sn kagome lattice layer and the Sn<sub>2</sub> honeycomb layer with atomic resolution in kagome antiferromagnet FeSn. On the Fe<sub>3</sub>Sn lattice, at the flat band energy determined by the angle resolved photoemission spectroscopy, tunneling spectroscopy detects an unusual state localized uniquely at the Fe kagome lattice network. We further show that the vectorial in-plane magnetic field manipulates the spatial anisotropy of the localization state within each kagome unit cell. Our results are consistent with the real-space flat band localization in the magnetic kagome lattice. We further discuss the magnetic tuning of flat band localization under the spin–orbit coupled magnetic kagome lattice model.

**Status:** published work in Communication Materials 2023, **4**, 17

# A platform for far-infrared spectroscopy of quantum materials at millikelvin temperatures

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<sup>1</sup>Department of Physics, Princeton University, Princeton, New Jersey 08544, USA; <sup>2</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, New Jersey 08544, USA; <sup>3</sup>Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA



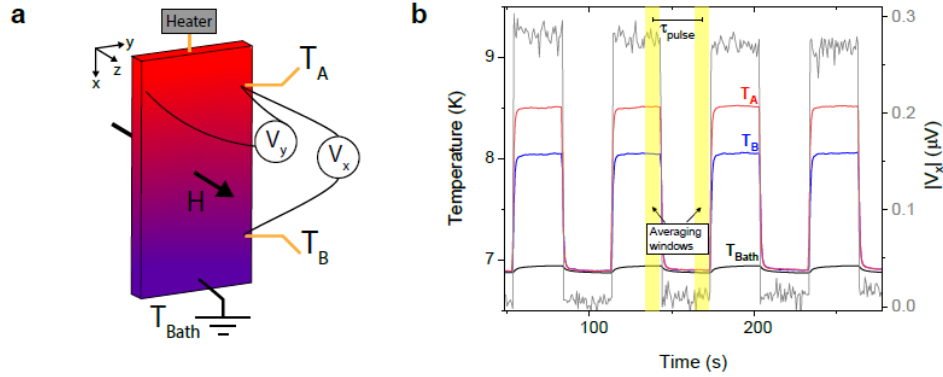
Optical spectroscopy of quantum materials at ultralow temperatures is rarely explored, yet it may provide critical characterizations of quantum phases not possible using other approaches. We describe the development of a novel experimental platform that enables optical spectroscopic studies, together with standard electronic transport, of materials at millikelvin temperatures inside a dilution refrigerator. The instrument is capable of measuring both bulk crystals and micrometer-sized two-dimensional van der Waals materials and devices. We demonstrate its performance by implementing photocurrent-based Fourier transform infrared spectroscopy on a monolayer WTe<sub>2</sub> device and a multilayer 1T-TaS<sub>2</sub> crystal, with a spectral range available from the near-infrared to the terahertz regime and in magnetic fields up to 5 T. In the far-infrared regime, we achieve spectroscopic measurements at a base temperature as low as  $\sim 43$  mK and a sample electron temperature of  $\sim 450$  mK. Possible experiments and potential future upgrades of this versatile instrumental platform are envisioned.

**Status:** published work in Rev. Sci. Instrum. 2023, **94**, 103903

## The vortex-Nernst effect in a superconducting infinite-layer nickelate

Nicholas P. Quirk,<sup>1</sup> Danfeng Li,<sup>2,3</sup> Bai Yang Wang,<sup>2,4</sup> Harold Y. Hwang,<sup>2,3</sup> and N. P. Ong<sup>1</sup>

<sup>1</sup>Department of Physics, Princeton University, Princeton, NJ 08544, USA; <sup>2</sup>Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA; <sup>3</sup>Department of Applied Physics, Stanford University, Stanford, CA 94305, USA; <sup>4</sup>Department of Physics, Stanford University, Stanford, CA 94305, USA.



We report measurements of the Nernst and Seebeck effects in  $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$  thin films near the superconducting transition temperature,  $T = 6.5 - 15$  K. Our main result is the observation of a vortex-Nernst signal  $S_{yx}(T, H)$  with a maximum at  $\mu_0 H = 5$  T and a tail that extends to  $\mu_0 H \approx 15$  T, which we identify as the upper-critical field  $H_{c2}$ . At  $T > T_c = 6.1$  K,  $H_{c2}$  remains large (15 T), up to the highest temperature we can resolve from  $S_{yx}$  (11 K). These results indicate the existence of a vortex-liquid state over a wide range of finite-resistance temperatures, as in the high- $T_c$  cuprates.

**Status:** work posted on arXiv.org: 2309.03170, 2023

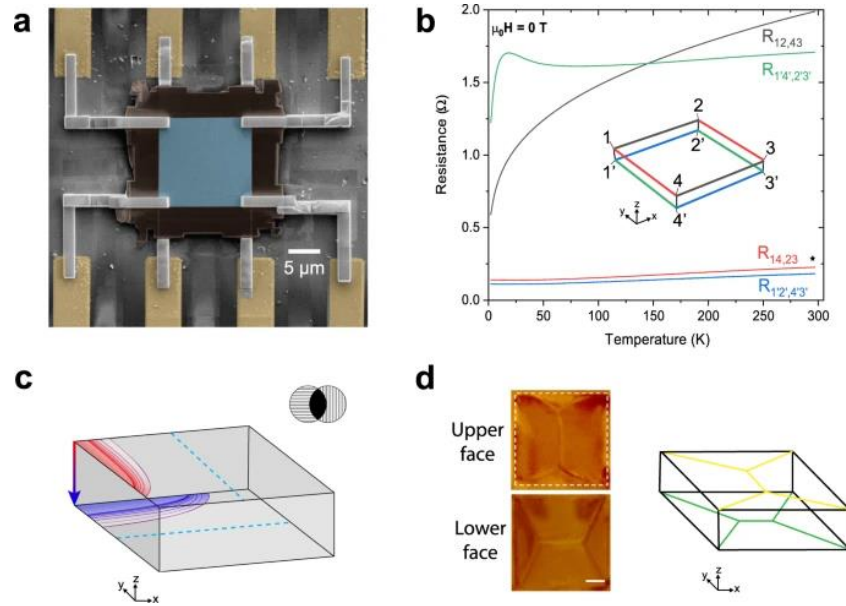
# Anisotropic resistance with a 90° twist in a ferromagnetic Weyl semimetal, $\text{Co}_2\text{MnGa}$

Nicholas P. Quirk,<sup>1</sup> Guangming Cheng,<sup>2</sup> Kaustuv Manna,<sup>3</sup> Claudia Felser,<sup>3</sup> Nan Yao,<sup>2</sup> N. P. Ong<sup>1</sup>

<sup>1</sup>Department of Physics, Princeton University, Princeton, NJ 08544, USA;

<sup>2</sup>Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, NJ 08544, USA;

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Weyl semimetals exhibit exotic magnetotransport phenomena such as the chiral anomaly and surface-to-bulk quantum oscillations (Weyl orbits) due to chiral bulk states and topologically protected surface states. Here we report a unique transport property in crystals of the ferromagnetic nodal-line Weyl semimetal  $\text{Co}_2\text{MnGa}$  that have been polished to micron thicknesses using a focused ion beam. These thin crystals exhibit a large planar resistance anisotropy ( $10 \times$ ) with axes that rotate by 90 degrees between opposite faces of the crystal. We use symmetry arguments and electrostatic simulations to show that the observed anisotropy resembles that of an isotropic conductor with surface states that are impeded from hybridization with bulk states. The origin of these states awaits further experiments that can correlate the surface bands with the observed 90° twist.

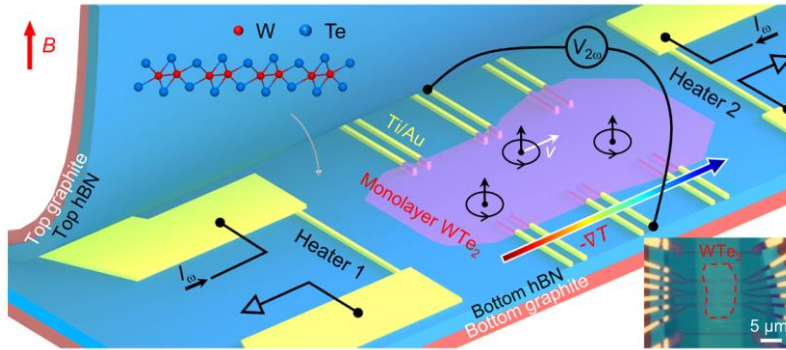
**Status:** published work in Nature Communications 2023, **14**, 6583



## Unconventional Superconducting Quantum Criticality in Monolayer WTe<sub>2</sub>

T. Song,<sup>1</sup> Y. Jia,<sup>1</sup> G. Yu,<sup>1,2</sup> Y. Tang,<sup>1</sup> P. Wang,<sup>1</sup> R. Singha,<sup>3</sup> X. Gui,<sup>3</sup> A. J. Uzan,<sup>1</sup>  
M. Onyszczyk,<sup>1</sup> K. Watanabe,<sup>4</sup> T. Taniguchi,<sup>5</sup> R. J. Cava,<sup>3</sup> L. M. Schoop,<sup>3</sup> N. P. Ong,<sup>1</sup> S. Wu<sup>1</sup>

<sup>1</sup>Department of Physics, Princeton University, Princeton, NJ, USA; <sup>2</sup>Department of Electrical and Computer Engineering, Princeton University, Princeton, NJ, USA; <sup>3</sup>Department of Chemistry, Princeton University, Princeton, NJ, USA; <sup>4</sup>Research Center for Functional Materials, National Institute for Materials Science, Tsukuba, Japan; <sup>5</sup>International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, Japan.



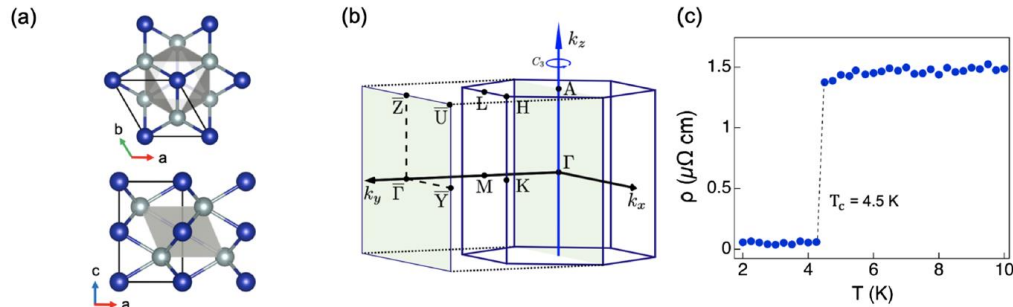
The superconductor to insulator or metal transition in two dimensions (2D) provides a valuable platform for studying continuous quantum phase transitions (QPTs) and critical phenomena. Distinct theoretical models have been developed, but many questions remain unsettled despite decades of research. Extending Nernst experiments down to millikelvin temperatures, we uncover anomalous quantum fluctuations and identify an unconventional superconducting quantum critical point (QCP) in a gate-tuned excitonic quantum spin Hall insulator (QSHI), the monolayer tungsten ditelluride (WTe<sub>2</sub>). The observed vortex Nernst effect reveals singular superconducting fluctuations in the resistive normal state induced by magnetic fields or temperature, even well above the transition. Near the doping-induced QCP, the Nernst signal driven by quantum fluctuations is exceptionally large in the millikelvin regime, with a coefficient of  $\sim 4,100 \mu\text{V}/\text{KT}$  at zero magnetic field, an indication of the proliferation of vortices. Surprisingly, the Nernst signal abruptly disappears when the doping falls below the critical value, in striking conflict with conventional expectations. This series of phenomena call for careful examinations of the mechanism of the QCP, including the possibility of a continuous QPT between two distinct ordered phases in the monolayer. Our experiments open a new avenue for studying unconventional QPTs and quantum critical matter.

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# Coexistence of Bulk-Nodal and Surface-Nodeless Cooper Pairings in a Superconducting Dirac Semimetal

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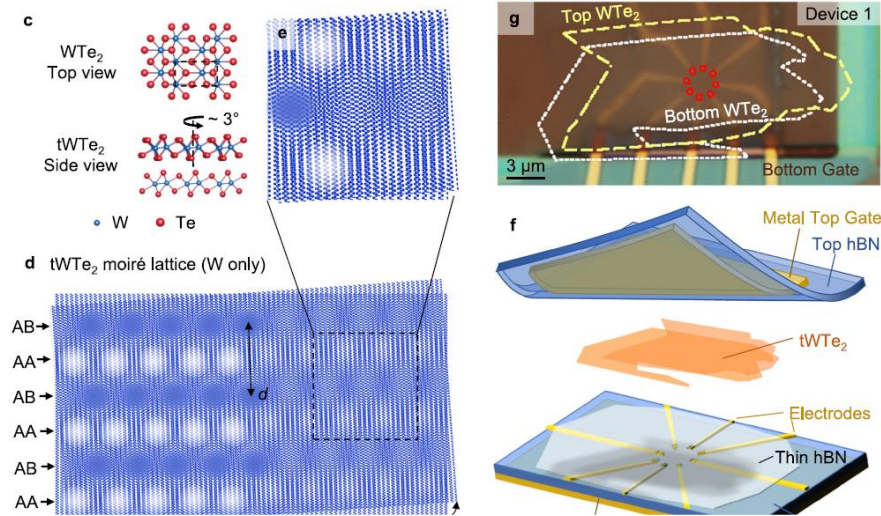
The interplay of nontrivial topology and superconductivity in condensed matter physics gives rise to exotic phenomena. However, materials are extremely rare where it is possible to explore the full details of the superconducting pairing. Here, we investigate the momentum dependence of the superconducting gap distribution in a novel Dirac material PdTe. Using high resolution, low temperature photoemission spectroscopy, we establish it as a spin-orbit coupled Dirac semimetal with the topological Fermi arc crossing the Fermi level on the (010) surface. This spin-textured surface state exhibits a fully gapped superconducting Cooper pairing structure below  $T_c \sim 4.5$  K. Moreover, we find a node in the bulk near the Brillouin zone boundary, away from the topological Fermi arc. These observations not only demonstrate the band resolved electronic correlation between topological Fermi arc states and the way it induces Cooper pairing in PdTe, but also provide a rare case where surface and bulk states host a coexistence of nodeless and nodal gap structures enforced by spin-orbit coupling.

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# Evidence for two dimensional anisotropic Luttinger liquids at millikelvin temperatures

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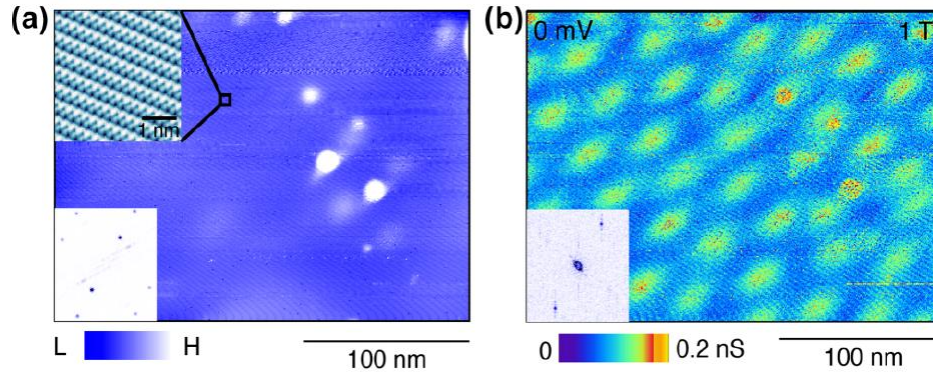
Interacting electrons in one-dimension (1D) are governed by the Luttinger liquid (LL) theory in which excitations are fractionalized. Can a LL-like state emerge in a 2D system as a stable zero-temperature phase? This question is crucial in the study of non-Fermi liquids. A recent experiment identified twisted bilayer tungsten ditelluride (tWTe<sub>2</sub>) as a 2D host of LL-like physics at a few kelvins. Here we report evidence for a 2D anisotropic LL state down to 50mK, spontaneously formed in tWTe<sub>2</sub> with a twist angle of  $\sim 3^\circ$ . While the system is metallic-like and nearly isotropic above 2 K, a dramatically enhanced electronic anisotropy develops in the millikelvin regime. In the anisotropic phase, we observe characteristics of a 2D LL phase including a power-law across-wire conductance and a zero-bias dip in the along-wire differential resistance. Our results represent a step forward in the search for stable LL physics beyond 1D.

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# Ultrahigh supercurrent density in a two-dimensional topological material

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Ongoing advances in superconductors continue to revolutionize technology thanks to the increasingly versatile and robust availability of lossless supercurrents. Here, we report the discovery of an unprecedentedly high superconducting critical current density in 1T'-WS<sub>2</sub>, exceeding those of all reported two-dimensional superconductors to date. 1T'-WS<sub>2</sub> features a strongly anisotropic superconducting state that violates the Pauli paramagnetic limit signaling the presence of unconventional superconductivity. Spectroscopic imaging of the vortices further substantiates the anisotropic nature of the superconducting state. More intriguingly, the normal state of 1T'-WS<sub>2</sub> carries topological properties. The band structure obtained via angle-resolved photoemission spectroscopy and first-principles calculations points to a Z<sub>2</sub> topological invariant. The concomitance of topology and superconductivity in 1T'-WS<sub>2</sub> establishes it as a topological superconductor candidate, which is promising for the development of quantum computing technology.

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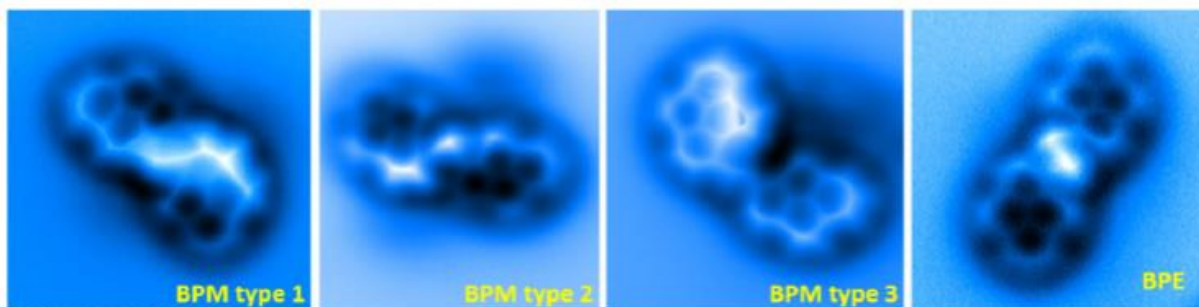
**Princeton Materials Institute**



## Sterical Structure of Molecules Determined by Scanning Probe Microscopy

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In this study, we investigated specially designed model compounds as proxies for archipelago structures in asphaltenes and heavy oils using HR-AFM. The experimental AFM images of BPM and BPE molecules were obtained using a CO-functionalized tip, in constant height scanning mode. The size of each AFM image is  $2.2 \times 2.2$  nm. The structure differences between BPM and BPE molecules was identified due to their different adsorption conformation and bonding. We identified various adsorption conformations of three different kinds of linkers in the BPM molecules (Figure 1), and their steric structure and fingerprints. With the steric fingerprint information of the linkers, we have addressed important questions related to the identification of molecular structures in chemistry and industrial applications. One example is the long-standing question of determining the molecular structures of petroleum pitch. With the help of this information, unknown molecules with similar linkers can be identified. For the nonplanar molecules, although AFM cannot resolve all the atoms and the bonding details of the molecules, the fingerprint-like features of each type bonding and adsorption configuration can be used as standard sample database for structure and conformation determination. Therefore, it provides a foundation for applying nc-AFM to solve unknown structures in petroleum-related studies and address a wide range of practical problems in the future.

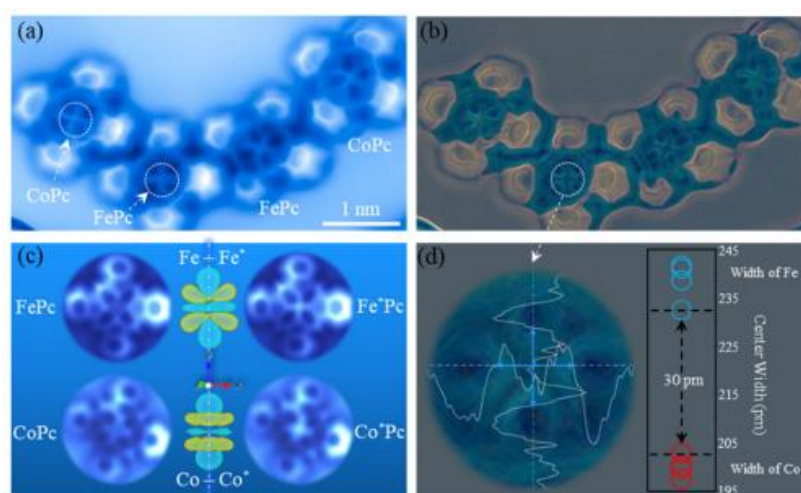
**Status:** published work in *Microscopy and Microanalysis* 2023, **29** (Suppl 1), 583



## Observation of electron orbital signatures of single atoms within metal-phthalocyanines using atomic force microscopy

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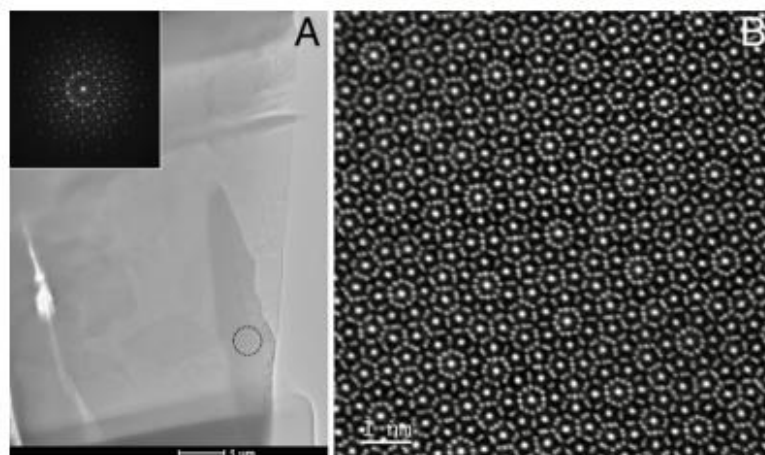
Resolving the electronic structure of a single atom within a molecule is of fundamental importance for understanding and predicting chemical and physical properties of functional molecules such as molecular catalysts. We report here the direct identification of two adjacent transition-metal atoms, Fe and Co, within phthalocyanine molecules using high-resolution noncontact atomic force microscopy (HR-AFM). HR-AFM imaging reveals that the Co atom is brighter and presents four distinct lobes on the horizontal plane whereas the Fe atom displays a “square” morphology. Our combined experimental and theoretical results demonstrate that both the distinguishable features in AFM images and the variation in the measured forces arise from Co’s higher electron orbital occupation above the molecular plane. The ability to directly observe orbital signatures using HR-AFM should provide a promising approach to characterizing the electronic structure of an individual atom in a molecular species.

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## Structure Evolution in Nature Quasicrystal Formed by Electrical Discharge

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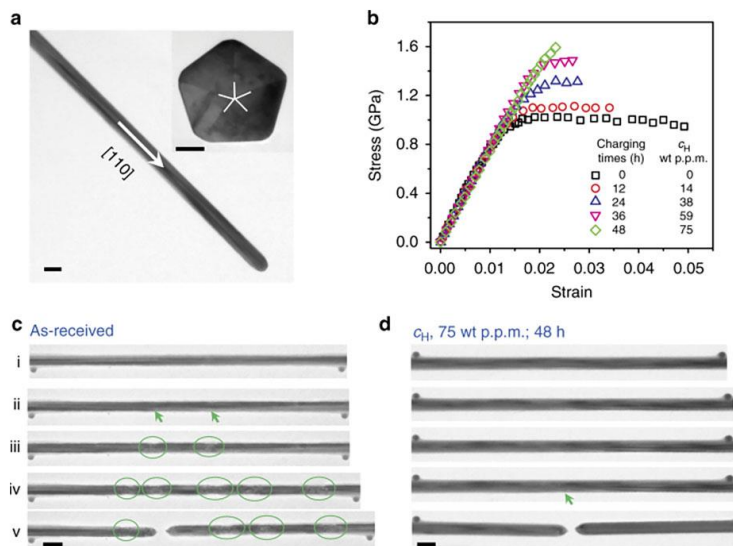
We report the details about the discovery of the quasicrystal in a fulgurite with rarely observed 12-fold symmetry and the microstructure evolution in the materials. In the case of a dodecagonal quasicrystal, the atomic structure consists of equally spaced atomic layers, each of which has crystallographically forbidden 12-fold symmetry, different from traditional crystal systems. To characterize these materials, a thin portion of the Mn-Si-Cr-Al-Ni fragment was extracted by means of the focused ion beam (FIB) technique and studied by electron microscopy. Together, these TEM/STEM results provide conclusive evidence of quasiperiodic translational order and crystallographically forbidden dodecagonal symmetry in a material formed by electrical discharge. Additionally, the dodecagonal quasicrystal also coexists with small portions of the hexagonal P6/mmm approximant similar to other dodecagonal quasicrystals that have been found to coexist with approximant crystals composed of the same local structural units as in the quasicrystal. The structure of the hexagonal approximant can be described as the tiling of two types of local structural units, namely an equilateral triangle and a square with the same edge length of 4.57 Å, which correspond to the A15-type structures in three dimensions, respectively.

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# Hydrogen Induced Transition of Failure Mode in Metallic Twinned Nanowires

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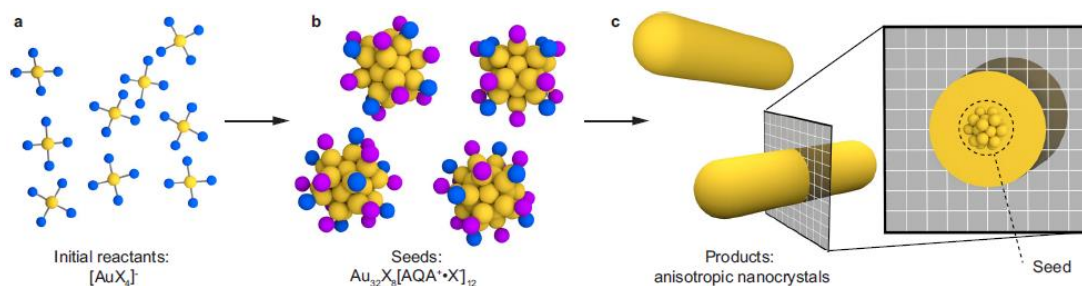
We use metallic nanowires (NW) as a platform to study hydrogen embrittlement in nanostructures where deformation and failure are dominated by dislocation nucleation. *In situ* transmission electron microscopy (TEM) tensile testing of NWs was performed on a microelectromechanical system (MEMS)-based tensile testing stage. Based on quantitative *in-situ* nanomechanical testing, we report enhanced yield strength and a transition in failure mechanism from distributed plasticity to localized necking in penta-twinned Ag NWs due to the presence of surface-adsorbed hydrogen. The yielding strength of the tested NWs increased from 0.95 to 1.54 GPa, whereas the failure strain decreased dramatically, indicating hydrogen-induced embrittlement in the tested NWs. In the NW with  $C_H = 75$  wt ppm., there were rare dislocation activities until the applied stress was close to the ultimate tensile strength and the NW fractured before substantial plastic deformation was activated. These results suggest that the presence of hydrogen adsorbed on the NW surface and diffusing into potential surface nucleation sources suppressed the nucleation of surface dislocations in the metallic NWs.

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## Atomically precise nanoclusters predominantly seed gold nanoparticle syntheses

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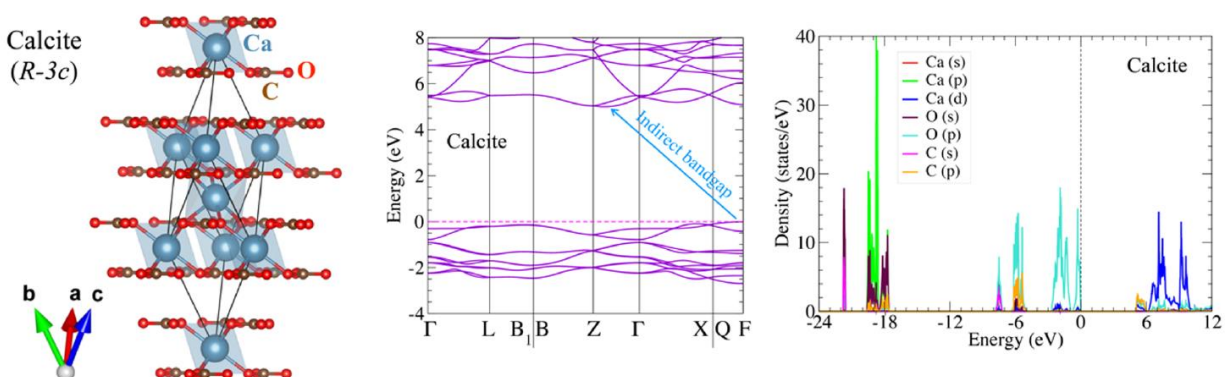
Seed-mediated synthesis strategies, in which small gold nanoparticle precursors are added to a growth solution to initiate heterogeneous nucleation, are among the most prevalent, simple, and productive methodologies for generating well-defined colloidal anisotropic nanostructures. However, the size, structure, and chemical properties of the seeds remain poorly understood, which partially explains the lack of mechanistic understanding of many particle growth reactions. Here, we identify the majority component in the seed solution as an atomically precise gold nanocluster, consisting of a 32-atom Au core with 8 halide ligands and 12 neutral ligands constituting a bound ion pair between a halide and the cationic surfactant:  $Au_{32}X_8[AQA^+\bullet X^-]_{12}$  ( $X = Cl, Br$ ;  $AQA =$  alkyl quaternary ammonium). Ligand exchange is dynamic and versatile, occurring on the order of minutes and allowing for the formation of 48 distinct  $Au_{32}$  clusters with AQAX (alkyl quaternary ammonium halide) ligands. Anisotropic nanoparticle syntheses seeded with solutions enriched in  $Au_{32}X_8[AQA^+\bullet X^-]_{12}$  show narrower size distributions and fewer impurity particle shapes, indicating the importance of this cluster as a precursor to the growth of well-defined nanostructures.

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## Differentiating the bonding states in calcium carbonate polymorphs by low-loss electron-energy-loss spectroscopy

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Calcium carbonate is one of the important building components in organisms, especially the two most common polymorphs, calcite and aragonite. Here, to understand the difference in bonding state, the two polymorphs are characterized by valence (low-loss) electron energy loss spectroscopy. 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 Ca  $M_{23}$  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 (spin-orbit coupling). This is because the atomic multiplet effect is much reduced for the Ca 3p orbital, which permits the corresponding Ca  $M_{23}$  edge to be compared with the PDOS results. Our findings show insights that PDOS can potentially be used to interpret the  $M_{23}$  edge of lighter 3d transition metals such as scandium, titanium, vanadium and chromium when such interpretation may not be achieved for their L edges.

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