

RESEARCH REPORT

Imaging and Analysis Center
PRISM



2021



A MESSAGE FROM THE DIRECTORS

Dear Friends of the PRISM Imaging and Analysis Center,

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

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

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

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

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



Nan Yao, Director of the Imaging and Analysis Center



Craig B. Arnold, Director of PRISM

Imaging and Analysis Center

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



Nanomaterials

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



Biomaterials

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



Electronic Materials

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



Ceramics and Glasses

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



Polymers

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



Metal Alloys

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

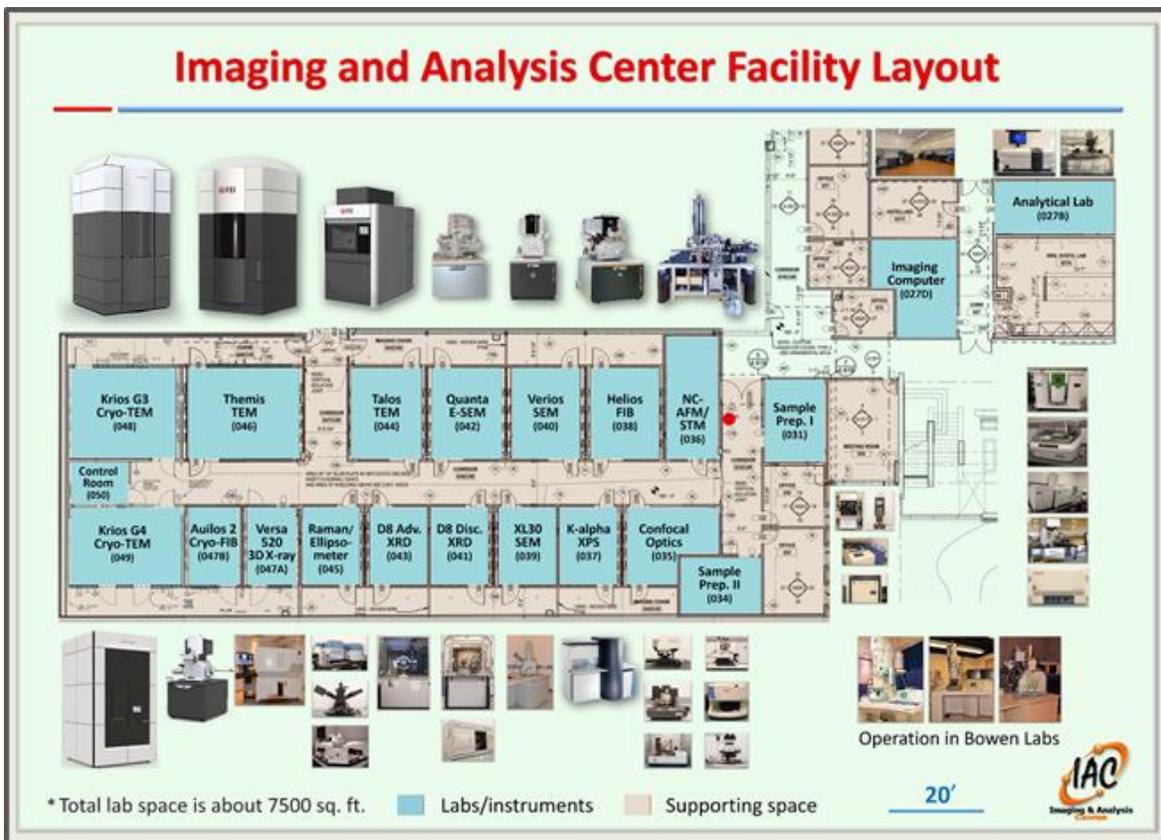
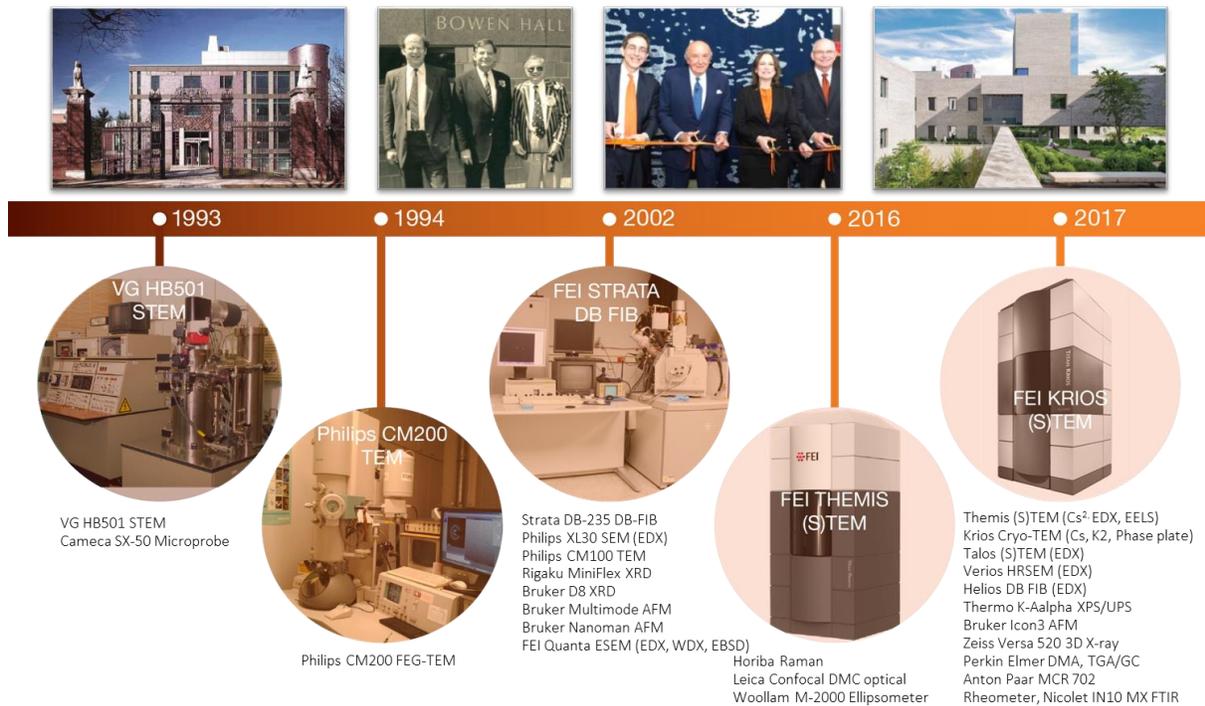


Pharmaceutical Materials

drug coating, toothpaste, molecular crystals, etc.

PRISM Imaging and Analysis Center (IAC)

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



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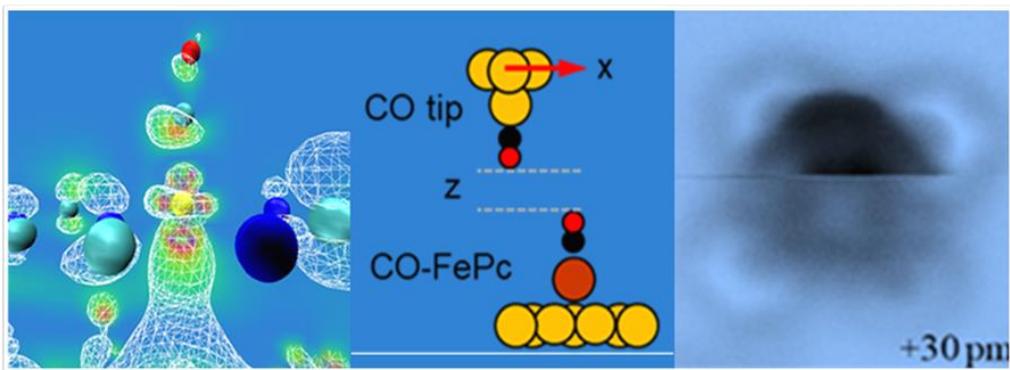
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IAC outside users from industry and other universities:



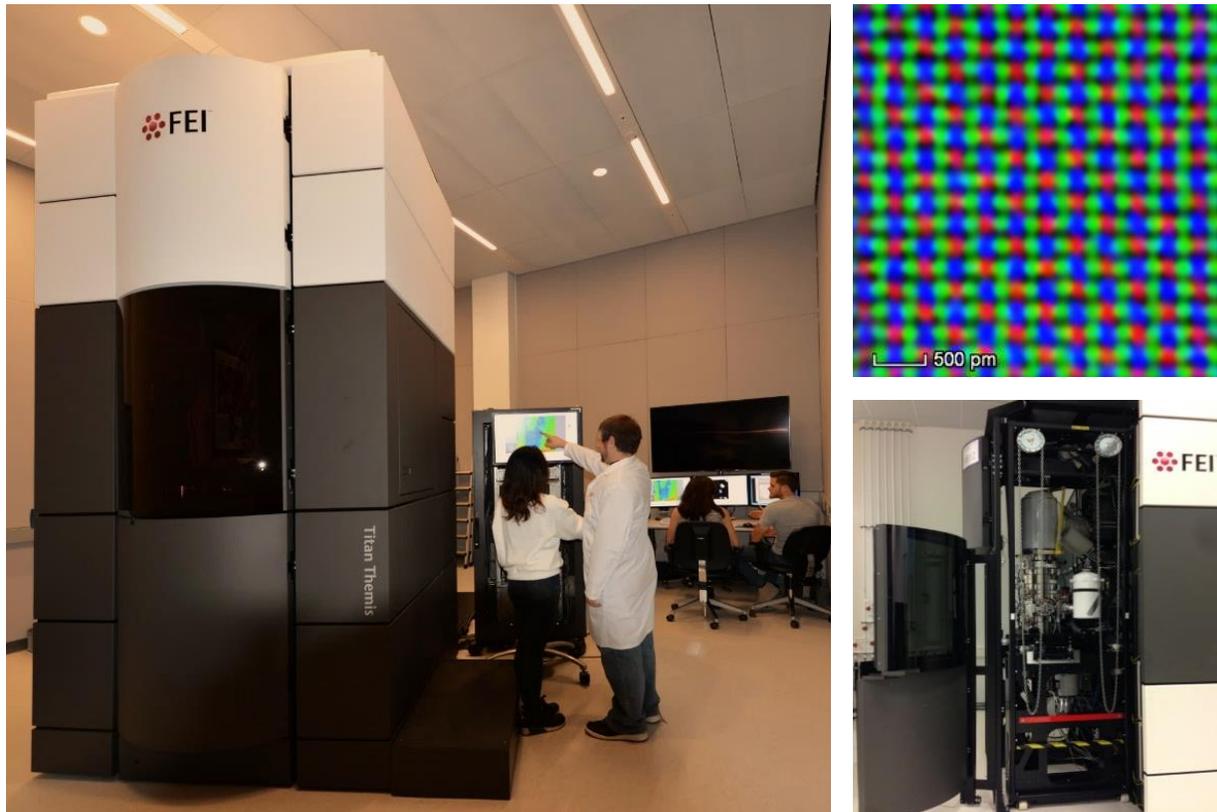
Images showing “Breaking a Dative Bond with Mechanical Forces”, Nature Communications 12 5635-5642 (2021). (Courtesy of P. Chen, D. Fan & N. Yao)

Acknowledgement:

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.

IAC instrumentation highlights:

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



(2) Titan Krios G3 Cryo-Transmission Electron Microscope

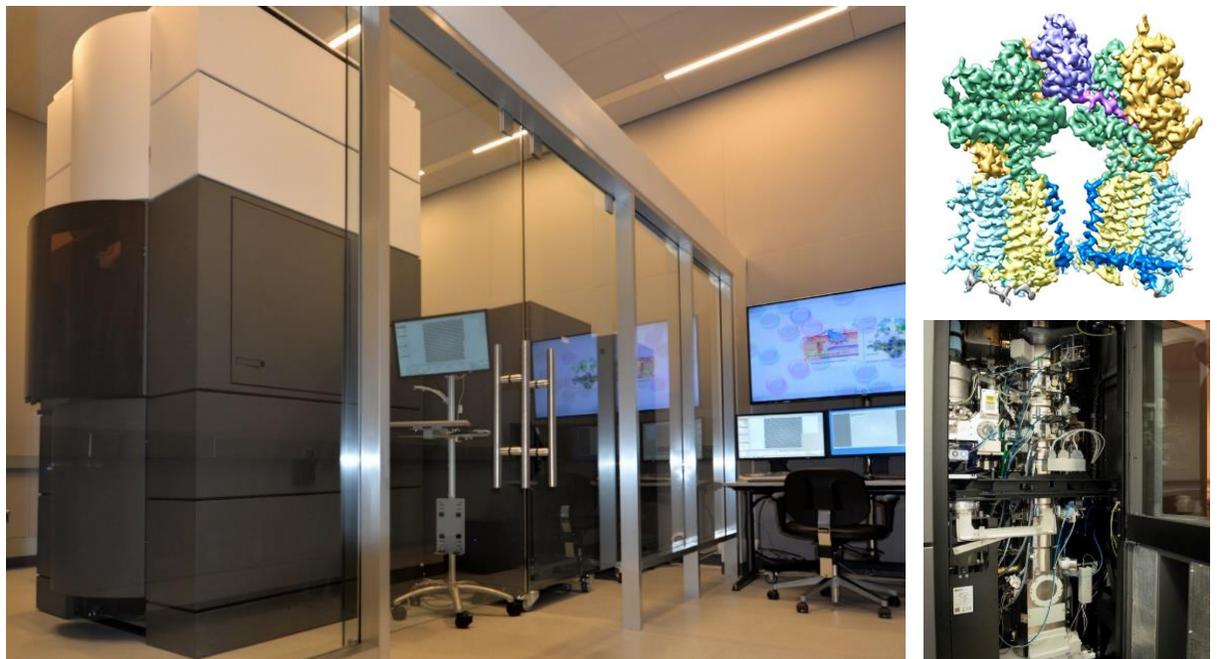


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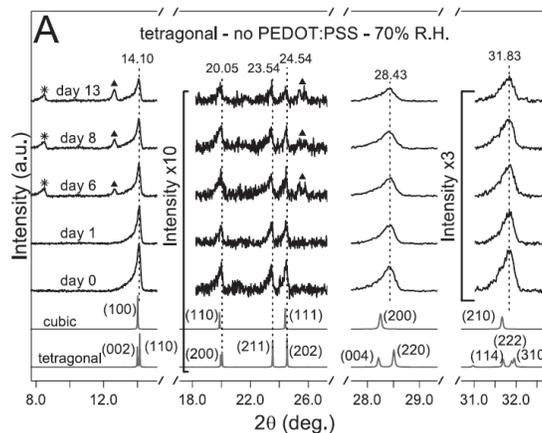
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Andlinger Center for Energy and Environment

Chemical and Structural Degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Propagate from PEDOT:PSS Interface in the Presence of Humidity

Sara A. Thomas,^{1,2} J. Clay Hamill Jr,³ Sarah Jane O. White,⁴ and Yueh-Lin Loo^{1,3}

¹Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544, USA; ²Department of Geosciences, Princeton University, Princeton, NJ 08544, USA; ³Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA; ⁴US Geological Survey, Reston, VA 20192, USA.



Understanding interfacial reactions that occur between the active layer and charge-transport layers can extend the stability of perovskite solar cells. In this study, the exposure of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) thin films prepared on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)-coated glass to 70% relative humidity (R.H.) leads to a perovskite crystal structure change from tetragonal to cubic within 2 days. Interface-sensitive photoluminescence measurements indicate that the structural change originates at the PEDOT:PSS/perovskite interface. During exposure to 30% R.H., the same structural change occurs over a much longer time scale (>200 days), and a reflection consistent with the presence of $(\text{CH}_3)_2\text{NH}_2\text{PbI}_3$ is detected. The authors propose that chemical interactions at the PEDOT:PSS/perovskite interface, facilitated by humidity, promote the formation of dimethylammonium, $(\text{CH}_3)_2\text{NH}_2^+$. The partial A-site substitution of CH_3NH_3^+ for $(\text{CH}_3)_2\text{NH}_2^+$ to produce a cubic $(\text{CH}_3\text{NH}_3)_{1-x}[(\text{CH}_3)_2\text{NH}_2]_x\text{PbI}_3$ phase explains the structural change from tetragonal to cubic during short-term humidity exposure. When $(\text{CH}_3)_2\text{NH}_2^+$ content exceeds its solubility limit in the perovskite during longer humidity exposures, a $(\text{CH}_3)_2\text{NH}_2^+$ -rich, hexagonal phase of $(\text{CH}_3\text{NH}_3)_{1-x}[(\text{CH}_3)_2\text{NH}_2]_x\text{PbI}_3$ emerges. These interfacial interactions may have consequences for device stability and performance beyond $\text{CH}_3\text{NH}_3\text{PbI}_3$ model systems.

Status: published work in Adv. Mater. Interfaces 2021, **8**, 2100505

Department of Chemical and Biological Engineering

Experimental verification of ion impact angle distribution at divertor surfaces using micro-engineered targets on DiMES at DIII-D

S. Abe,¹ C.H. Skinner,² I. Bykov,³ Y.W. Yeh,⁴ A. Lasa,⁵ J. Coburn,⁶ D.L. Rudakov,³ C. J. Lasnier,⁷ H.Q. Wang,⁸ A.G. McLean,⁷ T. Abrams,⁸ B.E. Koel¹

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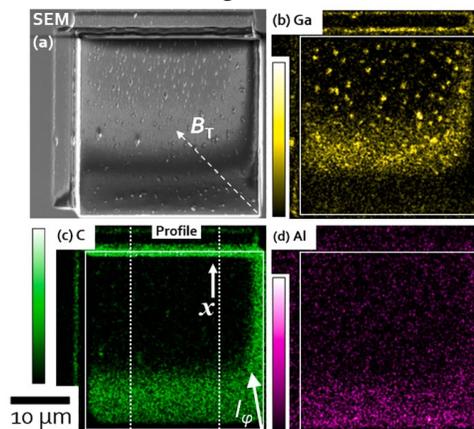
²Princeton Plasma Physics Laboratory, Princeton, NJ 08543, USA, ³Center for Energy Research, University of

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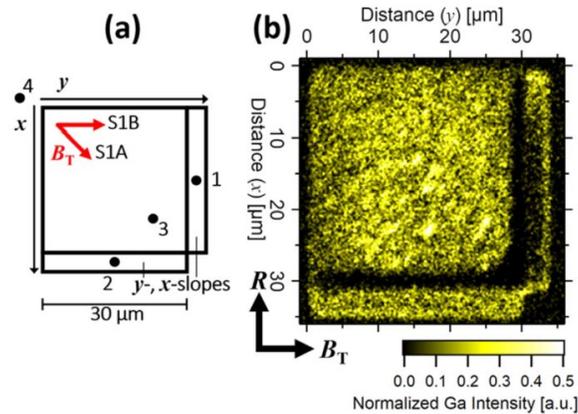
We report the first detailed experimental verification of the polar deuterium ion impact angle distribution (IAD) on the DIII-D divertor surface in L-mode plasmas using micro-engineered trenches in samples mounted on the DiMES probe. These trenches were fabricated via focused ion beam (FIB) milling of a silicon surface partially coated with aluminum. The sample surfaces were exposed to eight repeat L-mode deuterium discharges (30 s total exposure time). The samples were examined by scanning electron microscopy (SEM), which revealed changes on the trench floor due to material deposition and evidence for shadowing of the incident deuterium ions by the trench walls. The areal distribution of carbon and aluminum deposition was measured by energy-dispersive X-ray spectroscopy (EDS). One-dimensional profiles of this deposition are in agreement with net erosion profiles calculated from a Monte Carlo micro-patterning and roughness (MPR) code for ion sputtering using as input the polar and azimuthal deuterium IADs reported previously. The deposition profiles verified the characteristic shape of the polar IADs, which have a broad maximum from 79° to 86° , over the experimental range of 68° – 83° , where 0° is the surface normal direction.

Status: published work at Nuclear Materials and Energy 2021, **27**, 100965

Micro-trench measurements of the net deposition of carbon impurity ions in the DIII-D divertor and the resulting suppression of surface erosion

S. Abe,¹ C. H. Skinner,² I. Bykov,³ J. Guterl,⁴ A. Lasa,⁵ Y. W. Yeh,⁶ J. Coburn,⁷ D. L. Rudakov,³ C. J. Lasnier,⁸ H. Q. Wang,⁴ A. G. McLean,⁸ T. Abrams,⁴ and B. E. Koel¹

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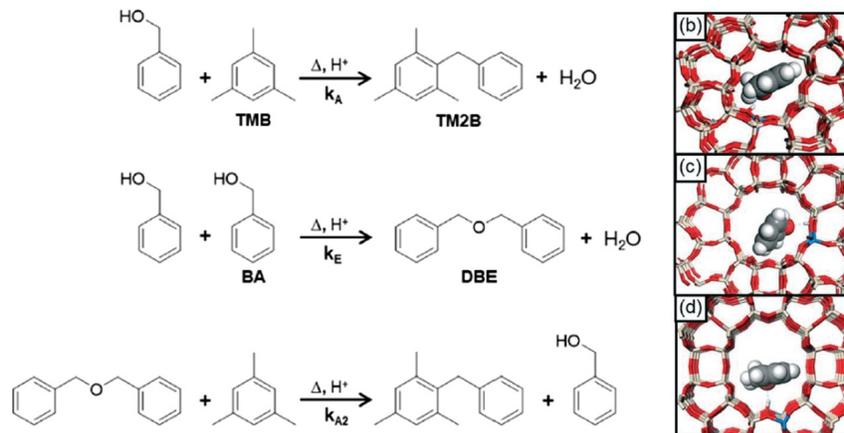
We report carbon impurity ion incident angles and deposition rates, along with silicon erosion rates, from measurements of micro-engineered trenches on a silicon surface exposed to L-mode deuterium plasmas at the DIII-D divertor. Post exposure ex-situ analysis determined elemental maps and concentrations, carbon deposition thicknesses, and erosion of silicon surfaces. Carbon deposition profiles on the trench floor showed carbon ion shadowing that was consistent with ERO calculations of average carbon ion angle distributions (IADs) for both polar and azimuthal angles. Measured silicon net erosion rates negatively correlated with the deposited carbon concentration at different locations. Differential erosion of surfaces on two different ion-downstream trench slope structures suggested that carbon deposition rate is affected by the carbon ion incident angle and significantly suppressed the surface erosion. The results suggest the C impurity ion incident angles, determined by the IADs and surface morphology, strongly affect erosion rates as well as the main ion (D, T, He) incident angles.

Status: published work at Physica Scripta 2021, **96**, 124039

Alkylation of poly-substituted aromatics to probe effects of mesopores in hierarchical zeolites with differing frameworks and crystal sizes

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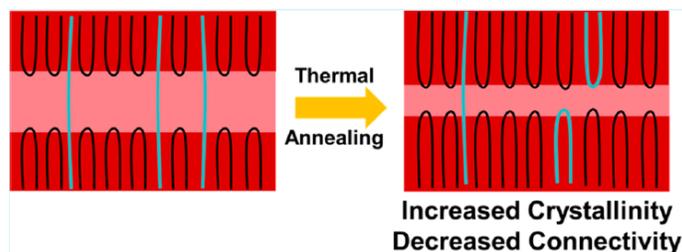
This study examines how the inherent diffusion constraints of MFI, BEA, and MOR zeolite architectures, at both nanocrystal and microcrystal scales, impact functions of mesopores in their hierarchical analogs. Reactivities, deactivation rates, and product selectivities were compared among zeolites, as well as to a mesoporous aluminosilicate control, during Friedel–Crafts alkylation of 1,3,5-trimethylbenzene with benzyl alcohol to form 1,3,5-trimethyl-2-benzylbenzene. Operation in the neat liquid phase ensured that the parallel BA self-etherification to yield dibenzyl ether occurred only at the expense of TM2B production when the alkylation reaction was impeded due to hindered access of TMB to confined protons. Investigation of secondary TM2B formation from reaction of DBE with TMB at low [BA]/[DBE] indicates an additional route of selectivity control for hierarchical zeolites that can achieve high BA conversion ($X_{BA} > 0.9$) with no DBE cofeed. These findings highlight a compounding advantage of increased diffusivity in mesopores that alter rates, extend lifetimes, and subsequently permit secondary reactions that enable significant shifts in product distribution. Fundamental insights into hierarchical zeolite reaction–diffusion–deactivation for alkylation of poly-substituted aromatics, as detailed here, can be applied broadly to reactions of other bulky species, including biomass-derived oxygenates, for more atom-efficient chemical and fuel production.

Status: published work at *Mol. Syst. Des. Eng.* 2021, **6**, 903

Role of Postdeposition Thermal Annealing on Intracrystallite and Intercrystallite Structuring and Charge Transport in Poly(3-hexylthiophene)

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The performance of electronic devices comprising conjugated polymers as the active layer depends not only on the intrinsic characteristics of the materials but also on the details of the extrinsic processing conditions. In this study, we examine the effect of postdeposition thermal treatments on the microstructure of poly(3-hexylthiophene) (P3HT) thin films and its impact on their electrical properties. Unsurprisingly, we find thermal annealing of P3HT thin films to generally increase their crystallinity and crystallite coherence length while retaining the same crystal structure. Despite such favorable structural improvements of the polymer active layers, however, thermal annealing at high temperatures can lead to a net reduction in the mobility of transistors, implicating structural changes in the intercrystallite amorphous regions of these semicrystalline active layers take place on annealing, and the simplistic picture that crystallinity governs charge transport is not always valid. Our results instead suggest tie-chain pullout, which occurs during crystal growth and perfection upon thermal annealing to govern charge transport, particularly in low-molecular-weight systems in which the tie-chain fraction is low. By demonstrating the interplay between intracrystallite and intercrystallite structuring in determining the macroscopic charge transport, we shed light on how structural evolution and charge-transport properties of nominally the same polymer can vary depending on the details of processing.

Status: published work at ACS Appl. Mater. Interfaces 2021, **13**, 999

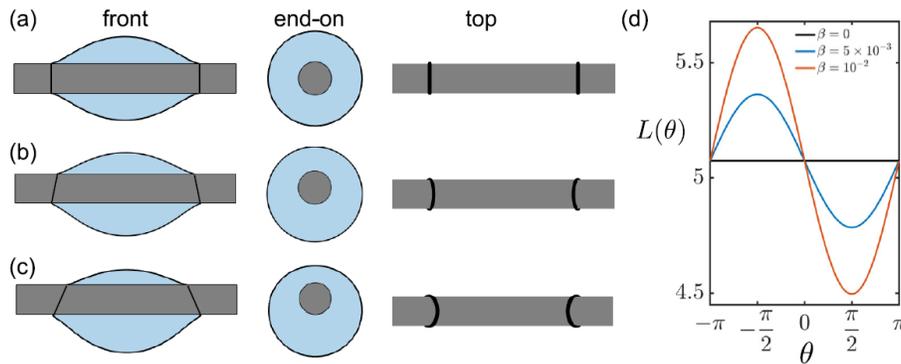
Effect of gravity on the shape of a droplet on a fiber: Nearly axisymmetric profiles with experimental validation

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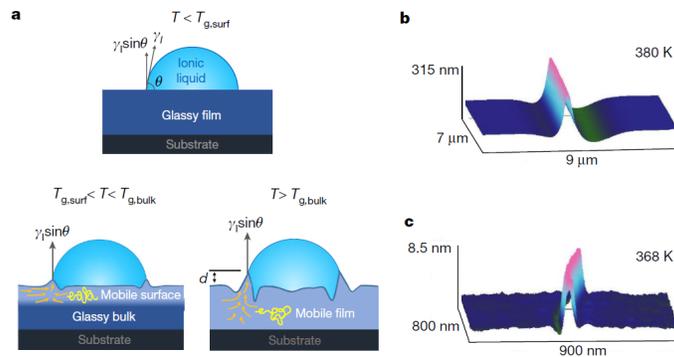
We study the effect of gravity on barrel-shaped droplets on fibers using theoretical analyses, numerical simulations, and experiments. By performing a perturbation analysis in the limit of small Bond numbers and small dimensionless droplet volumes, we formulate a nearly axisymmetric solution that describes the shape of the droplet. The leading-order solution yields the axisymmetric profile and the first-order correction incorporates the effect of gravity. Thus, we report the droplet shape as a function of dimensionless droplet volume, contact angle, and Bond number. We find that, due to gravity, the contact line position varies sinusoidally with the azimuthal angle around the fiber. We validate our solution by comparing droplet shape and contact line predictions with experiments and numerical simulations.

Status: published work at Phys. Rev. Fluids 2021, **6**, 063602

Mobility gradients yield rubbery surfaces on top of polymer glasses

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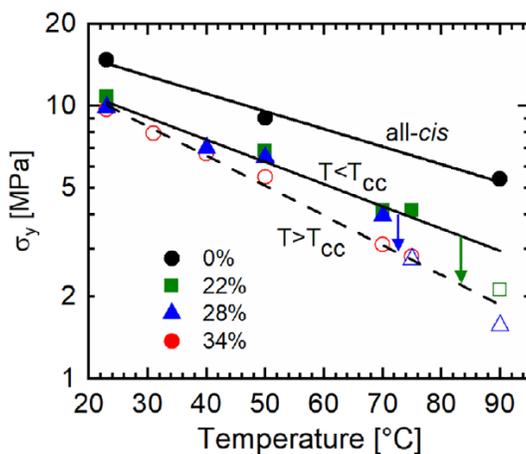
Many emerging materials, such as ultrastable glasses of interest for phone displays and OLED television screens, owe their properties to a gradient of enhanced mobility at the surface of glass-forming liquids. The discovery of this surface mobility enhancement has reshaped our understanding of the behaviour of glass formers and of how to fashion them into improved materials. In polymeric glasses, these interfacial modifications are complicated by the existence of a second length scale—the size of the polymer chain—as well as the length scale of the interfacial mobility gradient. Here we present simulations, theory and time-resolved surface nano-creep experiments to reveal that this two-scale nature of glassy polymer surfaces drives the emergence of a transient rubbery, entangled-like surface behaviour even in polymers comprised of short, subentangled chains. We find that this effect emerges from superposed gradients in segmental dynamics and chain conformational statistics. The lifetime of this rubbery behaviour extends as the material is cooled. The surface layers suffer a general breakdown in time–temperature superposition (TTS), a fundamental tenet of polymer physics and rheology. This finding may require a reevaluation of strategies for the prediction of long-time properties in polymeric glasses with high interfacial areas.

Status: published work in Nature 2021, **596**, 372

Controlling thermomechanical behavior of semicrystalline hydrogenated polynorbornene through the cis- to trans-cyclopentylene ratio

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Though polynorbornene synthesized by ring-opening metathesis polymerization has an intrinsically all-cis configuration of the cyclopentylene backbone rings, a fraction of these rings can be epimerized to the trans configuration during hydrogenation over suitable catalysts. By varying the method of hydrogenation, semicrystalline hydrogenated polynorbornenes (hPNs) with trans levels between 0 and 36% were obtained. With increasing trans content, the glass transition temperature, melting point, and enthalpy of melting decrease modestly. By contrast, the temperature at which the hPN crystal transitions into a rotationally disordered polymorph varies strongly with trans content, ranging from 126 °C (all-cis) to 71 °C at 27% trans; at trans contents of 34% and above, no rotationally-ordered phase is observed at any temperature. The room-temperature Young's modulus shows no dependence on trans content, while the yield stress drops by 20% at 1% trans content and slowly decreases further with additional epimerization. The temperature dependence of the Young's modulus differs for trans-containing versus all-cis polymers, while the temperature dependence of the yield stress is set by the polymorph type (rotationally ordered vs. disordered).

Status: published work in Journal of Polymer Science 2021, **XX**, XXX

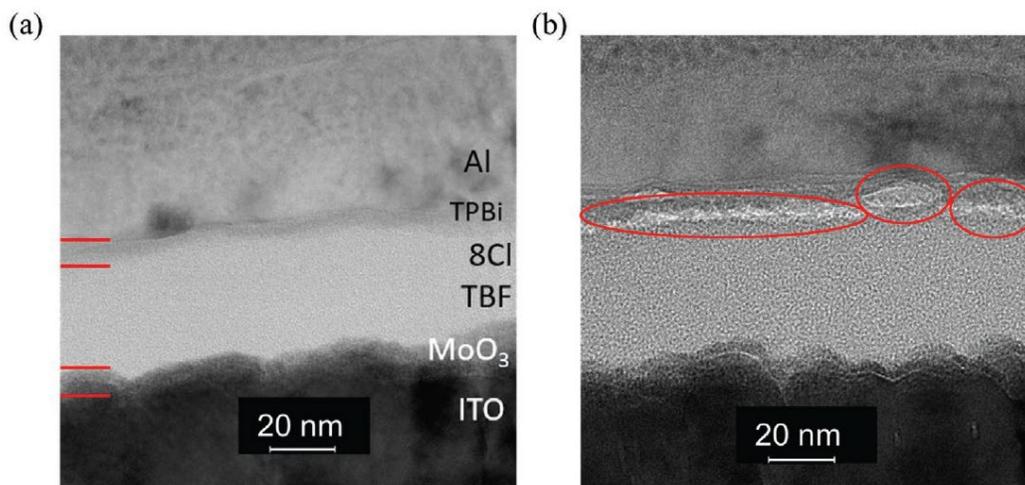
The Effects of Chromophore Halogenation on the Stability of UV-Absorbing Organic Solar Cells

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Transparent photovoltaics that harvest ultraviolet photons are promising point-of-use power sources for lower power applications, such as electrochromic windows that regulate the flow of visible and infrared photons for lighting and temperature regulation. Organic photovoltaic cells employing contorted hexabenzocoronene (cHBC) and its derivatives as chromophores have shown promise for transparent solar cells due to their high open-circuit voltages, large area scalability, and high photoactive layer transparency. Here, the operational stability of such devices is investigated and it is found that the solar cell active layers that include peripherally halogenated chromophores undergo rapid morphological degradation during operation, while control cells employing cHBC and other non-halogenated derivatives as donors with archetype C₇₀ as an acceptor are highly stable. This study suggests halogenation of chromophores can play an outsized role in determining the operational stability of devices comprising them, which should be considered during the molecular design process.

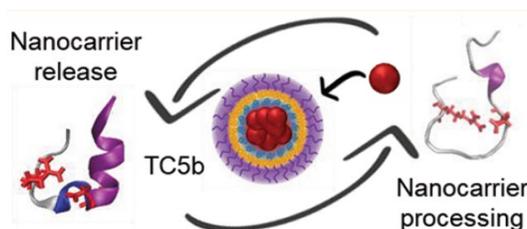
Status: published work at Adv. Energy Mater. 2021, **11**, 2100225

Stability of Protein Structure during Nanocarrier Encapsulation: Insights on Solvent Effects from Simulations and Spectroscopic Analysis

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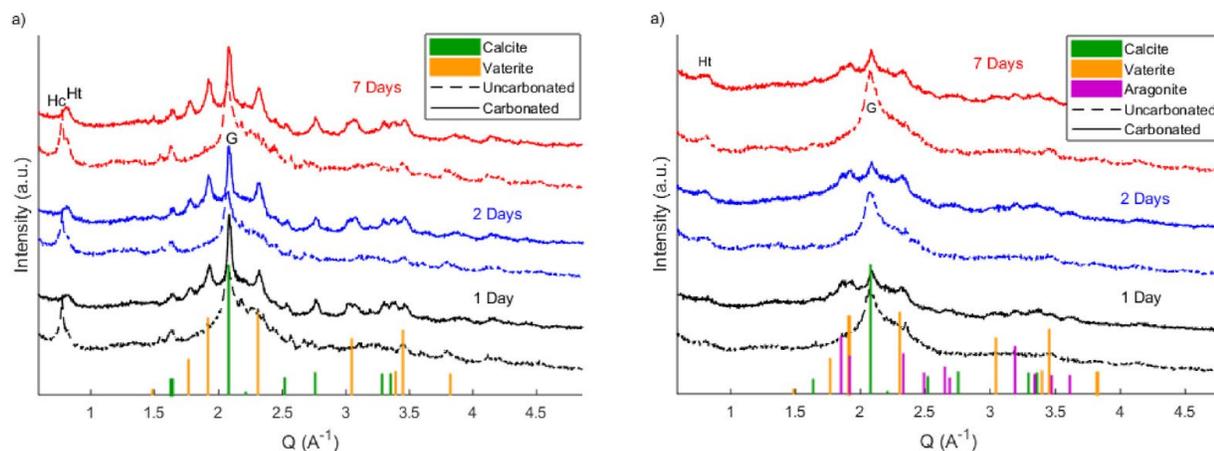
The dosing of peptide and protein therapeutics is complicated by rapid clearance from the blood pool and poor cellular membrane permeability. Encapsulation into nanocarriers such as liposomes or polymersomes has long been explored to overcome these limitations, but manufacturing challenges have limited clinical translation by these approaches. Recently, inverse Flash NanoPrecipitation (iFNP) has been developed to produce highly loaded polymeric nanocarriers with the peptide or protein contained within a hydrophilic core, stabilized by a hydrophobic polymer shell. Encapsulation of proteins with higher-order structure requires understanding how processing may affect their conformational state. We demonstrate a combined experimental/simulation approach to characterize protein behavior during iFNP processing steps using the Trp-cage protein TC5b as a model. Explicit-solvent fully atomistic molecular dynamics simulations with enhanced sampling techniques are coupled with two-dimensional heteronuclear multiple-quantum coherence nuclear magnetic resonance spectroscopy (2D-HMQC NMR) and circular dichroism to determine the structure of TC5b during mixed-solvent exposure encountered in iFNP processing. The simulations involve atomistic models of mixed solvents and protein to capture the complexity of the hydrogen bonding and hydrophobic interactions between water, dimethylsulfoxide (DMSO), and the protein. The combined analyses reveal structural unfolding of the protein in 11 M DMSO but confirm complete refolding after release from the polymeric nanocarrier back into an aqueous phase.

Status: published work in ACS Nano 2020, **14**, 16962

A parametric study of accelerated carbonation in alkali-activated slag

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Resistance to carbonation is one important attribute that low-CO₂ cement alternatives must possess, and is particularly crucial for cement alternatives subjected to aggressive CO₂ concentrations such as those used in construction of oil wells and wells for below ground carbon sequestration. Here, a parametric study of alkali-activated slag (AAS) carbonation in aggressive environments has been conducted to examine (i) calcium carbonate polymorphism using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy, and (ii) the extent of calcium carbonate formation and CO₂ adsorption using thermogravimetric analysis (TGA). A range of AASs have been studied by varying the magnesium content of the slag, the activator type (sodium hydroxide and sodium silicate), the activator concentration, and the curing time prior to carbonation. It was uncovered that both (i) magnesium from the slag and (ii) silica from the activating solution are needed to reduce the propensity for the sodium-containing calcium-alumino-silicate-hydrate gel to undergo decalcification.

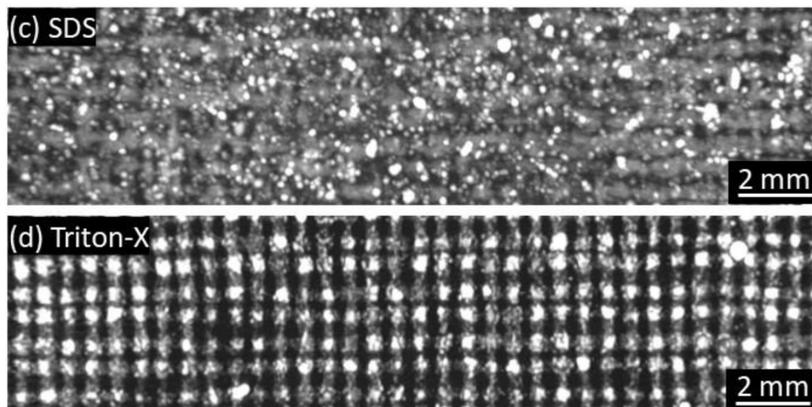
Status: published work at Cement and Concrete Research 2021, **145**, 106454

Visualizing Zinc Dendrites in Minimal Architecture Zinc Bromine Batteries via in-house Transmission X-ray Microscopy

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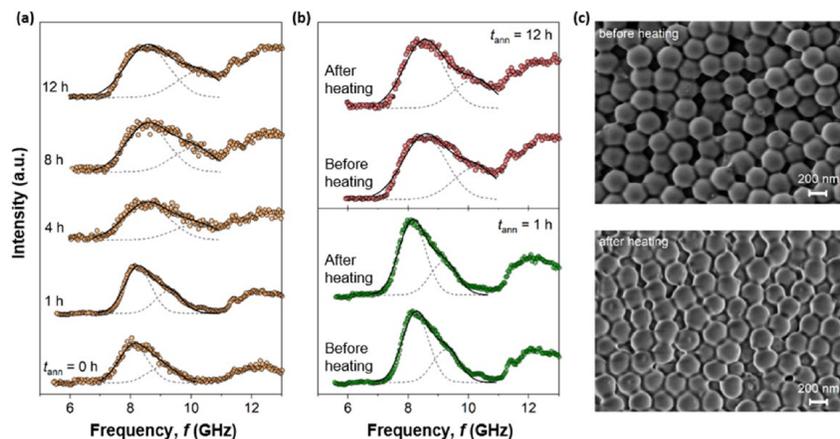
Development of low-cost (\$100/kWh), long-cycle life (>10,000) electrochemical energy storage devices or batteries is necessary for the transition toward the future of renewable energy. The electrochemical performance of batteries can be compromised by the formation of metal dendrites during cycling processes. Organic chemical additives in the electrolytes represent a useful strategy to mitigate dendrite formation, but a fuller understanding requires knowledge of the morphological effects of chemical additives during the cycling process. Traditional ex situ microscopy has been used extensively for studying energy materials and devices to obtain spatial and chemical information, but analysis requires disassembling materials from their native environments. In situ liquid cell transmission electron microscopy (TEM) enables obtaining more representative information that would otherwise be missing or misleading. However, the experimental conditions for specialized probing systems with modified battery structures may result in significant deviation from normal operating conditions of commercial batteries. Alternatively, in situ transmission X-ray microscopy (TXM) can provide three-dimensional (3D) morphological and chemical information on batteries in realistic operating conditions. In this work, we utilized an in-house TXM instrument to visualize the 3D growth morphology of zinc dendrites on carbon cloth electrodes during cycling in electrolytes containing organic additives within minimal architecture zinc bromine batteries (MA-ZBBs).

Status: published work in *Microscopy and Microanalysis* 2021, **27**, 2448

Direct Visualization and Characterization of Interfacially Adsorbed Polymer atop Nanoparticles and within Nanocomposites

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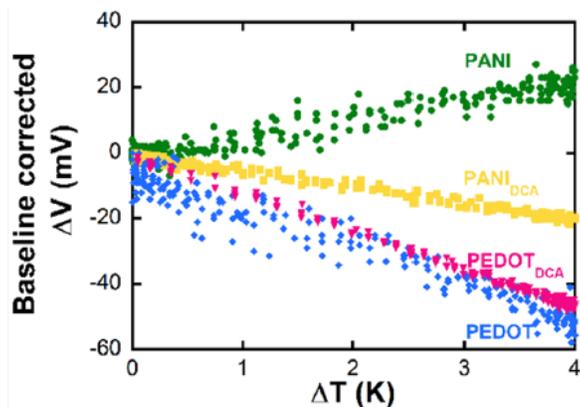
Irreversible adsorption at polymer/substrate interfaces has been reported to influence glassy properties in thin films. However, consideration has yet to be extended to the nanocomposite geometry, wherein a large interfacial area and high processing temperatures afford especially favorable conditions for irreversible adsorption at the polymer/nanoparticle interface. Here, we present an approach for directly measuring the site-specific glassy properties at the polystyrene (PS)-adsorbed layer interface in PS-silica nanocomposites. We achieved this using a stepwise assembly approach to localize fluorescent dyes within the nanocomposite adsorbed layer, subsequently measuring the glass transition temperature (T_g) via fluorescence. We found that PS adsorption within nanocomposites strongly influenced the local T_g . By measuring the thickness of the PS-adsorbed layers atop nanoparticles via transmission electron microscopy, we found a correlation between adsorbed layer T_g and thickness. Our results provide compelling evidence that adsorbed layer formation within polymer nanocomposites can have a profound impact on local interfacial properties.

Status: published work at *Macromolecules* 2021, **54**, 10224

Postdeposition Processing Influences the Relative Contributions of Electronic and Ionic Seebeck Effects in the Thermoelectric Response of Conducting Polymers

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The postdeposition solvent annealing of PEDOT:PSS and PANI–PAAMPSA thin films with dichloroacetic acid (DCA) induces structural modification that dramatically increases the electrical conductivity of these conducting polymers. Herein, we studied how such structural modification impacts the thermoelectric properties of PEDOT:PSS and PANI–PAAMPSA. DCA treatment increases the electronic Seebeck contribution to thermopower relative to the ionic Seebeck contribution for both conducting polymers. Interestingly, DCA treatment also induces a change in the sign of the electronic Seebeck coefficient of PANI–PAAMPSA from negative to positive. This switch in polarity of the Seebeck coefficient is likely to stem from an alteration of PANI's electronic structure with the morphological reorganization of PANI–PAAMPSA that takes place on DCA annealing. By relating the thermoelectric properties of PEDOT:PSS and PANI–PAAMPSA to the induced structural changes on DCA treatment, design rules have been generated to guide the optimization of thermoelectric response of conducting polymers per device architecture specification and application needs.

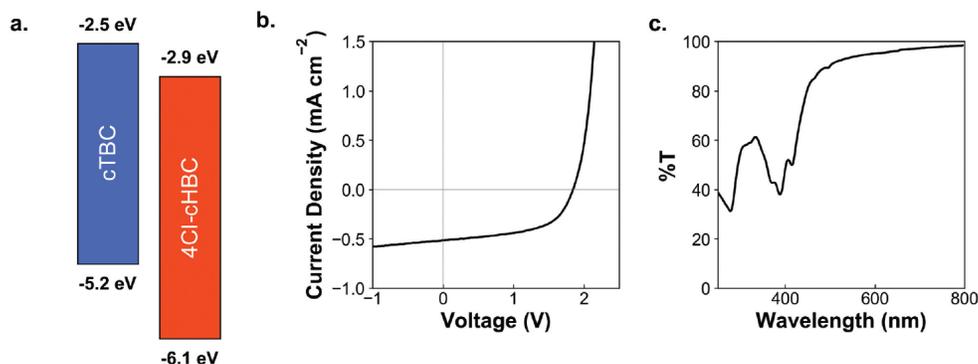
Status: published work in J. Phys. Chem. C 2021, **125**, 12289

Coronene derivatives for transparent organic photovoltaics through inverse materials design

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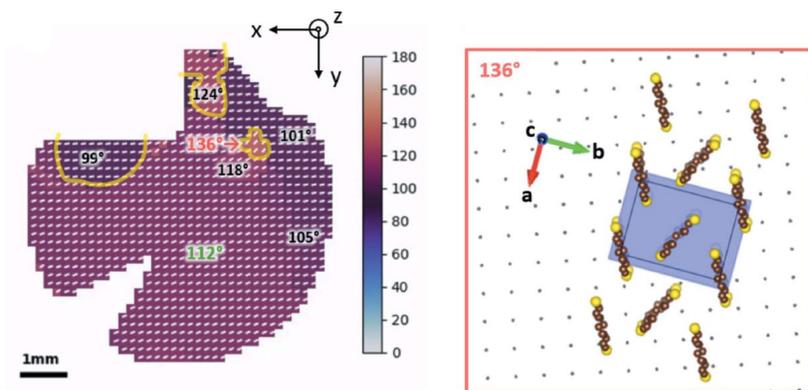
To accelerate materials discovery, computational methods such as inverse materials design have been proposed to predict the properties of target compounds of interest for specific applications. This *in silico* process can be used to guide subsequent synthesis and characterization. Inverse design is especially relevant for the field of organic molecules. With a target application of UV-absorbing, visibly transparent solar cells in mind, we calculated the orbital and transition energies of over 360 possible coronene derivatives. Our screening, or the constraints we imposed on the calculated series, resulted in the selection of three new derivatives, namely contorted pentabenzocoronene (cPBC), contorted tetrabenzocoronene (cTBC), and contorted tetrabenzofuranylbenzocoronene (cTBFBC) for synthesis and characterization. Our materials characterization found agreement between our calculated and experimental energy values, and we fabricated solar cells with an open-circuit voltage of 1.84 V and an average visible transparency of 88% of the active layer; both quantities exceed previous records for visibly transparent coronene-based solar cells. This work highlights the inverse materials design, as well as improvements to application of UV-targeted solar cells.

Status: published work in Journal of Materials Chemistry C 2021, **9**, 1310

Grazing-incidence X-ray diffraction tomography for characterizing organic thin films

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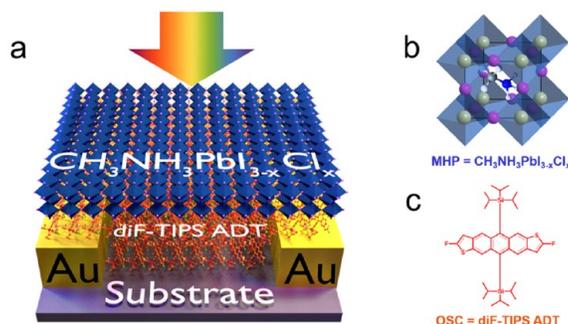
Characterization of thin films is of paramount importance for evaluating material processing outcomes/efficiency as well as establishing structure–property/performance relationships. This article introduces grazing-incidence diffraction tomography (GID tomography), a technique that combines grazing incidence X-ray scattering and computed tomography to quantitatively determine the dimension and orientation of crystalline domains in thin films without restrictions on the beam coherence, substrate type or film thickness. This computational method extends the capability of synchrotron beamlines by utilizing standard X-ray scattering experiment setups.

Status: published work in J. Applied Crystallography 2021, **54**, 1327

Photocurrent in Metal-Halide Perovskite/Organic Semiconductor Heterostructures: Impact of Microstructure on Charge Generation Efficiency

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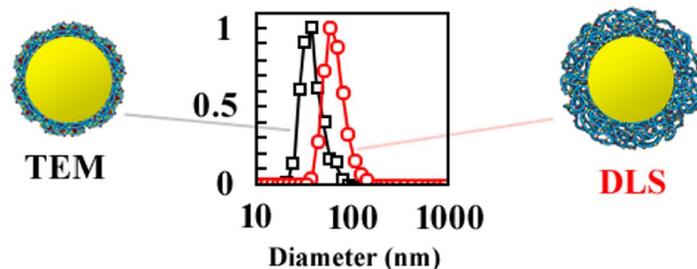
Hybrid organic–inorganic metal-halide perovskites have emerged as versatile materials for enabling low-cost, mechanically flexible optoelectronic applications. The progress has been commendable; however, technological breakthroughs have outgrown the basic understanding of processes occurring in bulk and at device interfaces. Here, we investigated the photocurrent at perovskite/organic semiconductor interfaces in relation to the microstructure of electronically active layers. We found that the photocurrent response is significantly enhanced in the bilayer structure as a result of a more efficient dissociation of the photogenerated excitons and triions in the perovskite layer. The increase in the grain size within the organic semiconductor layer results in reduced trapping and further enhances the photocurrent by extending the photocarriers' lifetime. The photodetector responsivity and detectivity have improved by 1 order of magnitude in the optimized samples, reaching values of $6.1 \pm 1.1 \text{ A W}^{-1}$, and $1.5 \times 10^{11} \pm 4.7 \times 10^{10}$ Jones, respectively, and the current–voltage hysteresis has been eliminated. Our results highlight the importance of fine-tuning film microstructure in reducing the loss processes in thin-film optoelectronics based on metal-halide semiconductors and provide a powerful interfacial design method to consistently achieve high-performance photodetectors.

Status: published work in ACS Appl. Mater. & Interfaces 2021, **13**, 10231

Nanoparticle size distribution quantification from transmission electron microscopy (TEM) of ruthenium tetroxide stained polymeric nanoparticles

Brian K. Wilson and Robert K. Prud'homme

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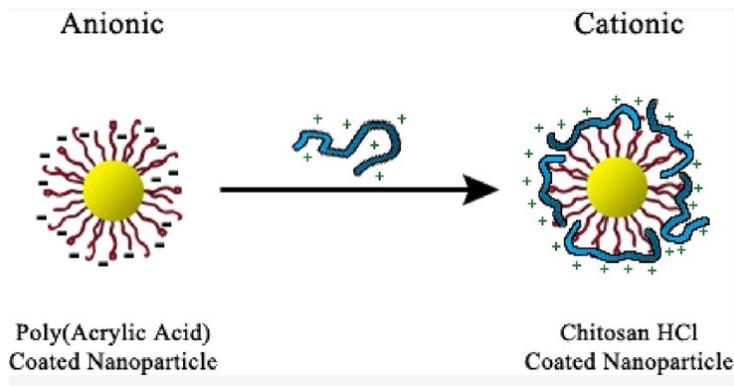
Hypothesis: Dynamic Light Scattering (DLS) generated particle size distributions (PSD) of polymer-stabilized nanoparticles are dependent on the optimization parameters used to generate an inversion solution fit to the measured autocorrelation function. The accuracy of the DLS PSD average and polydispersity can be determined by comparing analyzed Transmission Electron Microscopy (TEM) images with the DLS results if the TEM measured sizes can be corrected for the thickness of the hydrated polymer corona that impacts particle hydrodynamics but is a collapsed, desiccated shell in the TEM images. *Experiments:* Nanoparticles were prepared by Flash NanoPrecipitation with either poly(ethylene glycol) (PEG) or hydroxypropyl methylcellulose acetate succinate (HPMCAS) stabilizing polymers. Solvated nanoparticle size distributions were measured by DLS in aqueous media. The same nanoparticle dispersions were lyophilized onto TEM grids and stained by ruthenium tetroxide (RuO_4) vapor to improve electron contrast. Desiccated particle size distributions were generated by measuring a minimum of 300 particle diameters in the stained TEM images. *Findings:* Using our protocol for staining soft matter nanoparticles in TEM measurements, we have quantitatively analyzed the correlation between DLS and TEM generated PSDs. Average diameters disagree by the hydrated polymer corona thickness for each stabilizer due to the high-vacuum TEM environment, with 21.4 nm for PEG and 51.2 nm for HPMCAS. While corrected average diameter agrees within 10% for each technique, DLS consistently over-estimates the standard deviation of the PSD by 100% compared to the TEM measurement.

Status: published work in J. Colloid and Interface Sci. 2021, **604**, 208

Processing Chitosan for Preparing Chitosan-Functionalized Nanoparticles by Polyelectrolyte Adsorption

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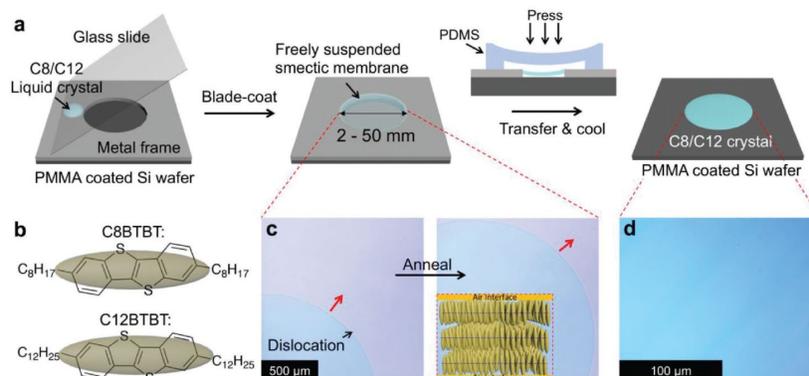
Chitosan-coated nanoparticles are a promising class of drug delivery vehicles that have been studied as tools for improving the gastrointestinal delivery of therapeutics. Here we present an analysis of chitosan-coated nanoparticles with an emphasis on characterizing the chitosan polymer properties. Cationic nanoparticles are produced by adsorbing a layer of chitosan HCl on an anionic (-40 mV ζ -potential) polyacrylic acid (PAA) coated primary nanoparticle. Commercially available chitosan (90% deacetylated) must be processed into a nearly completely deacetylated HCl salt form (99% deacetylation); otherwise, primary nanoparticle aggregation occurs. Deacetylated chitosan HCl produces stable, cationic ($+35$ mV ζ -potential) nanoparticles within 10% of the original anionic particle hydrodynamic diameter at a 1:2 molar ratio of chitosan glucosamine HCl monomers to PAA acrylic acid monomers.

Status: published work in *Langmuir* 2021, **37**, 8517

Solvent-Free Coating of Organic Semiconductor Membranes with Centimetric Crystalline Domains

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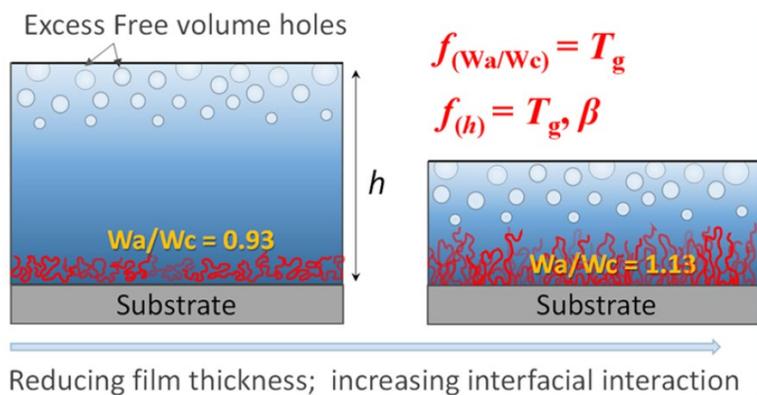
Organic semiconductors (OSCs) have shown great promise in a variety of applications. Although solution processing of OSCs has resulted in high quality films, exquisite control of structural development to minimize defect formation during large-scale fabrication remains formidable. Compounding this challenge is the use of halogenated organic solvents, which poses significant health and environmental hazards. However, the solvent-free techniques introduced thus far impose additional limitations on solidification kinetics; the resulting OSC thin films are often more defective than those processed from solution. Here, a solvent-free technique is reported to prepare OSC membranes with centimetric crystalline domains. Leveraging the tendency for liquid crystalline materials to preferentially orient, OSCs are “prealigned” by depositing them from the melt over a metal frame to form a freely suspended membrane. Crystallization from this prealigned phase affords membranes with unprecedented structural order across macroscopic distances. Field-effect transistors comprising membranes of dioctyl[1]-benzothieno[3,2-b][1]benzothiophene (C8BTBT) and didodecyl[1]-benzothieno[3,2-b][1]benzothiophene (C12BTBT) a hole mobility of $\approx 8.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, superseding the mobility of any transistors whose active layers are deposited from melt.

Status: published work at *Advanced Electronic Materials* 2021, **7**, 2000792

Decoupling Role of Film Thickness and Interfacial Effect on Polymer Thin Film Dynamics

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The film thickness and substrate interface are the two most common parameters to tune the dynamics of supported thin films. Here, we investigated the glass transition temperature (T_g) and thermal expansion of thin poly(methyl methacrylate) (PMMA) films with various thicknesses and different interfacial effects. We showed that, although the T_g of the thin films can be modulated equivalently by the two factors, their ability to change the expansivity (β) is quite different; that is, β increases notably with a reduction in the thickness, while it is insensitive to perturbations at the interface. We attribute the deviation in modulating β by the thickness and the interfacial effect to the disparate abilities to change the free volume content in the film by a free surface and substrate interface. This leads to a situation where thin films with dissimilar thicknesses and interfacial properties can have the same T_g but very different β values, suggesting that T_g alone cannot unequivocally quantify thin film dynamics.

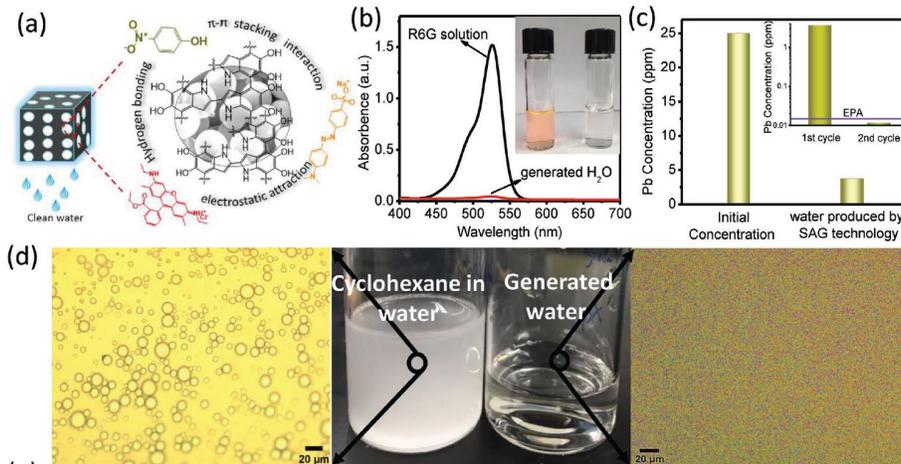
Status: published work in ACS Macro Lett. 2021, **10**, 1

A Bioinspired Elastic Hydrogel for Solar-Driven Water Purification

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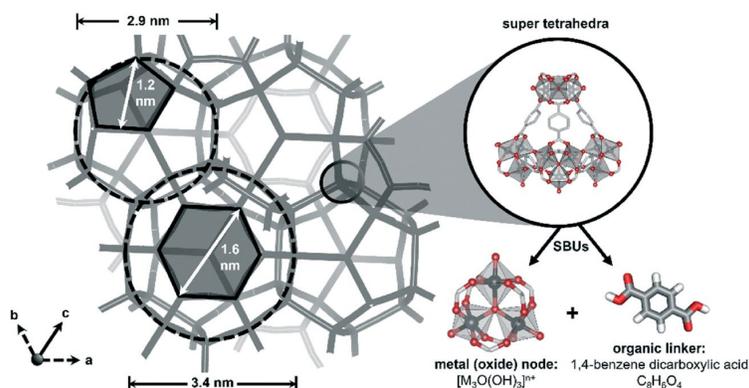
The global demand for clean and safe water will continue to grow well into the 21st century. Moving forward, the lack of access to clean water, which threatens human health and strains precious energy resources, will worsen as the climate changes. Therefore, future innovations that produce potable water from contaminated sources must be sustainable. Inspired by nature, a solar absorber gel (SAG) is developed to purify water from contaminated sources using only natural sunlight. The SAG is composed of an elastic thermoresponsive poly(N-isopropylacrylamide) (PNIPAm) hydrogel, a photothermal polydopamine (PDA) layer, and a sodium alginate (SA) network. Production of the SAG is facile; all processing is aqueous-based and occurs at room temperature. Remarkably, the SAG can purify water from various harmful reservoirs containing small molecules, oils, metals, and pathogens, using only sunlight. The SAG relies on solar energy to drive a hydrophilic/hydrophobic phase transformation at the lower critical solution temperature. Since the purification mechanism does not require water evaporation, an energy-intensive process, the passive solar water-purification rate is the highest reported. This discovery can be transformative in the sustainable production of clean water to improve the quality of human life.

Status: published work in *Advanced Materials* 2021, **33**, 2007833

Reaction pathways and deactivation mechanisms of isostructural Cr and Fe MIL-101 during liquid-phase styrene oxidation by hydrogen peroxide

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Isostructural Cr and Fe nanoporous MIL-101, synthesized without mineralizing agents, are investigated for styrene oxidation utilizing aqueous hydrogen peroxide to yield valuable oxygenates for chemical synthesis applications. Styrene conversion rates and oxygenate product distributions both depend on metal identity, as MIL-101(Fe) is more reactive for total styrene oxidation and is more pathway selective, preferring aldehyde formation at the α -carbon to the aromatic ring, where MIL-101(Cr) sustains epoxide production at the same α -carbon. We postulate that the higher reactivity of one of these surface intermediates, $Fe(IV)=O$ relative to $Cr(IV)=O$, leads to higher styrene oxidation rates for MIL-101(Fe), while higher electrophilicity of $Cr(III)-OOH$ intermediates translates to the higher styrene oxide selectivity observed for MIL-101(Cr). Secondary styrene oxide and benzaldehyde conversions are observed over both analogs, but the former is more prevalent over MIL-101(Fe) due to higher Lewis/Brønsted acid site density and strength compared to MIL-101(Cr). Recyclability experiments combined with characterization via XRD, SEM/EDXS, and FT-IR and UV-vis spectroscopies show that the nature of MIL-101(Fe) sites does not change significantly with each cycle, whereas MIL-101(Cr) suffers from metal leaching. Finally, examination of styrene conversion for three unique synthesized phases of MIL-101(Cr) rationalizes that nodal defects are largely responsible for observed reactivity and selectivity but predispose the framework to metal leaching as a predominant deactivation mechanism.

Status: published work in *Catal. Sci. Technol.* 2021, **11**, 5282

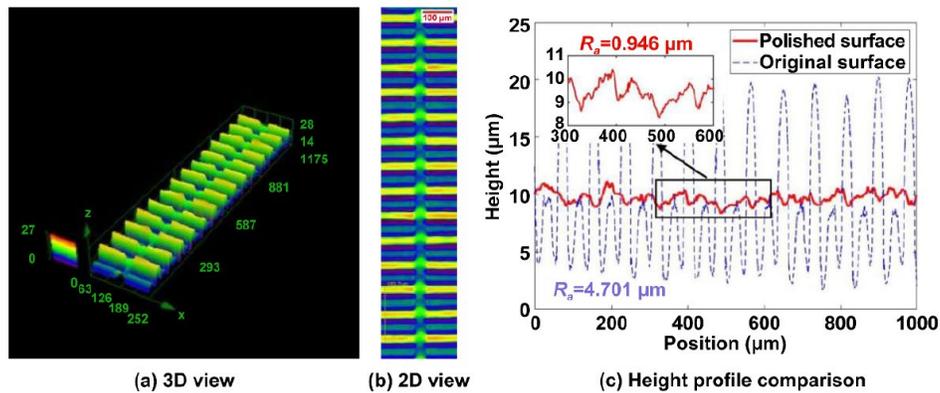
Implications of using two low-power continuous-wave lasers for polishing

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Laser polishing is widely employed to reduce the surface roughness of products with complex geometries. Traditional laser polishing techniques use a single high-power Gaussian beam to melt and smooth a thin layer of surface material. However, the reliance on high power lasers can present practical challenges such as minimizing surface evaporation or reducing overall cost. In this work, we combined two identical low-power laser beams with a spatial offset in between them to construct an elliptical beam. By changing the spatial offset, combined beams with different lengths along the major axis can be created. We observe over 20% improvement in line roughness reduction using this approach compared to a single Gaussian laser beam with the same total power. Additionally, both experiment and simulation results suggest such improvement is because this dual-laser set-up can create a longer molten pool compared to a single laser.

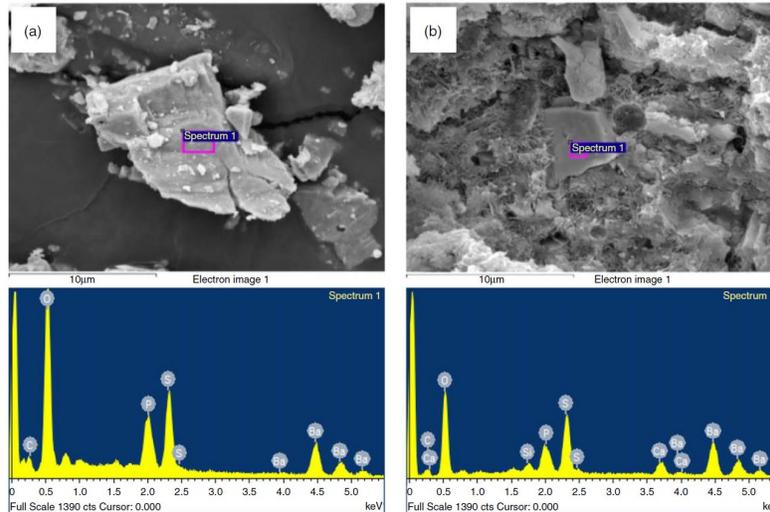
Status: published work at Int. J. Extrem. Manuf. 2020, **2**, 035101

Contamination of Oil-Well Cement with Conventional and Microemulsion Spacers

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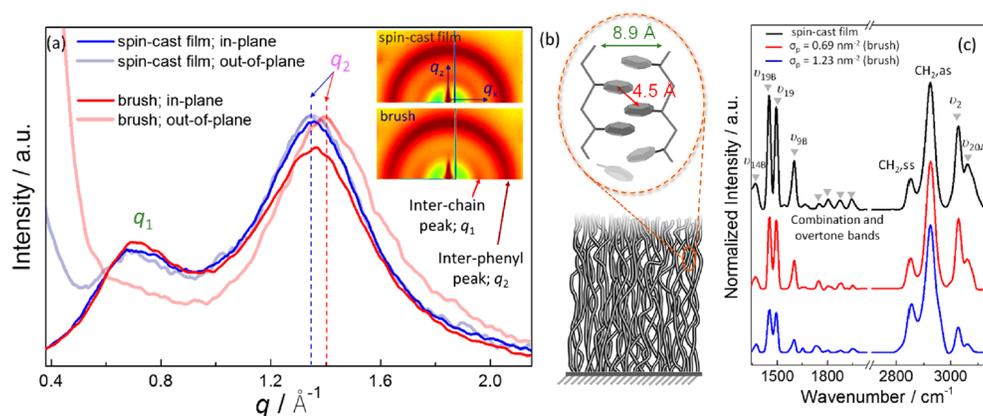
The performance of oil-well cement is altered if contaminated by spacers. Very few studies in the literature are found on this topic, in particular for newly developed microemulsion spacers. Therefore, it is worth investigating the properties of cement contaminated with spacers. In this study, material characterization techniques including chemical shrinkage, ultrasonic pulse velocity (UPV), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and nitrogen adsorption (NAD) were used to study the hydration and microstructure of contaminated cement. Results showed that the studied microemulsion spacer was less compatible with the cement slurry than the conventional one. The microemulsion spacer has complex effects on cement hydration: it slightly enhances hydration for the low dosage but can retard hydration at the early ages and accelerate hydration in the later ages with the increase of dosage. The conventional spacer caused early acceleration of cement hydration but had no effect at later ages. The presence of spacers in the cement slurry decreases the compressive strength and creates a more complex microstructure than is found for the neat cement. All these effects with the studied microemulsion spacer are worse than with the conventional spacer. Therefore, the presence of a microemulsion spacer in a cement slurry may cause long-term durability issues compromising the downhole zonal isolation.

Status: published work in SPE Journal 2020, **25**, 3002

Ultrastable Glassy Polymer Films with an Ultradense Brush Morphology

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Glassy polymer films with extreme stability could enable major advancements in a range of fields that require the use of polymers in confined environments. Yet, from a materials design perspective, we now know that the glass transition temperature (T_g) and thermal expansion of polymer thin films can be dramatically different from those characteristics of the bulk, i.e., exhibiting confinement-induced diminished thermal stability. Here, we demonstrate that polymer brushes with an ultrahigh grafting density, i.e., an ultradense brush morphology, exhibit a significant enhancement in thermal stability, as manifested by an exceptionally high T_g and low expansivity. For instance, a 5 nm thick polystyrene brush film exhibits an ~ 75 K increase in T_g and $\sim 90\%$ reduction in expansivity compared to a spin-cast film of similar thickness. Our results establish how morphology can overcome confinement and interfacial effects in controlling thin-film material properties and how this can be achieved by the dense packing and molecular ordering in the amorphous state of ultradense brushes prepared by surface-initiated atom transfer radical polymerization in combination with a self-assembled monolayer of initiators.

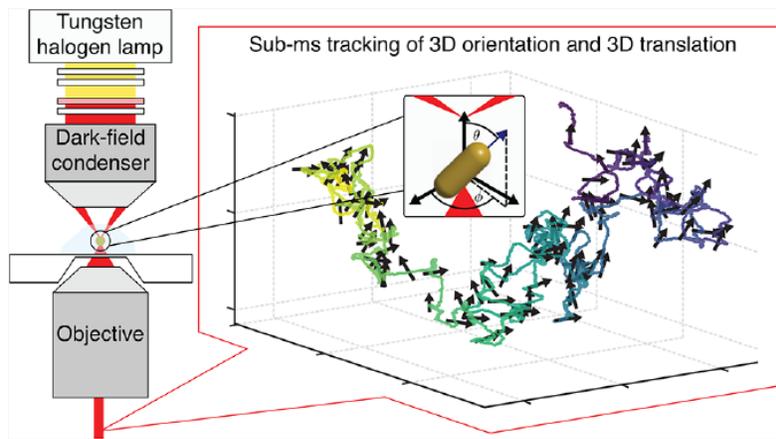
Status: published work in ACS Nano 2021, **15**, 9568

Department of Chemistry

Sub-millisecond Translational and Orientational Dynamics of a Freely Moving Single Nanoprobe

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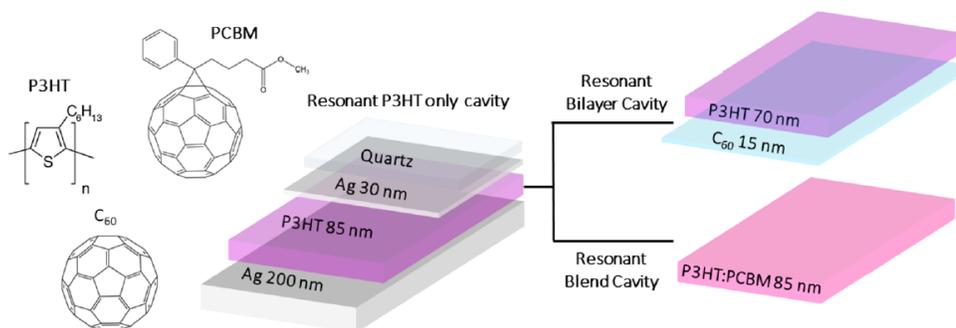
This paper presents a new experiment with which we are able to measure the 3D translational motion of a single particle at $10 \mu\text{s}$ time resolution and with $\sim 10 \text{ nm}$ spatial resolution while at the same time determining the 3D orientation of the same single particle with $250 \mu\text{s}$ time resolution. These high time resolutions are ~ 40 times greater than previous simultaneous measurements of 3D position and 3D orientation. Detailed numerical simulations and experiments are used to demonstrate that the technique can measure 3D orientation at the shot-noise limit. The microscope is also able to simultaneously measure the length or width (with the other assumed) of the plasmonic nanorods used here in situ and nondestructively, which should yield a greater understanding of the underlying dynamics. This technique should be applicable to a broad range of problems where environments which change in space and time may perturb physical and chemical dynamics.

Status: published work at *J. Phys. Chem. B* 2021, **125**, 13436

Polariton Decay in Donor–Acceptor Cavity Systems

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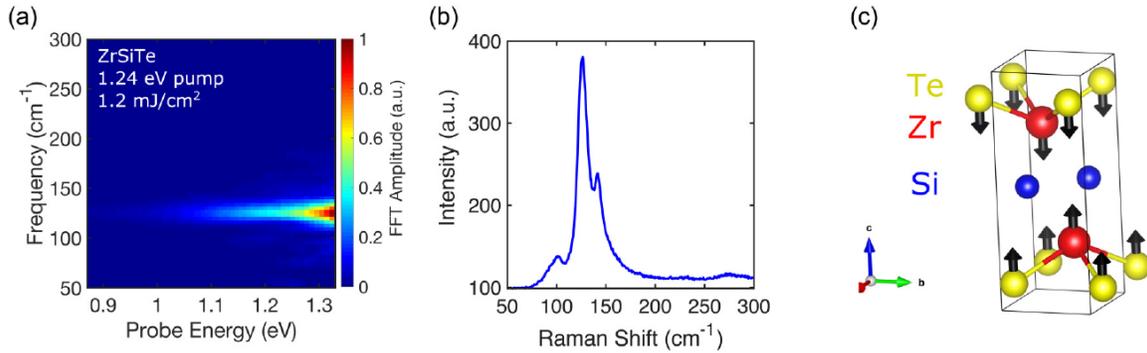
Enhanced delocalization is beneficial for absorbing molecules in organic solar cells, and in particular bilayer devices, where excitons face small diffusion lengths as a barrier to reaching the charge-generating donor – acceptor interface. As hybrid light – matter states, polaritons offer exceptional delocalization which could be used to improve the efficiency of bilayer organic photovoltaics. Polariton delocalization can aid in delivering excitons to the donor – acceptor interface, but the subsequent charge transfer event must compete with the fast decay of the polariton. To evaluate the viability of polaritons as tools to improve bilayer organic solar cells, we studied the decay of the lower polariton in three cavity systems: a donor only, a donor–acceptor bilayer, and a donor–acceptor blend. Using several spectroscopic techniques, we identified an additional decay pathway through charge transfer for the polariton in the bilayer cavity, demonstrating charge transfer from the polariton is fast enough to outcompete the decay to the ground state.

Status: published work at J. Phys. Chem. Lett. 2021, **12**, 9774

Signature of an ultrafast photoinduced Lifshitz transition in the nodal-line semimetal ZrSiTe

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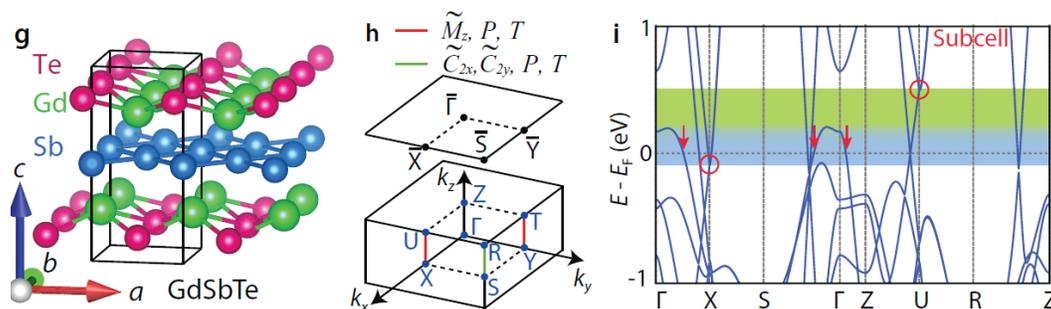


Here we report an ultrafast optical spectroscopic study of the nodal-line semimetal ZrSiTe. Our measurements reveal that, converse to other compounds of the family, the sudden injection of electronic excitations results in a strongly coherent response of an A_{1g} phonon mode that dynamically modifies the distance between Zr and Te atoms and Si layers. “Frozen phonon” density functional theory calculations, in which band structures are calculated as a function of nuclear position along the phonon mode coordinate, show that large displacements along this mode alter the material’s electronic structure significantly, forcing bands to approach and even cross the Fermi energy. The incoherent part of the time-domain response reveals that a delayed electronic response at low fluence discontinuously evolves into an instantaneous one for excitation densities larger than $3.43 \times 10^{17} \text{ cm}^{-3}$. This sudden change of the dissipative channels for electronic excitations is indicative of an ultrafast Lifshitz transition, which we tentatively associate with a change in topology of the Fermi surface driven by a symmetry-preserving A_{1g} phonon mode.

Status: published work at Phys. Rev. B 2021, **103**, 205138

Band Engineering of Dirac Semimetals Using Charge Density Waves

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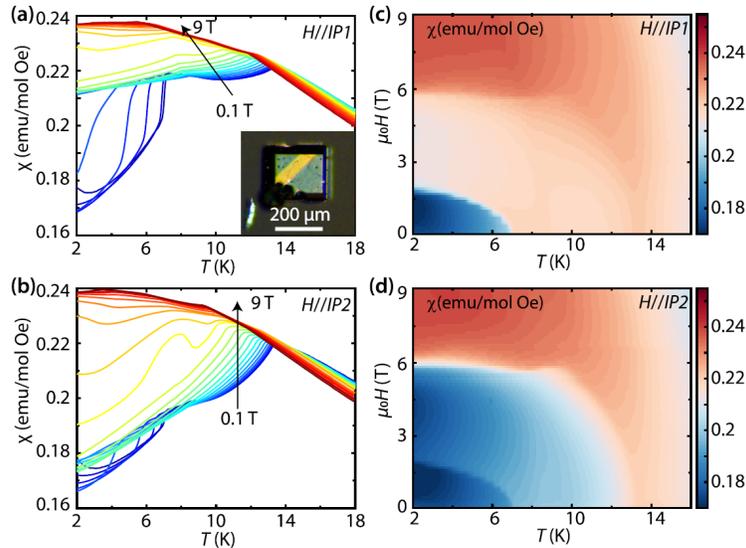
New developments in the field of topological matter are often driven by materials discovery, including novel topological insulators, Dirac semimetals, and Weyl semimetals. Large efforts have been made to classify all known inorganic materials with respect to their topology. A large number of topological materials suffer from non-ideal band structures. Topological bands are frequently convoluted with trivial ones, and band structure features of interest can appear far below the Fermi level. This leaves just a handful of materials that are intensively studied. Finding strategies to design new topological materials is a solution. Here, a new mechanism is introduced, which is based on charge density waves and non-symmorphic symmetry, to design an idealized Dirac semimetal. It is then shown experimentally that the antiferromagnetic compound $\text{GdSb}_{0.46}\text{Te}_{1.48}$ is a nearly ideal Dirac semimetal based on the proposed mechanism, meaning that most interfering bands at the Fermi level are suppressed. Its highly unusual transport behavior points to a thus far unknown regime, in which Dirac carriers with Fermi energy very close to the node seem to gradually localize in the presence of lattice and magnetic disorder.

Status: published work at *Advanced Materials* 2021, **33**, 2101591

Complex magnetic phases enriched by charge density waves in the topological semimetals $\text{GdSb}_x\text{Te}_{2-x-\delta}$

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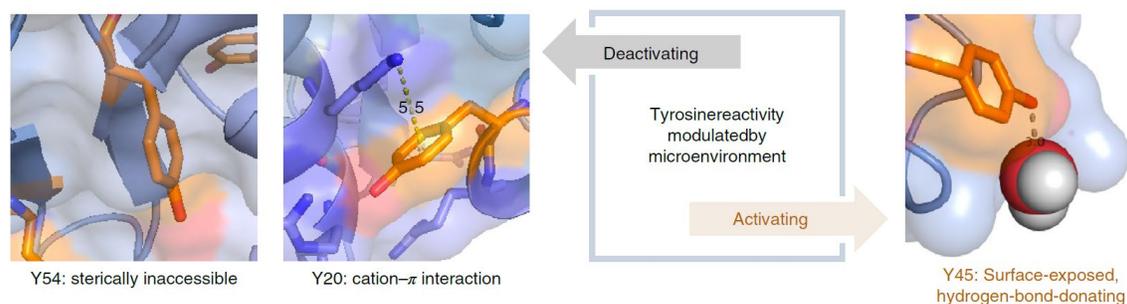
The interplay of crystal symmetry, magnetism, band topology, and electronic correlation can be the origin of quantum phase transitions in condensed matter. Particularly, square-lattice materials have been serving as a versatile platform to study the rich phenomena resulting from that interplay. In this work we report a detailed magnetic study on the square-lattice-based magnetic topological semimetal $\text{GdSb}_x\text{Te}_{2-x-\delta}$. We report the H - T magnetic phase diagrams along three crystallographic orientations and show that, for those materials where a charge density wave distortion is known to exist, many different magnetic phases are identified. In addition, the data hints towards the existence of an antiferromagnetic skyrmion phase, which has been theoretically predicted but not experimentally confirmed in a bulk material yet.

Status: published work at Phys Rev B 2021, **103**, 134418

Site-selective tyrosine bioconjugation via photoredox catalysis for native-to-bioorthogonal protein transformation

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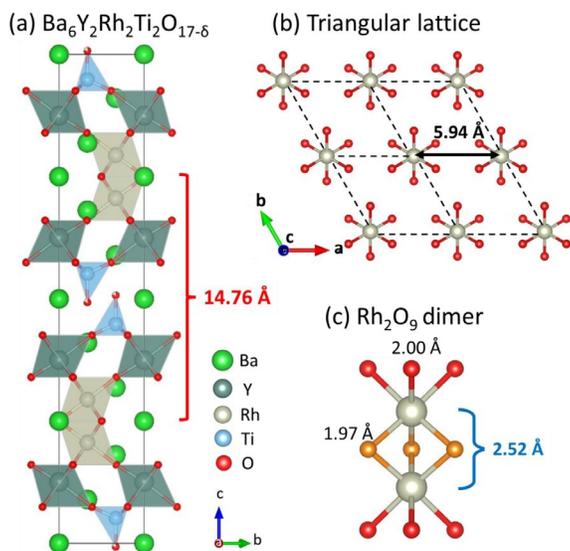
The growing prevalence of synthetically modified proteins in pharmaceuticals and materials has exposed the need for efficient strategies to enable chemical modifications with high site-selectivity. While genetic engineering can incorporate non-natural amino acids into recombinant proteins, regioselective chemical modification of wild-type proteins remains a challenge. Herein, we use photoredox catalysis to develop a site-selective tyrosine bioconjugation pathway that incorporates bioorthogonal formyl groups, which subsequently allows for the synthesis of structurally defined fluorescent conjugates from native proteins. A water-soluble photocatalyst, lumiflavin, has been shown to induce oxidative coupling between a previously unreported phenoxazine dialdehyde tag and a single tyrosine site, even in the presence of multiple tyrosyl side chains, through the formation of a covalent C–N bond. A variety of native proteins, including those with multiple tyrosines, can successfully undergo both tyrosine-specific and single-site-selective labelling. This technology directly introduces aldehyde moieties onto native proteins, enabling rapid product diversification using an array of well-established bioorthogonal functionalization protocols including the alkyne–azide click reaction.

Status: published work at Nature Chemistry 2021, **13**, 902

Widely Spaced Planes of Magnetic Dimers in the $\text{Ba}_6\text{Y}_2\text{Rh}_2\text{Ti}_2\text{O}_{17-8}$ Hexagonal Perovskite

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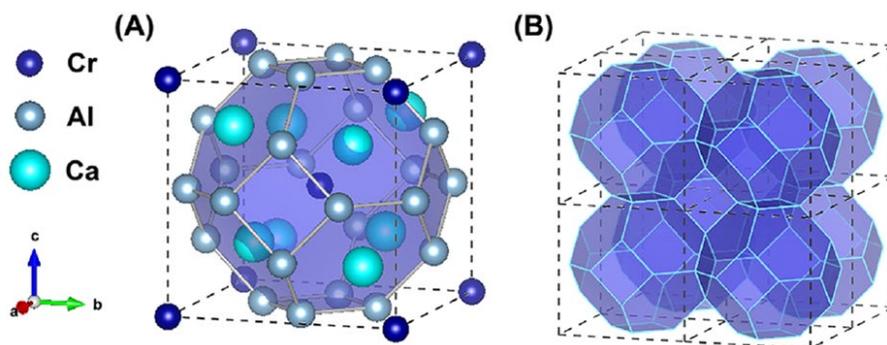
We report the synthesis and initial characterization of $\text{Ba}_6\text{Y}_2\text{Rh}_2\text{Ti}_2\text{O}_{17-8}$, a previously unreported material with a hexagonal symmetry structure. Face-sharing RhO_6 octahedra form triangular planes of Rh_2O_9 dimers that are widely separated in the perpendicular direction. The material displays a small effective magnetic moment, due to the Rh ions present, and a negative Curie-Weiss temperature. The charge transport and optical band gaps are very similar, near 0.16 eV. A large upturn in the heat capacity at temperatures below 1 K, suppressed by applied magnetic fields larger than $\mu_0 H = 2$ Tesla, is observed. A large T-linear term in the specific heat ($\gamma=166$ mJ/mol f.u. K^2) is seen, although the material is insulating at low temperatures. These results suggest the possibility of a spin liquid ground state in this material.

Status: published work in Physical Review Materials 2021, **5**, 034419

Magnetic Frustration in a Zeolite

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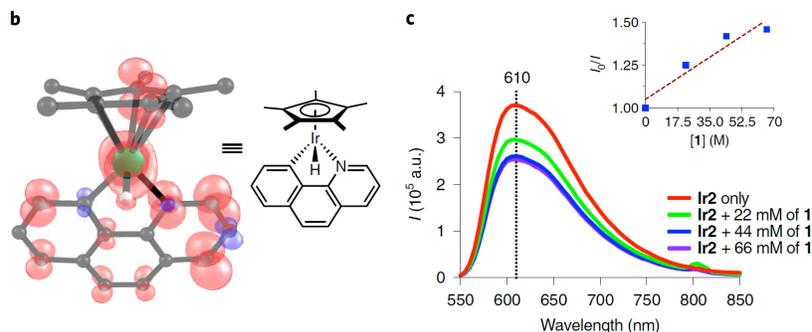
Zeolites are so well known in real-world applications and after decades of scientific study that they hardly need any introduction: their importance in chemistry cannot be overemphasized. Here, we add to the remarkable properties that they display by reporting our discovery that the simplest zeolite, sodalite, when doped with Cr^{3+} in the β -cage, is a frustrated magnet. Soft X-ray absorption spectroscopy and magnetic measurements reveal that the Cr present is Cr(III). Cr(III), with its isotropic $3d^3$ valence electron configuration, is well known as the basis for many geometrically frustrated magnets, but it is especially surprising that a material like the $\text{Ca}_8\text{Al}_{12}\text{Cr}_2\text{O}_{29}$ zeolite is a frustrated magnet. This finding illustrates the value of exploring the properties of even well-known material families.

Status: published work in Chemistry of Materials 2021, **33**, 9725

Visible light enables catalytic formation of weak chemical bonds with molecular hydrogen

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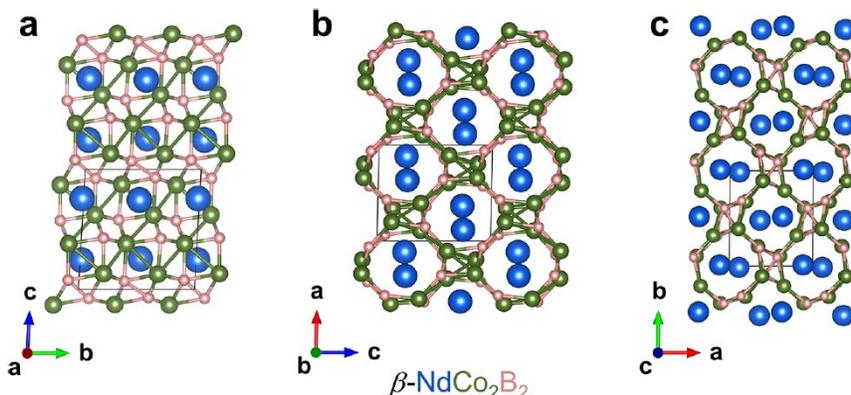


The synthesis of weak chemical bonds at or near thermodynamic potential is a fundamental challenge in chemistry, with applications ranging from catalysis to biology to energy science. Proton-coupled electron transfer using molecular hydrogen is an attractive strategy for synthesizing weak element–hydrogen bonds, but the intrinsic thermodynamics presents a challenge for reactivity. Here we describe the direct photocatalytic synthesis of extremely weak element–hydrogen bonds of metal amido and metal imido complexes, as well as organic compounds with bond dissociation free energies as low as 31 kcal mol⁻¹. Key to this approach is the bifunctional behaviour of the chromophoric iridium hydride photocatalyst. Activation of molecular hydrogen occurs in the ground state and the resulting iridium hydride harvests visible light to enable spontaneous formation of weak chemical bonds near thermodynamic potential with no by-products. Photophysical and mechanistic studies corroborate radical-based reaction pathways and highlight the uniqueness of this photodriven approach in promoting new catalytic chemistry.

Status: published work in Nature Chemistry 2021, **13**, 969

Metastable β -NdCo₂B₂: A Triclinic Polymorph with Magnetic Ordering

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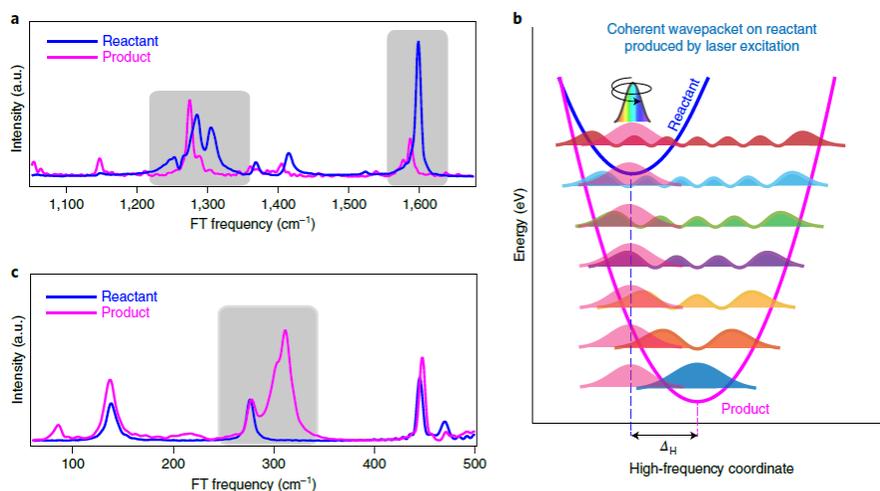
Metastable phases increase the diversity of structure–property relationships, facilitating the study and comparison of materials. In this article, we present the synthesis and characterization of a metastable polymorph of NdCo₂B₂, synthesized by arc melting, which we designate as β -NdCo₂B₂. Single-crystal X-ray diffraction reveals that it crystallizes in a new triclinic structure type with space group $P\bar{1}(\#2)$. The structure is composed of 3D Co–B channels filled by Nd zigzags, a large departure from the thermodynamically stable tetragonal ThCr₂Si₂-type polymorph. β -NdCo₂B₂ is closely related to the BaRh₂Si₂ structure type, providing a connection to the “122-type” channel-containing RM₂B₂ compounds (R = rare-earth element, M = Ni, Ru, Os, and Ir) that was previously absent for rare-earth cobalt borides of this stoichiometry. Differential scanning calorimetry shows that this new polymorph transforms irreversibly into the tetragonal form upon heating above 530 °C. β -NdCo₂B₂ displays metallic conductivity and magnetically orders into a complex ferromagnetic or ferrimagnetic state at 7.7 K. We present density functional theory calculations throughout to further explore the stability, magnetism, and electronic structure. β -NdCo₂B₂ demonstrates that new compounds with interesting structural and magnetic properties can be found even in well-studied chemical systems, such as the ternary transition metal borides.

Status: published work in *Chemistry of Materials* 2021, **33**, 6374

Interplay of vibrational wavepackets during an ultrafast electron transfer reaction

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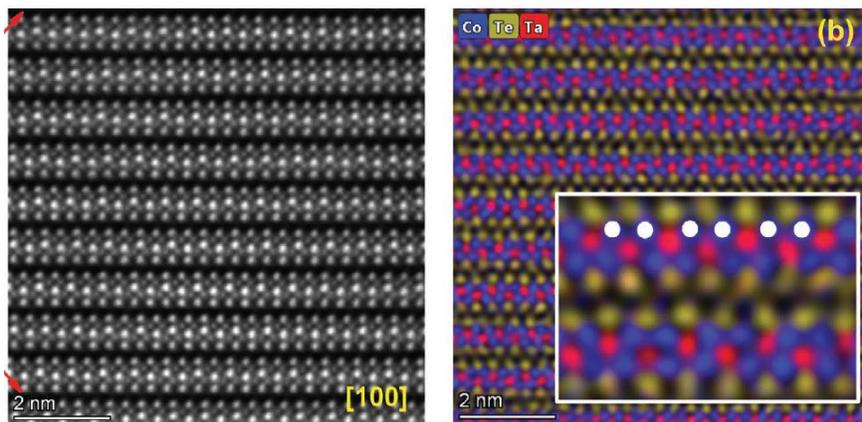
Electron transfer reactions facilitate energy transduction and photoredox processes in biology and chemistry. Recent findings show that molecular vibrations can enable the dramatic acceleration of some electron transfer reactions, and control it by suppressing and enhancing reaction paths. Here, we report ultrafast spectroscopy experiments and quantum dynamics simulations that resolve how quantum vibrations participate in an electron transfer reaction. We observe ballistic electron transfer (~ 30 fs) along a reaction coordinate comprising high-frequency promoting vibrations. Along another vibrational coordinate, the system becomes impulsively out of equilibrium as a result of the electron transfer reaction. This leads to the generation (by the electron transfer reaction, not the laser pulse) of a new vibrational coherence along this second reaction coordinate in a mode associated with the reaction product. These results resolve a complex reaction trajectory composed of multiple vibrational coordinates that, like a sequence of ratchets, progressively diminish the recurrence of the reactant state.

Status: published work at Nature Chemistry 2021, **13**, 70

TaCo₂Te₂: An Air-Stable, High Mobility Van der Waals Material with Probable Magnetic Order

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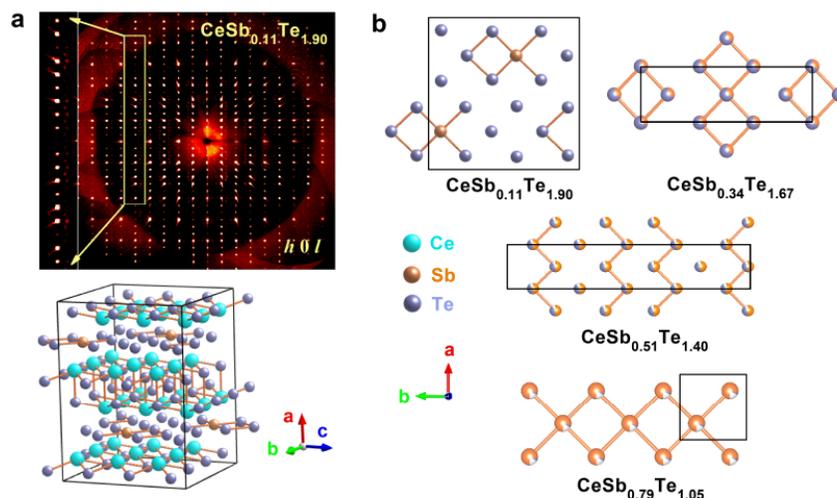
Van der Waals (vdW) materials are an indispensable part of functional device technology due to their versatile physical properties and ease of exfoliating to the low-dimensional limit. Among all the compounds investigated so far, the search for magnetic vdW materials has intensified in recent years, fueled by the realization of magnetism in 2D. However, metallic magnetic vdW systems are still uncommon. In addition, they rarely host high-mobility charge carriers, which is an essential requirement for high-speed electronic applications. Another shortcoming of 2D magnets is that they are highly air sensitive. Using chemical reasoning, TaCo₂Te₂ is introduced as an air-stable, high-mobility, magnetic vdW material. It has a layered structure, which consists of Peierls distorted Co chains and a large vdW gap between the layers. It is found that the bulk crystals can be easily exfoliated and the obtained thin flakes are robust to ambient conditions after 4 months of monitoring using an optical microscope. Signatures of canted antiferromagnetic behavior are also observed at low-temperature. TaCo₂Te₂ shows a metallic character and a large, nonsaturating, anisotropic magnetoresistance. Furthermore, the Hall data and quantum oscillation measurements reveal the presence of both electron- and hole-type carriers and their high mobility.

Status: published work at *Advanced Functional Materials* 2021, 2108920

Evolving Devil's staircase magnetization from tunable charge density waves in nonsymmorphic Dirac semimetals

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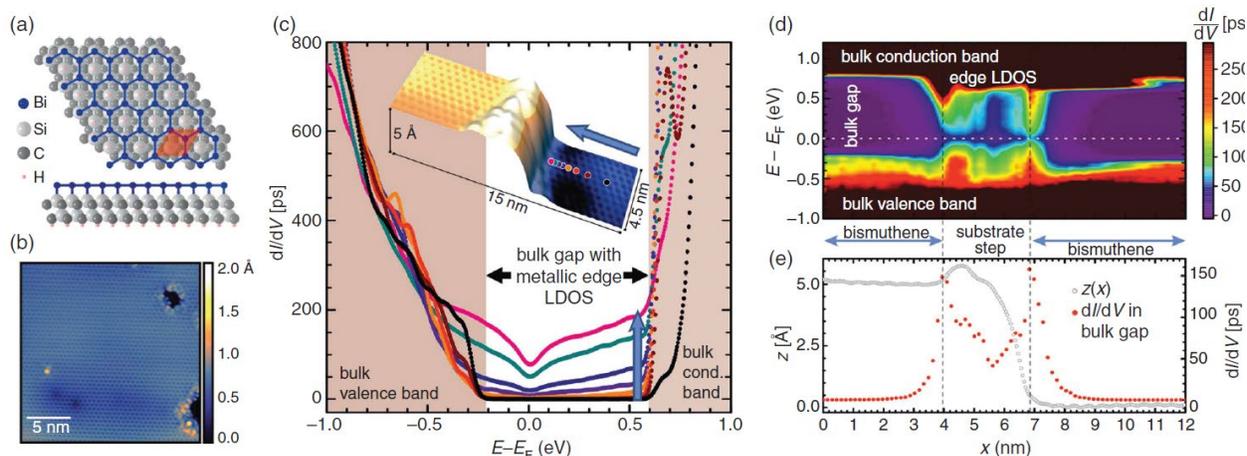
While several magnetic topological semimetals have been discovered in recent years, their band structures are far from ideal, often obscured by trivial bands at the Fermi energy. Square-net materials with clean, linearly dispersing bands show potential to circumvent this issue. CeSbTe, a square-net material, features multiple magnetic field-controllable topological phases. Here, it is shown that in this material, even higher degrees of tunability can be achieved by changing the electron count at the square-net motif. Increased electron filling results in structural distortion and formation of charge density waves (CDWs). The modulation wave-vector evolves continuously leading to a region of multiple discrete CDWs and a corresponding complex “Devil's staircase” magnetic ground state. A series of fractionally quantized magnetization plateaus are observed, which implies direct coupling between CDW and a collective spin-excitation. It is further shown that the CDW creates a robust idealized non-symmorphic Dirac semimetal, thus providing access to topological systems with rich magnetism.

Status: published work at *Advanced Materials* 2021, **33**, 2103476

The properties and prospects of chemically exfoliated nanosheets for quantum materials in two dimensions

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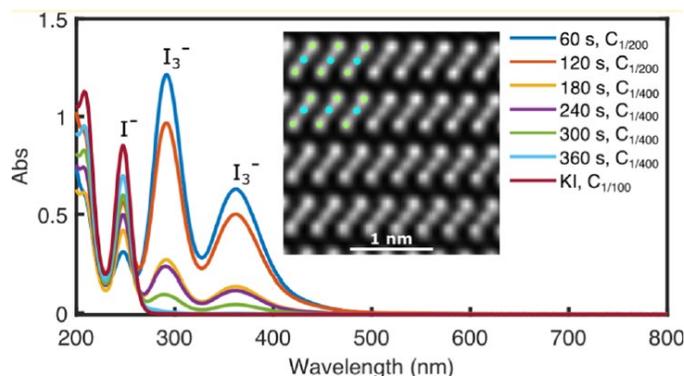
The aim of this review is to elucidate the potential of chemically exfoliated sheets for the field of quantum matter. Quantum materials are loosely defined as materials that do not follow the laws of classical physics; the family commonly includes complex magnets, topological materials, or superconductors. Two-dimensional (2D) materials have been key in driving the field of quantum matter forward due to the high degree of tunability they offer. However, progress has largely been made with mechanically exfoliated sheets while chemically exfoliated sheets have been mostly ignored. The latter offer a wide range of advantages, for example, chemical exfoliation gives access to 2D materials that are unobtainable with other methods. In this review, we highlight the progress that has been made in exploring properties that can be associated with quantum materials of chemically exfoliated nanosheets. We will cover magnetic chemically exfoliated sheets, their use in transistors, their potential as 2D topological insulators, and opportunities that arise for the emerging field of *twistronics*. We will highlight both the advantages and current shortcomings of chemically exfoliated quantum materials and address how shortcomings might be overcome in the future. We conclude that while the prospects of chemically exfoliated sheets for quantum materials are still underexplored, they offer a large potential for having an impact in that field.

Status: published work at Appl. Phys. Rev. 2021, **8**, 011312

Kinetics and Evolution of Magnetism in Soft-Chemical Synthesis of CrSe₂ from KCrSe₂

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Cation deintercalation with soft-chemical methods provides a route to synthesize new layered compounds with emergent physical and chemical properties. One example is CrSe₂, a van der Waals (vdW) material that is promising as an air-stable two-dimensional (2D) magnet. Cation deintercalation has rarely been studied mechanistically, and optimized reaction pathways to yield high-quality materials are often poorly understood. In this work, we perform a detailed study of the oxidative deintercalation process of KCrSe₂. We prove for the first time using high-resolution scanning transmission electron microscopy (STEM) that even though CrSe₂ indeed exists in a true vdW layered structure, K-intercalated crystalline defects exist in the final product. We then study the kinetics of the oxidative deintercalation process, showing that it is a zeroth-order reaction with an activation energy of 0.27(6) eV, where the solid-state diffusion of K⁺ cations in the potassium deintercalation process is the rate-limiting step. Finally, we study the relationship between Cr–Cr distances and the change in magnetic order by tracking how the properties change as a function of varying potassium content due to deintercalation. These data suggest that it might be possible to switch between magnetic states in CrSe₂ monolayers by varying its lattice parameters with methods, such as applying strain. Our study also provides a deeper understanding of the cation deintercalation process from a mechanistic perspective that will be helpful for the future development of synthetic methodology that can lead to other new layered materials.

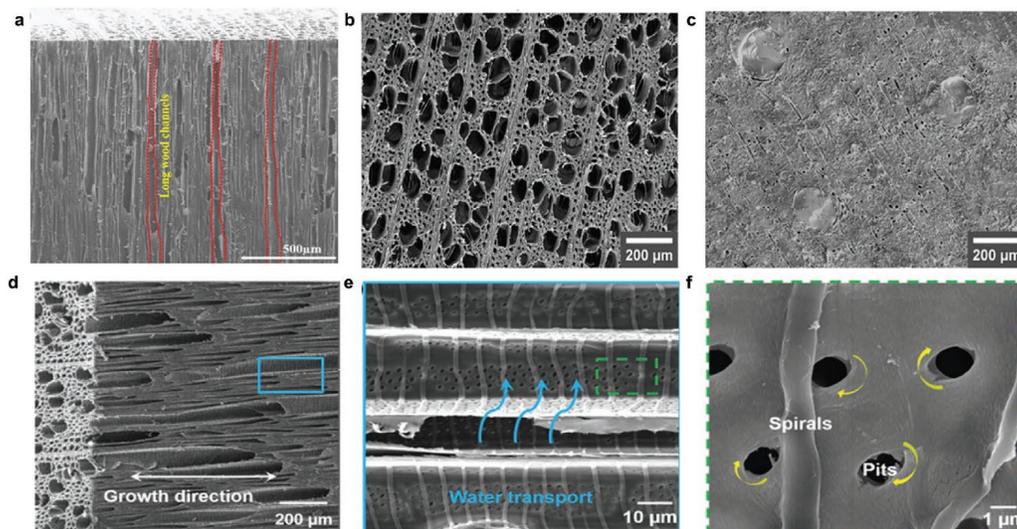
Status: published work at Chem. Mater. 2021, **33**, 8070

Department of Civil and Environmental Engineering

Advanced Nanowood Materials for the Water–Energy Nexus

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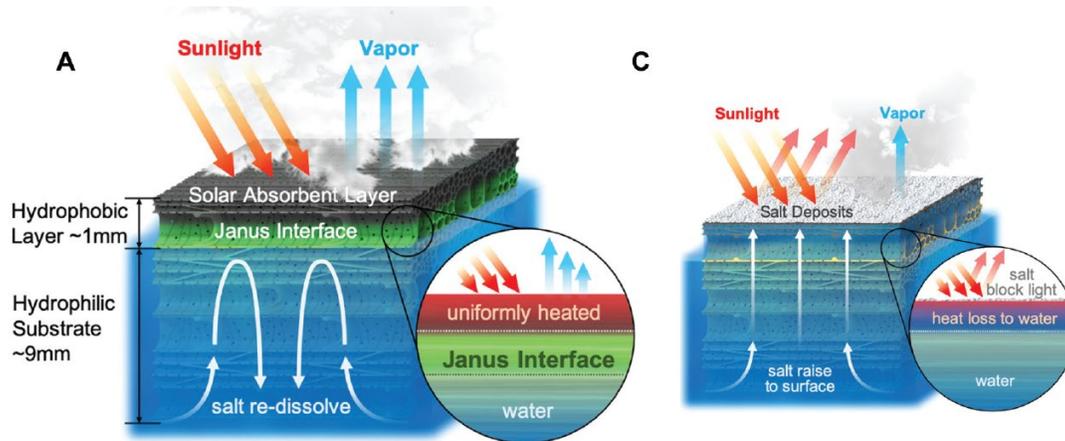
Wood materials are being reinvented to carry superior properties for a variety of new applications. Cutting-edge nanomanufacturing transforms traditional bulky and low-value woods into advanced materials that have desired structures, durability, and functions to replace nonrenewable plastics, polymers, and metals. Here, a first prospect report on how novel nanowood materials have been developed and applied in water and associated industries is provided, wherein their unique features and promises are discussed. First, the unique hierarchical structure and associated properties of the material are introduced, and then how such features can be harnessed and modified by either bottom-up or top-down manufacturing to enable different functions for water filtration, chemical adsorption and catalysis, energy and resource recovery, as well as energy-efficient desalination and environmental cleanup are discussed. The study recognizes that this is a nascent but very promising field; therefore, insights are offered to encourage more research and development. Trees harness solar energy and CO₂ and provide abundant carbon-negative materials. Once harvested and utilized, it is believed that advanced wood materials will play a vital role in enabling a circular water economy.

Status: published work at *Advanced Materials* 2021, **33**, 2001240

Sustainable off-grid desalination of hypersaline waters using Janus wood evaporators

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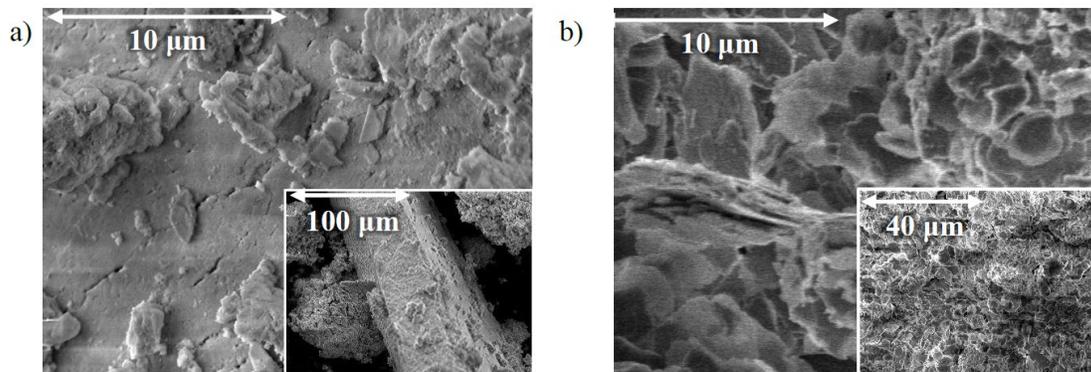
Solar-thermal evaporation is a promising technology for energy-efficient desalination, but salt accumulation on solar absorbers and system longevity are the major challenges that hinder its widespread application. In this study, we present a sustainable Janus wood evaporator that overcomes these challenges and achieves a record-high evaporation efficiencies in hypersaline water, one of the most difficult water sources to treat via desalination. The Janus wood evaporator has asymmetric surface wettability, where the top layer acts as a hydrophobic solar absorber with water blockage and salt resistance, while the bottom hydrophilic wood layer allows for rapid water replenishment and superior thermal insulation. An evaporation efficiency of 82.0% is achieved for 20% NaCl solution under 1 sun, and persistent salt-resistance is observed during a 10-cycle long-term test. To ensure the environmental impact of the Janus wood evaporator, for the first time, a life cycle assessment (LCA) is conducted to compare this Janus wood evaporator with the emerging Janus evaporators, indicating a functional and more sustainable opportunity for off-grid desalination and humanitarian efforts.

Status: published work at Energy Environ. Sci 2021, 14, 5347

Synthesis and characterization of Ca-based layered double hydroxides as solid sorbents for carbon capture

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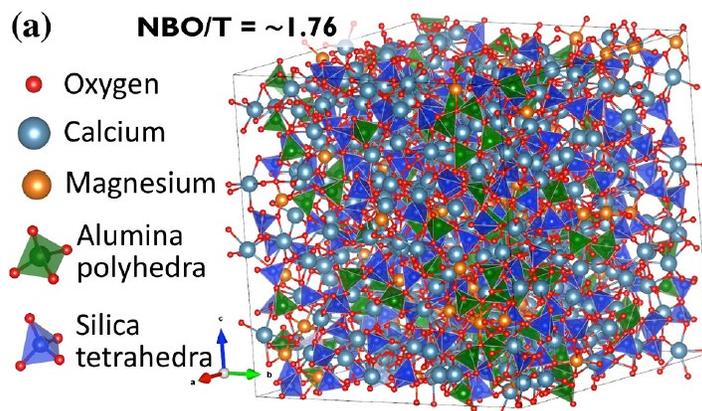
The development of new sorbents for carbon capture that are (i) widely available, (ii) low cost, and (iii) require less energy for rejuvenation compared with current sorbent technologies is an area of significant interest to industries with point-source CO₂ emissions and those pursuing direct air capture (DAC). Here, we synthesized high purity Ca-based layered double hydroxides (LDHs) and performed a preliminary evaluation of their low-temperature carbon capture potential at high relative humidity (85 %). In particular, CaFe- and CaAl-LDHs with chloride as the interlayer anion were obtained through addition of a trivalent cation (Fe³⁺ or Al³⁺) to a Ca(OH)₂ suspension in an inert environment. Characterization of the reaction products was carried out using scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, where preliminary results showed successful synthesis of high-purity Ca-based LDHs. The synthesized samples were carbonated at 30 °C for 1 hr in a controlled environment with 85 % RH and 1 % CO₂. The carbonated samples were characterized using XRD and ATR-FTIR analysis, and subsequently subjected to thermal decomposition via TGA where the evolved gases were studied concurrently using FTIR analysis. Our results show that the chemical tailoring of Ca(OH)₂ may not only reduce its regeneration energy but also lead to an improved adsorption capacity.

Status: published work at Proceedings of GHGT-15, 2021

Predicting CaO-(MgO)-Al₂O₃-SiO₂ glass reactivity in alkaline environments from force field molecular dynamics simulations

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In this investigation, force field-based molecular dynamics (MD) simulations have been employed to generate detailed structural representations for a range of amorphous quaternary CaO-MgO-Al₂O₃-SiO₂ (CMAS) and ternary CaO-Al₂O₃-SiO₂ (CAS) glasses. Comparison of the simulation results with select experimental X-ray and neutron total scattering and literature data reveals that the MD-generated structures have captured the key structural features of these CMAS and CAS glasses. Based on the MD-generated structural representations, we have developed two structural descriptors, specifically (i) average metal oxide dissociation energy (AMODE) and (ii) average self-diffusion coefficient (ASDC) of all the atoms at melting. Both structural descriptors are seen to more accurately predict the relative glass reactivity than the commonly used degree of depolymerization parameter, especially for the eight synthetic CAS glasses that span a wide compositional range. Hence these descriptors hold great promise for predicting CMAS and CAS glass reactivity in alkaline environments from compositional information.

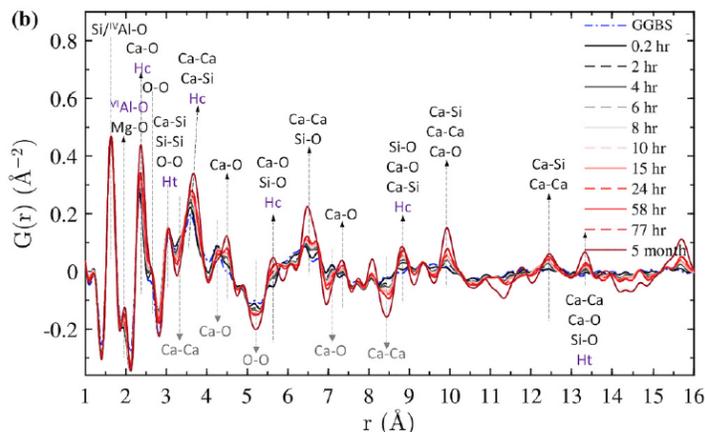
Status: published work at Cement and Concrete Research 2021, **150**, 106588

Time-dependent phase quantification and local structure analysis of hydroxide-activated slag via X-ray total scattering and molecular modeling

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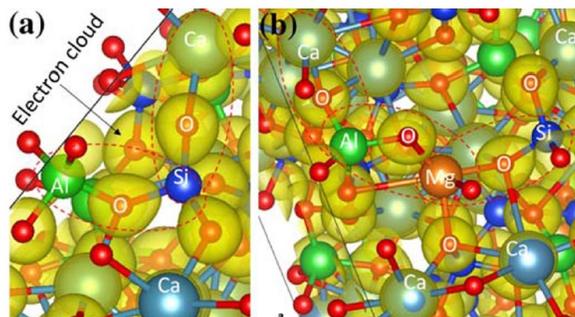
Here, an approach to quantify the amorphous-to-disordered/crystalline transformation occurring in NaOH-activated ground granulated blast-furnace slag (GGBS) is outlined that combines atomistic modeling with in situ pair distribution function (PDF) analysis. Firstly, by using force-field molecular dynamics (MD) simulations, a detailed structural representation is generated for the amorphous GGBS that is in agreement with experimental X-ray scattering data. Use of this structural representation along with literature-derived structures for the reaction products allows for real space X-ray PDF refinement of the alkaline activation of GGBS, resulting in the quantification of all phases and the degree of reaction (DOR) as a function of reaction time. All phases and the DOR are seen to approximately follow a logarithmic-type time-dependent behavior up to 5 months, while at the early age (up to 11 h), the DOR is accurately captured by a modified pseudo-single step first-order reaction model. Lastly, the evolution of DOR is found to agree with several other complementary in situ data containing quantitative reaction information, including isothermal conduction calorimetry, Fourier transform infrared spectroscopy, and quasi-elastic neutron scattering.

Status: published work at Cement and Concrete Research 2022, **151**, 106642

Density functional modeling and total scattering analysis of the atomic structure of a quaternary CaO-MgO-Al₂O₃-SiO₂ (CMAS) glass: Uncovering the local environment of calcium and magnesium

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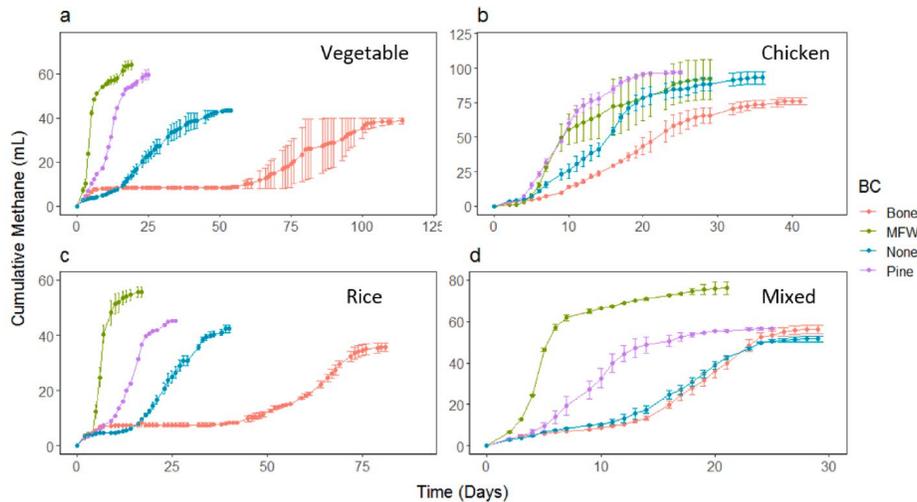
Quaternary CaO-MgO-Al₂O₃-SiO₂ (CMAS) glasses are important constituents of the Earth's lower crust and mantle, and they also have important industrial applications such as in metallurgical processes, concrete production, and emerging low-CO₂ cement technologies. In particular, these applications rely heavily on the composition-structure-reactivity relationships for CMAS glasses, which are not yet well established. In this study, we combined force-field molecular dynamics (MD) simulations and density functional theory (DFT) calculations to generate detailed structural representations for a CMAS glass. The generated structures are not only thermodynamically favorable but also agree with experiments. Detailed analysis of the final structure enabled existing discrepancies in the literature to be reconciled and has revealed important structural information on the CMAS glass, specifically (i) the unambiguous assignment of medium-range atomic ordering, (ii) the preferential role of Ca atoms as charge compensators and Mg atoms as network modifiers, (iii) the proximity of Mg atoms to free oxygen sites, and (iv) clustering of Mg atoms. Electronic property calculations suggest higher reactivity for Ca atoms as compared with Mg atoms, and that the reactivity of oxygen atoms varies considerably depending on their local bonding environment. Overall, this information may enhance our mechanistic understanding on CMAS glass dissolution behavior in the future, including dissolution-related mechanisms occurring during the formation of low-CO₂ cements.

Status: published work at Physical Review Materials 2021, **5**, 015603

Circular utilization of food waste to biochar enhances thermophilic codigestion performance

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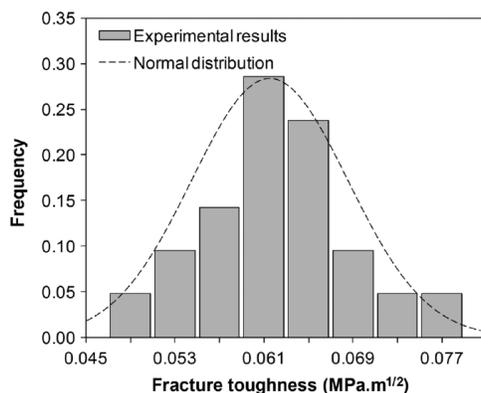
Codigestion is an emerging approach to improve wastewater sludge biogas production and valorize food waste (FW). This study explores FW-derived biochar as a codigestion amendment for the first time and reports a matrix experiment using four diverse biochar amendments (mixed food waste, pinewood, bonechar, unamended control) across four FW types (vegetable, rice, chicken, mixed). It demonstrated that biochar derived from mixed FW can greatly improve the performance of biogas production and yield relative to unamended control and other biochars. The mixed food waste (MFW) biochar amendment led to 34.5%, 35.6%, and 47.5% increase in methane production from mixed FW compared to biochars made of wood, bone and non-amendment control, and the maximum methane production rate of MFW biochar reactors could be up to 6.7–9.9 times of the control. These results suggest that a more circular utilization of FW by integrating biochar production with codigestion can bring great benefits to FW management.

Status: published work at *Bioresource Technology* 2021, **332**, 125130

Assessment of Ceramic Water Filters for the Removal of Bacterial, Chemical, and Viral Contaminants

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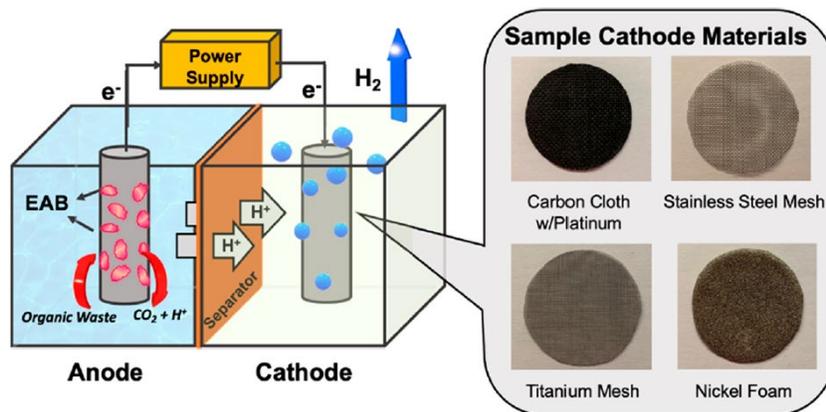
In this study, a comprehensive assessment of doped ceramic water filters (doping with hydroxyapatite and alumina) was conducted for potential application in household water treatment. The efficiency/reliability was assessed via statistical data analysis and normal distributions. It was found that the doped ceramic water filters had high porosity ($63.25\% \pm 0.31\%$ by volume) and a substantial flow rate ($14.76 \pm 1.43 \text{ L} \cdot \text{h}^{-1}$). The removal of bacterial contaminants [i.e., log reduction value (LRV)] was also found to be associated with the percentage of porosity. Hence, the doped filters were both efficient and reliable in removing bacterial contaminants (LRV of 4.69 ± 0.19). The removal of chemical/viral contaminants was related to the doping with hydroxyapatite and alumina. Due to kinetics, the removal of viral contaminants also depended on the flow rate of the doped ceramic water filters. This resulted in high efficiency in the removal of viral contaminants (LRV of 3.47 ± 0.35) and high reliability in the removal of chemical contaminants (LRV of 2.26 ± 0.07). The current results suggest that the doped filters are suitable materials for application in household water treatment.

Status: published work in Journal of Environmental Engineering 2020, **146**, 04020066

Cathode Material Development in the Past Decade for H₂ Production from Microbial Electrolysis Cells

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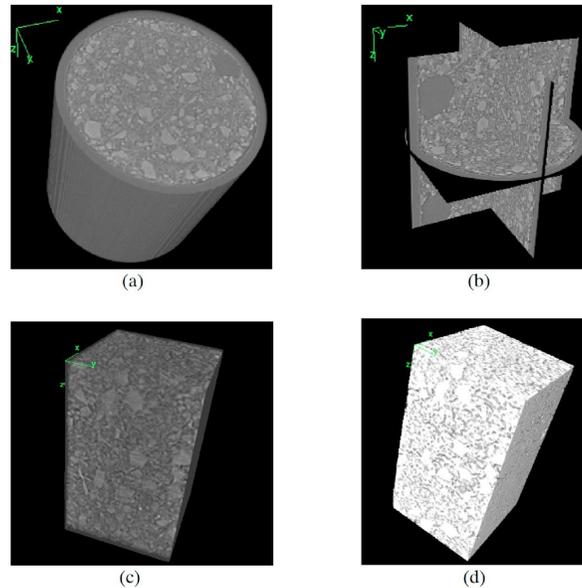
Cathode materials are critical for microbial electrolysis cell (MEC) development and its contribution to achieving a circular hydrogen economy. There are numerous reports on the progress in MEC cathode development during the past decade, but a comprehensive review on the quantitative comparisons and critical assessments of these works is lacking. This Review summarizes and analyzes the published literature on MEC cathode and catalyst development in the past decade, providing an overview of new materials examined during this time period and quantitative analyses on system performance and trends in materials development. Collected data indicate that hybrid materials have become the most popular catalyst candidate while nickel materials also attract increasing interest and exploration. However, the dilemma between higher H₂ production rate and larger MEC volume remains and still requires more investigation of novel MEC cathode catalysts and configurations to offer a solution.

Status: published work in Journal 2021, XX, XXX

Effects of magnesium content and carbonation on the multiscale pore structure of alkali-activated slags

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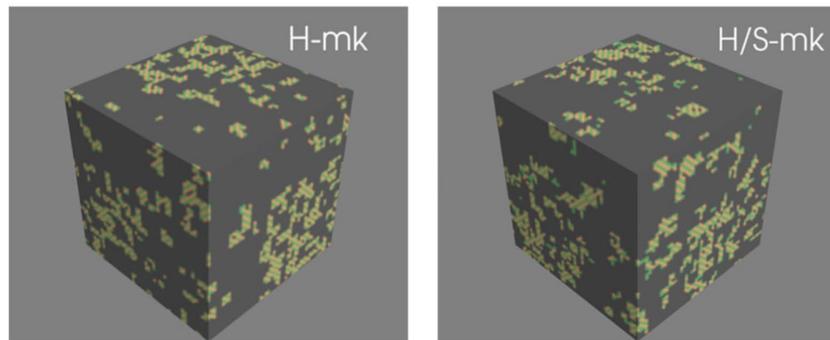
While CO₂-resistant cement materials are crucial in oil and gas industries, the CO₂ emissions associated with manufacturing oil-well cements have necessitated the development of lower-CO₂ alternatives with enhanced carbonation resistance. A higher magnesium content blast furnace slag precursor for alkali-activated slag (AAS) has been shown to increase resistance to accelerated carbonation-induced degradation. This investigation assesses the effects of sample age, AAS magnesium content, and carbonation (exposure to 100% CO₂) on the multiscale pore structure of AASs (nanometers to microns). The pore size distributions and diffusion tortuosities of ordinary Portland cement (OPC) and silicate-activated slag pastes are obtained through the techniques of nitrogen sorption, mercury intrusion porosimetry, and X-ray microtomography. These pore morphology properties show AAS to be more resistant to pore structural degradation following accelerated carbonation than OPC, and increased magnesium content in AAS is shown to improve its resistance to gel decalcification and capillary pore formation during carbonation.

Status: published work at Cement and Concrete Research 2020, **130**, 105979

Multiscale pore structure determination of cement paste via simulation and experiment: The case of alkali-activated metakaolin

Kengran Yang, Claire E. White

Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544, USA and Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544, USA.



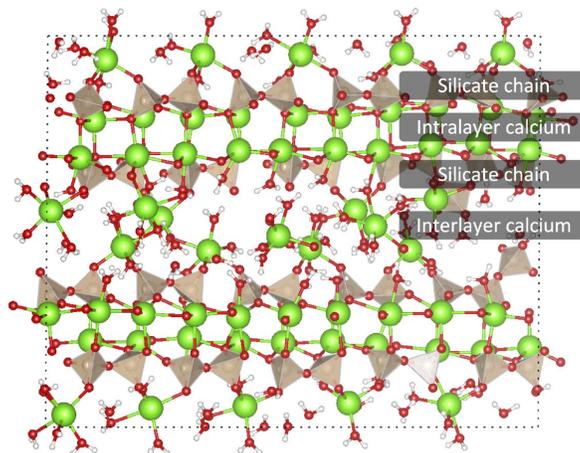
Alkali-activated metakaolin (AAMK) is a type of aluminosilicate-rich material often regarded as a potential alternative to ordinary Portland cement due to a smaller carbon footprint. However, the multiscale pore structure of AAMK, and how it is influenced by availability of free silica from the activator, remains largely unknown. Here, a Monte Carlo simulation approach is employed to generate the pore structure of AAMKs with different activator silicate moduli ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio). The simulation-derived pore size distributions are compared with experimental data obtained using nitrogen sorption (NAD) to assess the validity of the simulation results where qualitative agreement is obtained. The larger length scale pores in AAMKs are characterized using NAD and mercury intrusion porosimetry. This study stresses the importance of using complementary pore characterization techniques when investigating materials with multiscale pore structures, and shows the promise of the simulation approach to predict key transport properties of AAMKs and other cementitious materials.

Status: published work in *Cement and Concrete Research* 2020, **137**, 106212

Modeling of aqueous species interaction energies prior to nucleation in cement-based gel systems

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Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544, USA*



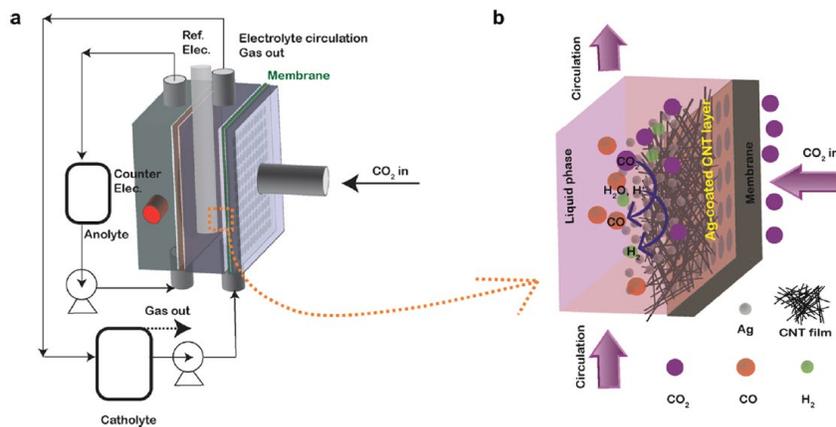
Arguably the most ubiquitous construction material in modern civilization, concrete is enabling the development of megacities around the globe together with increasing living standards in developing nations. However, the exact formation mechanisms of the strength-giving calcium-rich gels remain a topic of debate. Using density functional modeling, we simulate the fundamental solution-based building blocks of cement hydrates (calcium ions and silicate and aluminate monomers) and their propensity to form pair-wise complexes with bonding environments characteristic of those found in calcium-silicate-hydrate, calcium-alumino-silicate-hydrate and sodium-containing calcium-alumino-silicate-hydrate gels, as assessed from Gibbs free energies of chemical reactions. By accurately simulating the high pH pore solution chemistry in Portland cements and related systems, along with discrete solvation of the species, we hypothesize potential early age formation routes of the gels and discuss limitations and future work associated with this approach.

Status: published work in *Cement and Concrete Research* 2021, **139**, 106266

Electrocatalytic Membranes for Tunable Syngas Production and High-Efficiency Delivery to Biocompatible Electrolytes

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The integration of electrochemical and biological CO₂ reduction in artificial photosynthetic processes holds great promise to alleviate the current environmental stress of carbon-intensive industries and enable a circular carbon economy. The advancement of these devices hinges on the development of highly stable and selective CO₂ reduction catalysts. We fabricated a porous silver gas diffusion electrode (GDE) on the carbon nanotube (CNT)-supported hydrophobic membrane for tunable electrochemical syngas production. We then tested its performance under the direct gas delivery mode, different chamber thicknesses, and different microbial–electrolyte compositions. CO₂ was directly flowed through the GDE and electrochemically converted to syngas and delivered into the electrolyte. The optimized reactor with the narrower chamber enabled higher CO faradic efficiencies (FEs) (~92 vs ~42%) and larger tunable CO/H₂ ratios. The impact of complex microbial growth media on electrocatalysis was also investigated: systems achieved consistent >90% FE for syngas production, but nutrient ingredients such as NH₄Cl and yeast extract led to much higher H₂ production due to the significant increase in proton availability from these species. The culmination of these findings helps address key limitations at the microbial–electrode interface that aid in the development of practical artificial photosynthetic technologies toward the sustainable production of green fuels and chemicals.

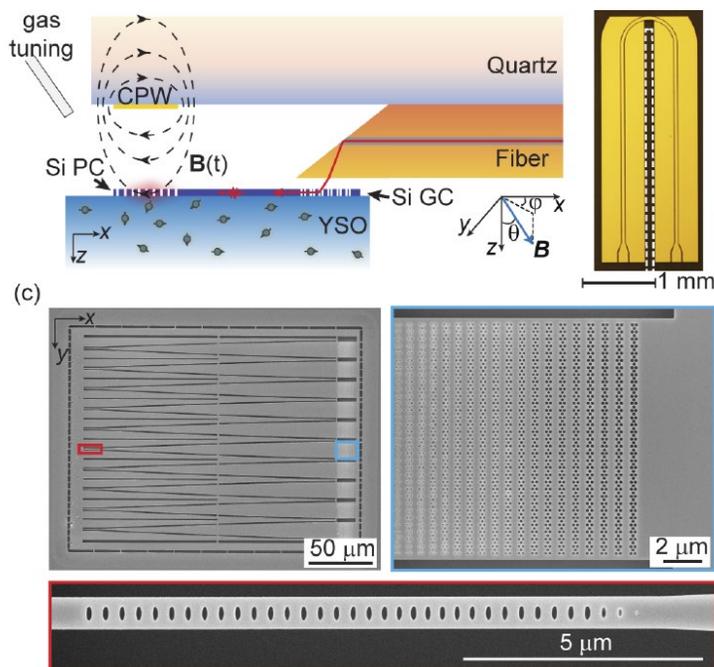
Status: published work at ACS Sustainable Chemistry and Engineering 2021, **9**, 6012

Department of Electrical and Computer Engineering

Hybrid microwave-optical scanning probe for addressing solid-state spins in nanophotonic cavities

S.T. Chen, S. Ourari, M. Raha, C.M. Phenicie, M.T. Uysal, and J.D. Thompson

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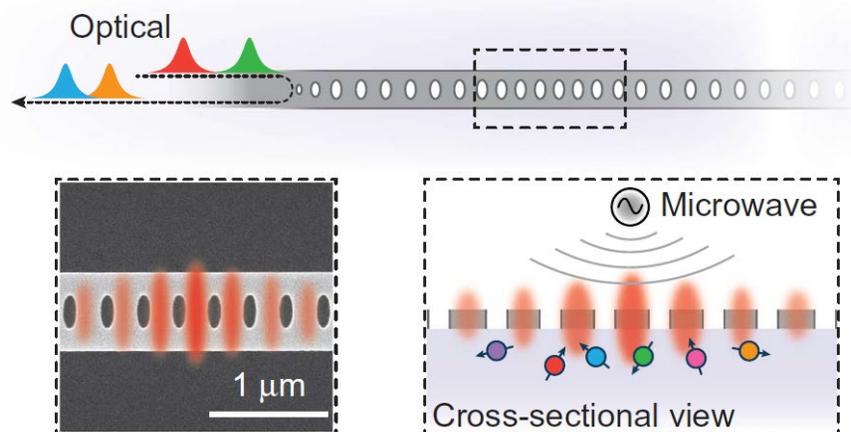


Spin-photon interfaces based on solid-state atomic defects have enabled a variety of key applications in quantum information processing. To maximize the light-matter coupling strength, defects are often placed inside nanoscale devices. Efficiently coupling light and microwave radiation into these structures is an experimental challenge, especially in cryogenic or high vacuum environments with limited sample access. In this work, we demonstrate a fiber-based scanning probe that simultaneously couples light into a planar photonic circuit and delivers high power microwaves for driving electron spin transitions. The optical portion achieves 46% one-way coupling efficiency, while the microwave portion supplies an AC magnetic field with strength up to 9 Gauss at 10 Watts of input microwave power. The entire probe can be scanned across a large number of devices inside a ^3He cryostat without free-space optical access. We demonstrate this technique with silicon nanophotonic circuits coupled to single Er^{3+} ions.

Status: published work at Optics Express 2021, **29**, 4902

Parallel single-shot measurement and coherent control of solid-state spins below the diffraction limit

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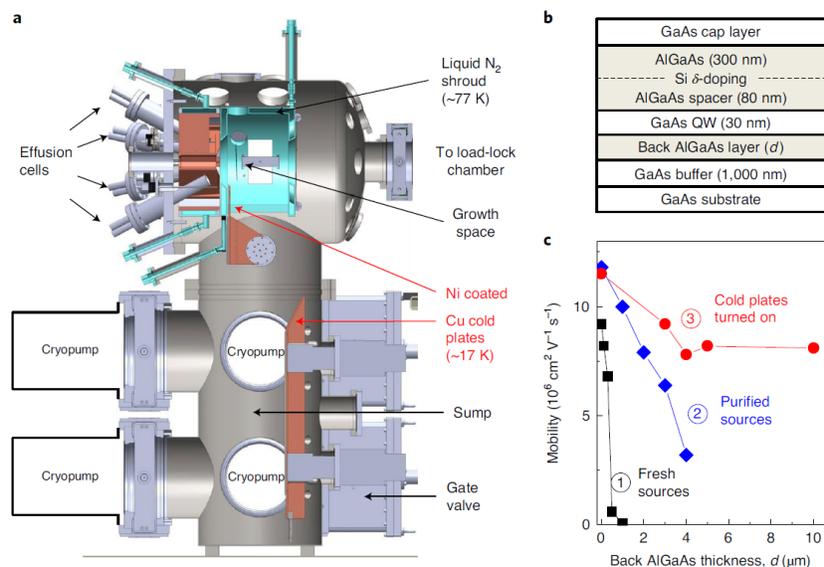
Solid-state spin defects are a promising platform for quantum science and technology. The realization of larger-scale quantum systems with solid-state defects will require high-fidelity control over multiple defects with nanoscale separations, with strong spin-spin interactions for multi-qubit logic operations and the creation of entangled states. We demonstrate an optical frequency-domain multiplexing technique, allowing high-fidelity initialization and single-shot spin measurement of six rare-earth (Er^{3+}) ions, within the subwavelength volume of a single, silicon photonic crystal cavity. We also demonstrate subwavelength control over coherent spin rotations by using an optical AC Stark shift. Our approach may be scaled to large numbers of ions with arbitrarily small separation and is a step toward realizing strongly interacting atomic defect ensembles with applications to quantum information processing and fundamental studies of many-body dynamics.

Status: published work at Science 2020, **370**, 592

Ultra-high-quality two-dimensional electron systems

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



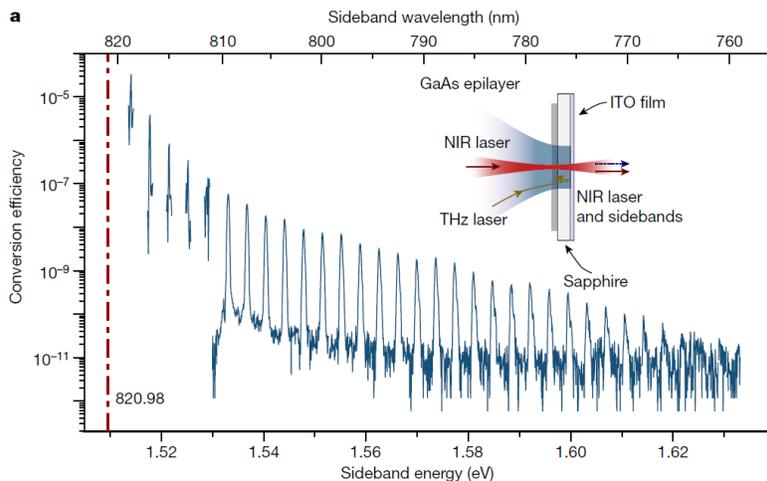
Two-dimensional electrons confined to GaAs quantum wells are hallmark platforms for probing electron–electron interactions. Many key observations have been made in these systems as sample quality has improved over the years. Here, we present a breakthrough in sample quality via source-material purification and innovation in GaAs molecular beam epitaxy vacuum chamber design. Our samples display an ultra-high mobility of $44 \times 10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electron density of $2.0 \times 10^{11} \text{ cm}^{-2}$. These results imply only 1 residual impurity for every 10^{10} Ga/As atoms. The impact of such low impurity concentration is manifold. Robust stripe and bubble phases are observed, and several new fractional quantum Hall states emerge. Furthermore, the activation gap (Δ) of the fractional quantum Hall state at the Landau-level filling (ν) = 5/2, which is widely believed to be non-Abelian and of potential use for topological quantum computing, reaches $\Delta \approx 820 \text{ mK}$. We expect that our results will stimulate further research on interaction-driven physics in a two-dimensional setting and substantially advance the field.

Status: published work at Nature Materials 2021, **20**, 632

Reconstruction of Bloch wavefunctions of holes in a semiconductor

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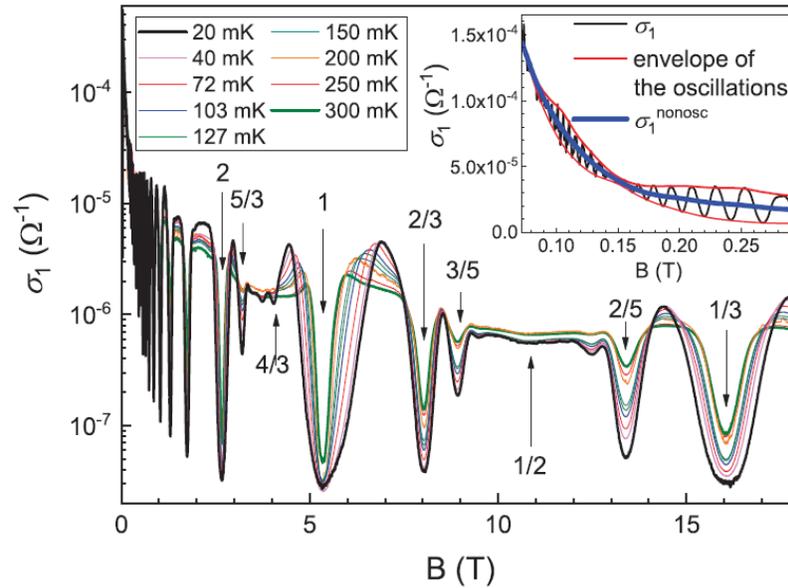


A central goal of condensed-matter physics is to understand how the diverse electronic and optical properties of crystalline materials emerge from the wavelike motion of electrons through periodically arranged atoms. However, more than 90 years after Bloch derived the functional forms of electronic waves in crystals (Bloch wavefunctions), rapid scattering processes have so far prevented their direct experimental reconstruction. In high-order sideband generation, electrons and holes generated in semiconductors by a near-infrared laser are accelerated to a high kinetic energy by a terahertz field, and recollide to emit near-infrared sidebands before they are scattered. Here we reconstruct the Bloch wavefunctions of two types of hole in gallium arsenide at wavelengths much longer than the spacing between atoms by experimentally measuring sideband polarizations and introducing a theory that ties those polarizations to quantum interference between different recollision pathways. These Bloch wavefunctions are compactly visualized on the surface of a sphere. High-order sideband generation can be observed from any direct-gap semiconductor or insulator. We expect that the method introduced here can be used to reconstruct low-energy Bloch wavefunctions in many of these materials, enabling important insights into the origin and engineering of the electronic and optical properties of condensed matter.

Status: published work at Nature 2021, **599**, 57

Dresselhaus spin-orbit interaction in the p-AlGaAs/GaAs/AlGaAs structure with a square quantum well: Surface acoustic wave study

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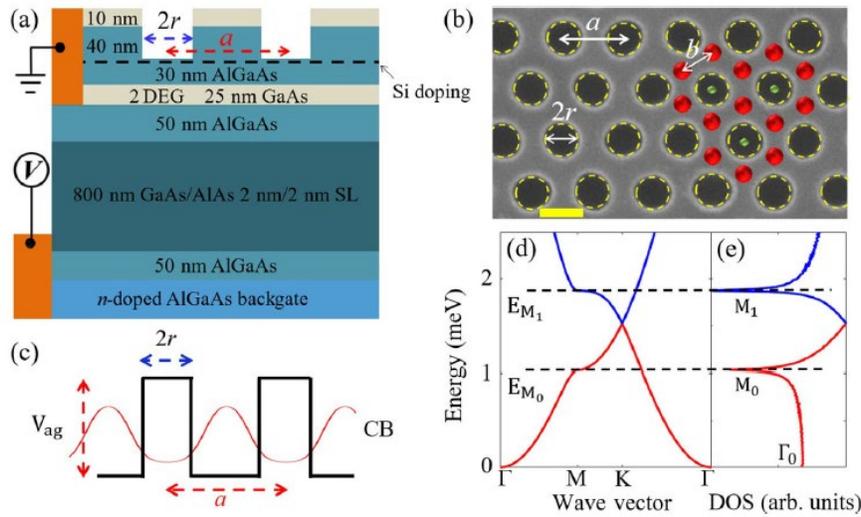
The effect of spin-orbit interaction was studied in a high-quality *p*-AlGaAs/GaAs/AlGaAs structure with a square quantum well using acoustic methods. The structure grown on a GaAs(100) substrate was symmetrically doped with carbon on both sides of the quantum well. Shubnikov–de Haas–type oscillations of the ac conductance of two-dimensional holes were measured. At a low magnetic field $B < 2$ T, conductance oscillations undergo beating induced by a spin-orbit interaction. Analysis of the beating character made it possible to separate the conductance contributions from the two heavy-hole subbands split by the spin-orbit interaction. For each of the subbands the values of the effective masses and quantum relaxation times were determined, and then the energy of the spin-orbit interaction was obtained. The quantum well profile, as well as the small magnitude of the spin-orbit interaction, allowed us to conclude that the spin-orbit splitting is governed by the Dresselhaus mechanism.

Status: published work in Physical Review B 2021, **104**, 155302

Observation of Flat Bands in Gated Semiconductor Artificial Graphene

Lingjie Du,^{1,2} Ziyu Liu,³ Shalom J. Wind,² Vittorio Pellegrini,⁴ Ken W. West,⁵ Saeed Fallahi,⁶ Loren N. Pfeiffer,⁵ Michael J. Manfra,⁶ and Aron Pinczuk^{2,3}

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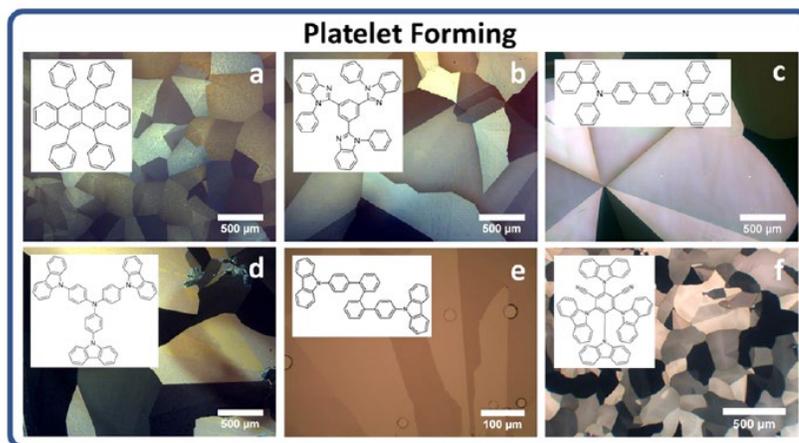
Flat bands near M points in the Brillouin zone are key features of honeycomb symmetry in artificial graphene (AG) where electrons may condense into novel correlated phases. Here we report the observation of van Hove singularity doublet of AG in GaAs quantum well transistors, which presents the evidence of flat bands in semiconductor AG. Two emerging peaks in photoluminescence spectra tuned by backgate voltages probe the singularity doublet of AG flat bands and demonstrate their accessibility to the Fermi level. As the Fermi level crosses the doublet, the spectra display dramatic stability against electron density, indicating interplays between electron-electron interactions and honeycomb symmetry. Our results provide a new flexible platform to explore intriguing flat band physics.

Status: published work at JGR Solid Earth 2019, **124**, 12799

Thermal Properties, Molecular Structure, and Thin-Film Organic Semiconductor Crystallization

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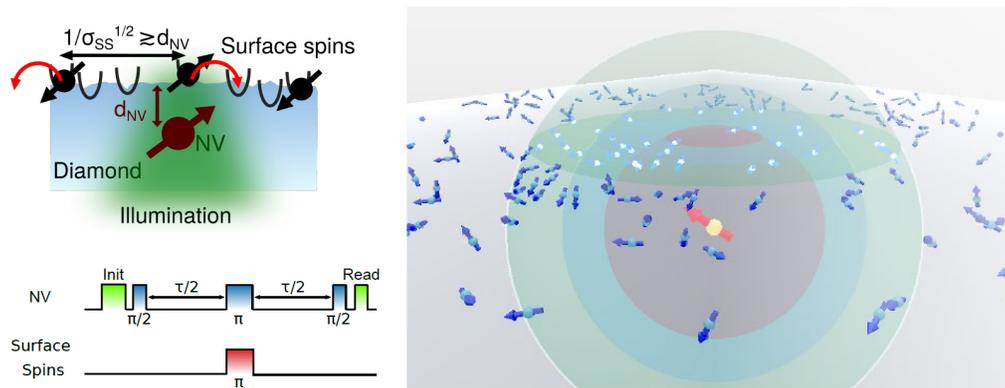
The crystallinity of a group of organic small molecules is investigated by vapor depositing the materials into thin films followed by a thermal annealing step. The materials are categorized into three groups: platelet-forming, spherulite-forming, and those that resist crystallization. Differential scanning calorimetry is utilized to determine the bulk thermal properties of these materials, which provide a reliable indicator of a material's crystallization motif. Platelet-forming materials tend to be characterized by high melting points (T_m) and high magnitude crystallization driving force at the material's crystallization temperature (ΔG_c). The materials that resist crystallization as a thin film have small ΔG_c . These results provide guidelines that can help determine which organic molecules have a greater likelihood of growing into large-scale crystalline frameworks, a key step for improving the charge carrier mobility and exciton diffusion length in organic semiconductors.

Status: published work at J. Phys. Chem. C 2020, **124**, 27213

Probing spin dynamics on diamond surfaces using a single quantum sensor

B. L. Dwyer,¹ L. V. H. Rodgers,² E. K. Urbach,¹ D. Bluvstein,¹ S. Sangtawesin,³ H. Zhou,¹ Y. Nassab,² M. Fitzpatrick,² Z. Yuan,² K. De Greve,¹ E. L. Peterson,¹ J.-P. Chou,⁴ A. Gali,^{5,6} V. V. Dobrovitski,⁷ M. D. Lukin,¹ N. P. de Leon,²

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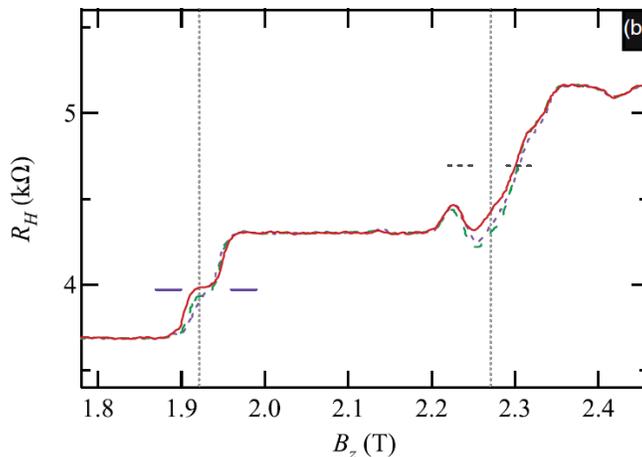
Understanding the dynamics of a quantum bit's environment is essential for the realization of practical systems for quantum information processing and metrology. We use single nitrogen-vacancy (NV) centers in diamond to study the dynamics of a disordered spin ensemble at the diamond surface. Specifically, we tune the density of "dark" surface spins to interrogate their contribution to the decoherence of shallow NV center spin qubits. 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, but some of them reconfigure between measurements. In particular, we observe a depth-dependent critical time associated with a dynamical transition from Gaussian ($n = 2$) decay to $n = 2/3$. These observations demonstrate the potential of a local sensor for understanding complex systems and elucidate pathways for improving and controlling spin qubits at the surface.

Status: published work at arXiv 2021, 2103.12757

Anomalous nematic state to stripe phase transition driven by in-plane magnetic fields

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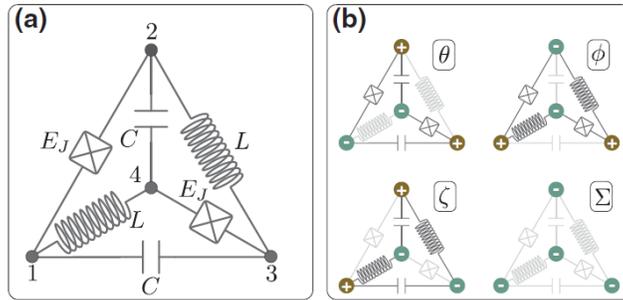
Anomalous nematic states, recently discovered in ultraclean two-dimensional electron gas, emerge from quantum Hall stripe phases upon further cooling. These states are hallmarked by a local minimum (maximum) in the hard (easy) longitudinal resistance and by an incipient plateau in the Hall resistance in nearly half-filled Landau levels. Here, we demonstrate that a modest in-plane magnetic field, applied either along $\langle 110 \rangle$ or $\langle 1-10 \rangle$ crystal axis of GaAs, destroys anomalous nematic states and restores quantum Hall stripe phases aligned along their native $\langle 110 \rangle$ direction. These findings confirm that anomalous nematic states are distinct from other ground states and will assist future theories to identify their origin.

Status: published work in Phys. Rev. B 2021, **104**, L081301

Experimental Realization of a Protected Superconducting Circuit Derived from the 0– π Qubit

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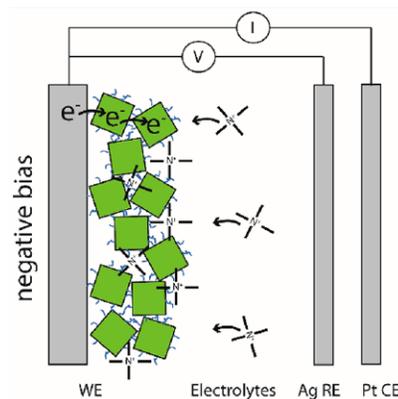
Encoding a qubit in logical quantum states with wave functions characterized by disjoint support and robust energies can offer simultaneous protection against relaxation and pure dephasing. One of the most promising candidates for such a fully protected superconducting qubit is the 0– π circuit. Here we realize the proposed circuit topology in an experimentally obtainable parameter regime, where the ground-state degeneracy is lifted but the qubit is still largely noise protected. More precisely, the logical states of this qubit feature disjoint support and are exponentially protected against relaxation and exponentially (first order) protected against dephasing due to charge (flux) noise. We name the resultant device the “soft 0– π qubit.” Multitone spectroscopy measurements reveal the energy-level structure of the system, which can be precisely described by a simple two-mode Hamiltonian. Using a Raman-type protocol, we exploit a higher-lying charge-insensitive energy level of the device to realize coherent population transfer and logical operations. The measured relaxation ($T_1 = 1.6$ ms) and dephasing ($T_R = 9$ μ s, $T_{2E} = 25$ μ s) times demonstrate that the soft 0– π circuit not only broadens the family of superconducting qubits but also constitutes an important step toward quantum computing with intrinsically protected superconducting qubits.

Status: published work at PRX Quantum 2021, **2**, 010339

Electrochemically n-Doped CsPbBr₃ Nanocrystal Thin Films

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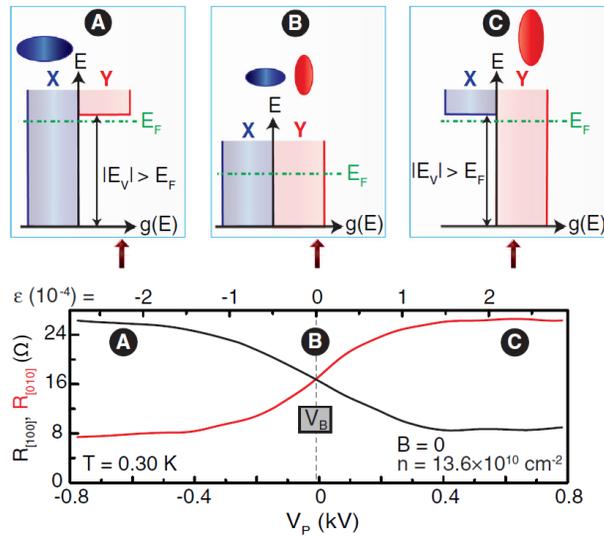
Electrochemical doping is a promising strategy to dope halide perovskites without introducing impurities into the lattice. However, n-type doping of halide perovskites remains challenging due to intrinsically limited electrochemical stability. Herein, we report electrochemically n-doped CsPbBr₃ nanocrystal (NC) films within electrochemically stable potential windows (−0.9–0.5 V vs Ag/AgNO₃). Compared to bulk films with limited accessible surface area for cation charge compensation, NC films show more efficient n-doping properties due to their porous nature. Electrochemically doped NC films exhibit Fermi level shifts, confirmed via electrochemical measurements, vacuum-Kelvin probe contact potential difference, and photoelectron spectroscopy. As a result, in situ conductivity measurements show increases when films are p- or n-doped. Furthermore, n-doped films show a photoluminescence intensity increase. Given that we remain within the electrochemically stable window, we suspect this is due to an alleviation of electron traps, likely a result of altering the charge state of the interstitial Br population.

Status: published work in ACS Energy Letters 2022, 7, 221

Spontaneous Valley Polarization of Itinerant Electrons

Md. S. Hossain, M. K. Ma, K. A. Villegas-Rosales, Y. J. Chung, L. N. Pfeiffer, K.W. West, K.W. Baldwin, and M. Shayegan

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Memory or transistor devices based on an electron's spin rather than its charge degree of freedom offer certain distinct advantages and comprise a cornerstone of spintronics. Recent years have witnessed the emergence of a new field, valleytronics, which seeks to exploit an electron's valley index rather than its spin. An important component in this quest would be the ability to control the valley index in a convenient fashion. Here we show that the valley polarization can be switched from zero to 1 by a small reduction in density, simply tuned by a gate bias, in a two-dimensional electron system. This phenomenon, which is akin to Bloch spin ferromagnetism, arises fundamentally as a result of electron-electron interaction in an itinerant, dilute electron system. Essentially, the kinetic energy favors an equal distribution of electrons over the available valleys, whereas the interaction between electrons prefers single-valley occupancy below a critical density. The gate-bias-tuned transition we observe is accompanied by a sudden, twofold change in sample resistance, making the phenomenon of interest for potential valleytronic transistor device applications. Our observation constitutes a quintessential demonstration of valleytronics in a very simple experiment.

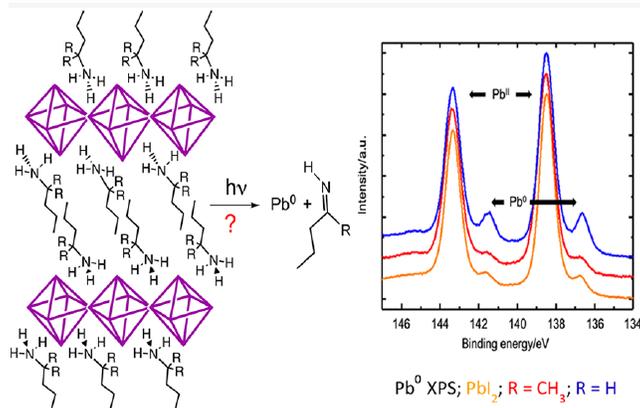
Status: published work in Phys. Rev. Lett. 2021, **127**, 116601

Organoammonium-Ion-based Perovskites Can Degrade to Pb⁰ via Amine–Pb(II) Coordination

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The degradation of alkylammonium Pb^{II} halide perovskites, in the dark and upon irradiation near room temperature, involves coordinated amine as the dominant reducing agent to yield Pb⁰ near room temperature, as determined by X-ray photoelectron spectroscopy (XPS). The reduction of Pb^{II} first involves amine coordination, supported by ²⁰⁷Pb nuclear magnetic resonance (NMR) analysis. It is shown that a Pb^{II}–amide complex is the immediate precursor of PbII reduction. Its oxidized counterpart, the imine, is formed and is characterized by NMR and gas chromatography–mass spectrometry. The “redox” process requires a β-C–H bond of the alkylamine. Amine species devoid of this moiety do not similarly reduce Pb^{II} to Pb⁰. The conversion of an alkylammonium moiety to the Pb^{II}–amide is proposed to occur through a sequence of photoassisted proton-transfer reactions to a lead-coordinated ligand, which is substantiated through XPS-observed Pb^{II} reduction in a family of lead bromide/iodide 2D perovskites.

Status: published work at ACS Energy Letters 2021, **6**, 2262

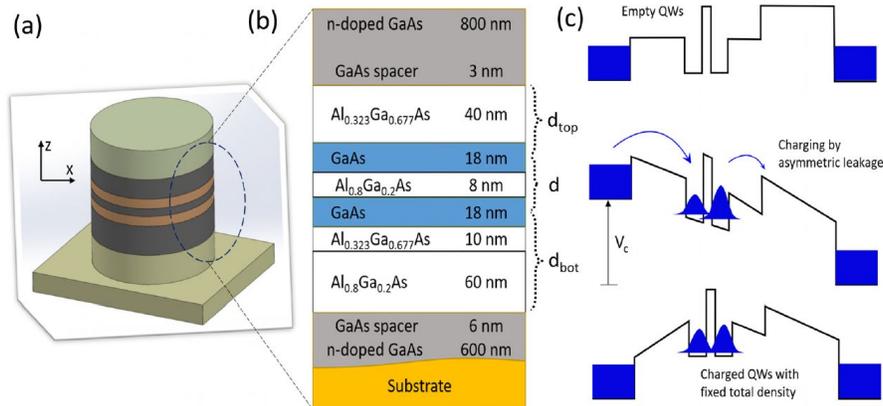
Strong interlayer charge transfer due to exciton condensation in an electrically isolated GaAs quantum well bilayer

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We introduce a design of electrically isolated “floating” bilayer GaAs quantum wells (QW), in which application of a large gating voltage controllably and highly reproducibly induces charges that remain trapped in the bilayer after removal of the gating voltage. At smaller gate voltages, the bilayer is fully electrically isolated from external electrodes by thick insulating barriers. This design permits full control of the total and differential densities of two coupled 2D electron systems. The floating bilayer design provides a unique approach for studying systems inaccessible by simple transport measurements. It also provides the ability to measure the charge transfer between the layers, even when the in-plane resistivities of the 2D systems diverge. We measure the capacitance and inter-layer tunneling spectra of the QW bilayer with independent control of the top and bottom layer electron densities. Our measurements display strongly enhanced inter-layer tunneling current at $\nu_T = 1$, a signature of exciton condensation of a strongly interlayer-correlated bilayer system. With fully tunable densities of individual layers, the floating bilayer QW system provides a versatile platform to access previously unavailable information on the quantum phases in electron bilayer systems.

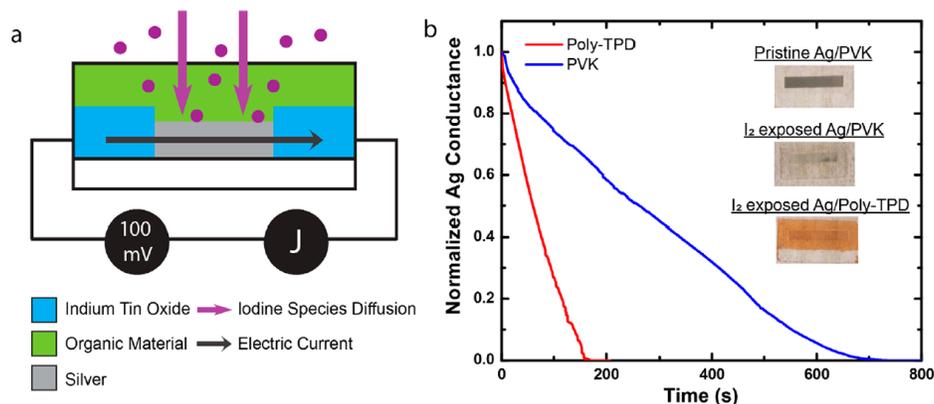
Status: published work in Applied Physics Letters 2021, **118**, 202110

Organic Hole Transport Material Ionization Potential Dictates Diffusion Kinetics of Iodine Species in Halide Perovskite Devices

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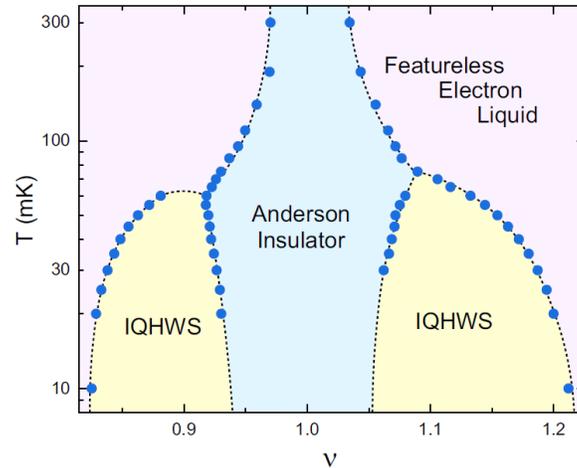
Iodine-containing volatiles are major degradation products of halide perovskite materials under irradiation, yet iodine diffusion kinetics into and throughout organic hole transport materials (HTMs) and consequent reactions are largely unexplored. Here, we modify the Ca:O₂ corrosion test to Ag:I₂ to quantify I₂ transmission rates through common organic HTMs. We observe I₂ permeability to inversely correlate with HTM ionization energy, or the highest occupied molecular orbital (HOMO) energy. Tracking electronic conductance during exposure to I₂ confirms shallow HOMO HTMs are strongly oxidized (i.e., doped), leading to substantial I₂ uptake and increased transmission rates. Finally, relationships between HOMO level, doping, and transmission rate are maintained when methylammonium lead triiodide (MAPbI₃) photolysis products are the only source of iodine. While HTM energetics influence the initial performance of halide perovskite devices by selective charge extraction, our results further suggest they will affect device stability; deeper HOMO energy HTMs will suppress iodine migration and associated degradation mechanisms.

Status: published work at ACS Energy Letters 2021, **6**, 501

Magnetotransport patterns of collective localization near $\nu = 1$ in a high-mobility two-dimensional electron gas

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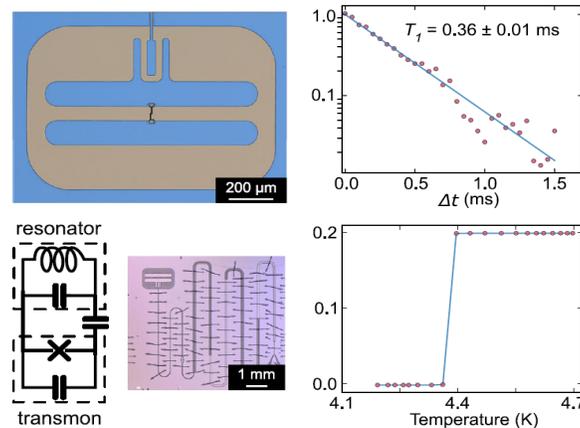
We report complex magnetotransport patterns of the $\nu = 1$ integer quantum Hall state in a GaAs/AlGaAs sample from the newest generation with a record high electron mobility. The reentrant integer quantum Hall effect in the flanks of the $\nu = 1$ plateau indicates the formation of the integer quantum Hall Wigner solid, a collective insulator. Moreover, at a fixed filling factor, the longitudinal resistance versus temperature in the region of the integer quantum Hall Wigner solid exhibits a sharp peak. Such sharp peaks in the longitudinal resistance versus temperature so far were only detected for bubble phases forming in high Landau levels but were absent in the region of the Anderson insulator. We suggest that in samples of sufficiently low disorder, sharp peaks in the longitudinal resistance versus temperature traces are universal transport signatures of all isotropic electron solids that form in the flanks of integer quantum Hall plateaus. We discuss possible origins of these sharp resistance peaks and we draw a stability diagram for the insulating phases in the ν - T phase space.

Status: published work in Physical Review B 2021, **104**, 045311

New material platform for superconducting transmon qubits with coherence times exceeding 0.3 milliseconds

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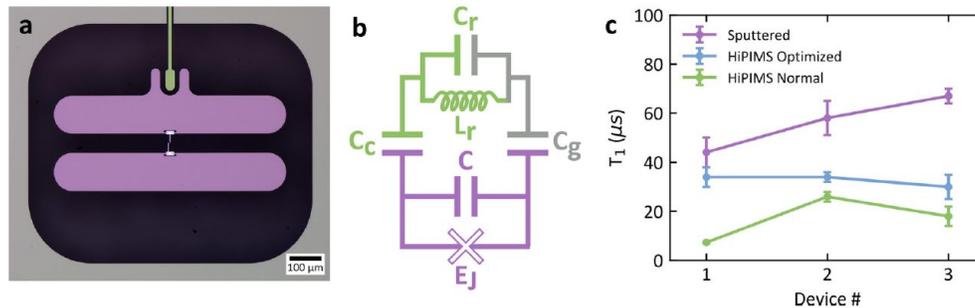
The superconducting transmon qubit is a leading platform for quantum computing and quantum science. Building large, useful quantum systems based on transmon qubits will require significant improvements in qubit relaxation and coherence times, which are orders of magnitude shorter than limits imposed by bulk properties of the constituent materials. This indicates that relaxation likely originates from uncontrolled surfaces, interfaces, and contaminants. Previous efforts to improve qubit lifetimes have focused primarily on designs that minimize contributions from surfaces. However, significant improvements in the lifetime of two-dimensional transmon qubits have remained elusive for several years. Here, we fabricate two-dimensional transmon qubits that have both lifetimes and coherence times with dynamical decoupling exceeding 0.3 milliseconds by replacing niobium with tantalum in the device. We have observed increased lifetimes for seventeen devices, indicating that these material improvements are robust, paving the way for higher gate fidelities in multi-qubit processors.

Status: published work at Nature Communications 2021, **12**, 1779

Microscopic relaxation channels in materials for superconducting qubits

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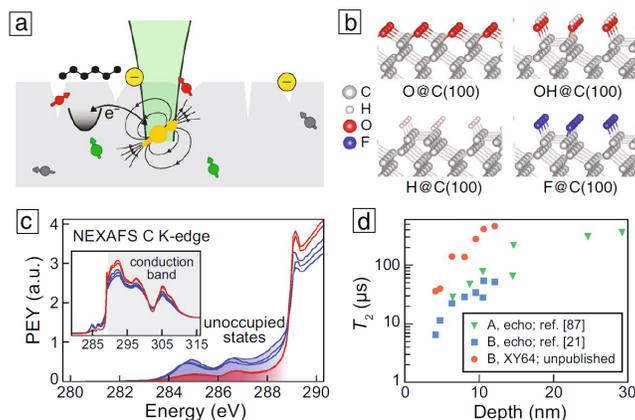
Despite mounting evidence that materials imperfections are a major obstacle to practical applications of superconducting qubits, connections between microscopic material properties and qubit coherence are poorly understood. Here, we combine measurements of transmon qubit relaxation times (T_1) with spectroscopy and microscopy of the polycrystalline niobium films used in qubit fabrication. By comparing films deposited using three different techniques, we reveal correlations between T_1 and intrinsic film properties such as grain size, enhanced oxygen diffusion along grain boundaries, and the concentration of suboxides near the surface. Qubit and resonator measurements show signatures of two-level system defects, which we propose to be hosted in the grain boundaries and surface oxides. We also show that the residual resistance ratio of the polycrystalline niobium films can be used as a figure of merit for qubit lifetime. This comprehensive approach to understanding qubit decoherence charts a pathway for materials-driven improvements of superconducting qubit performance.

Status: published work in *Comms. Mater.* 2021, **2**, 72

Materials challenges for quantum technologies based on color centers in diamond

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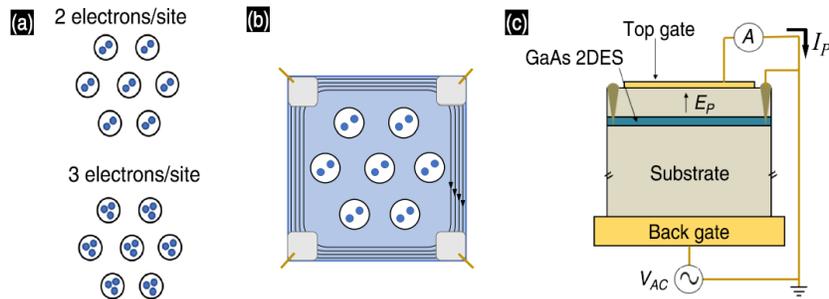
Emerging quantum technologies require precise control over quantum systems of increasing complexity. Defects in diamond, particularly the negatively charged nitrogen-vacancy center, are a promising platform with the potential to enable technologies ranging from ultra-sensitive nanoscale quantum sensors, to quantum repeaters for long distance quantum networks, to simulators of complex dynamical processes in many-body quantum systems, to scalable quantum computers. While these advances are due in large part to the distinct material properties of diamond, the uniqueness of this material also presents difficulties, and there is a growing need for novel materials science techniques for characterization, growth, defect control, and fabrication dedicated to realizing quantum applications with diamond. In this article we identify and discuss the major materials science challenges and opportunities associated with diamond quantum technologies.

Status: published work in MRS Bulletin 2021, **46**, 623

Melting phase diagram of bubble phases in high Landau levels

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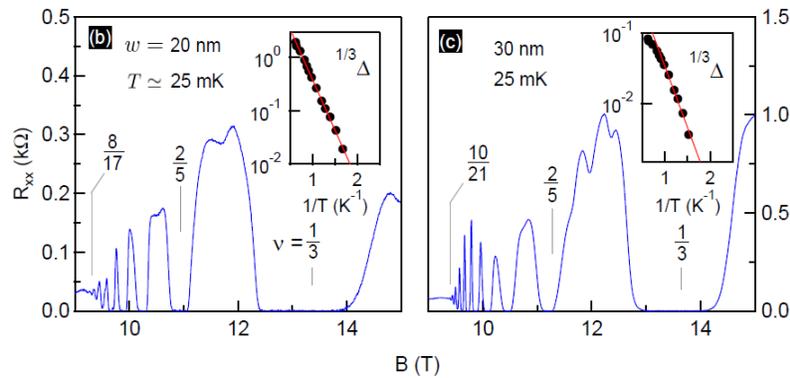
A low-disorder, two-dimensional electron system (2DES) subjected to a large perpendicular magnetic field and cooled to very low temperatures provides a rich platform for studies of many-body quantum phases. The magnetic field quenches the electrons' kinetic energy and quantizes the energy into a set of Landau levels, allowing the Coulomb interaction to dominate. In excited Landau levels, the fine interplay between short- and long-range interactions stabilizes bubble phases, Wigner crystals with more than one electron per unit cell. Here, we present the screening properties of bubble phases, probed via a simple capacitance technique where the 2DES is placed between a top and a bottom gate and the electric field penetrating through the 2DES is measured. The bubbles formed at very low temperatures screen the electric field poorly as they are pinned by the residual disorder potential, allowing a large electric field to reach the top gate. As the temperature is increased, the penetrating electric field decreases and, surprisingly, exhibits a pronounced minimum at a temperature that appears to coincide with the melting temperature of the bubble phase. We deduce a quantitative phase diagram, as a function of Landau level filling factor (ν) and temperature, for the transition from the bubble to liquid phases for $4 \leq \nu \leq 5$.

Status: published work in Phys. Rev. B 2021, **104**, L121110

Fractional quantum Hall effect energy gaps: role of electron layer thickness

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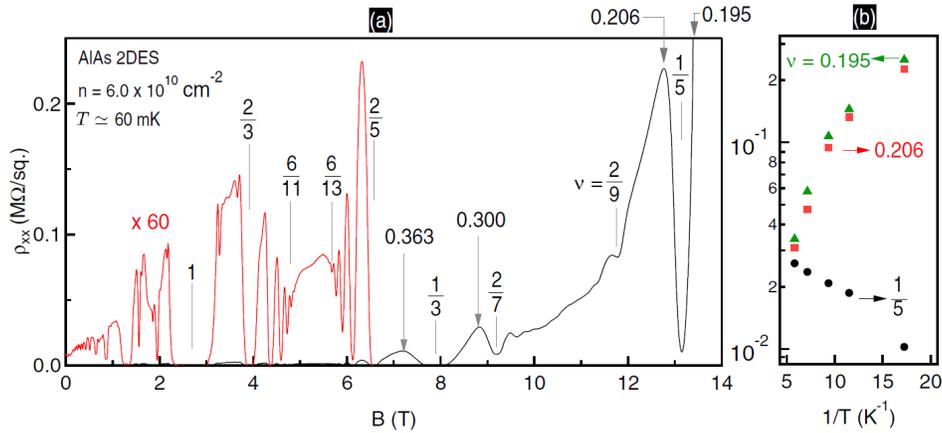
The fractional quantum Hall effect (FQHE) stands as a quintessential manifestation of an interacting two-dimensional electron system. One of FQHE's most fundamental characteristics is the energy gap separating the incompressible ground state from its excitations. Yet, despite nearly four decades of investigations, a quantitative agreement between the theoretically calculated and experimentally measured energy gaps is lacking. Here we report a quantitative comparison between the measured energy gaps and the available theoretical calculations that take into account the role of finite layer thickness and Landau level mixing. Our systematic experimental study of the FQHE energy gaps uses very high-quality two-dimensional electron systems confined to GaAs quantum wells with varying well widths. All the measured energy gaps fall below the calculations, but as the electron layer thickness increases, the results of experiments and calculations come closer. Accounting for the role of disorder in a phenomenological manner, we find the measured energy gaps to be in reasonable quantitative agreement with calculations, although some discrepancies remain.

Status: published work in Phys. Rev. Lett. 2021, **127**, 056801

Competition between fractional quantum Hall liquid and Wigner solid at small fillings: Role of layer thickness and Landau level mixing

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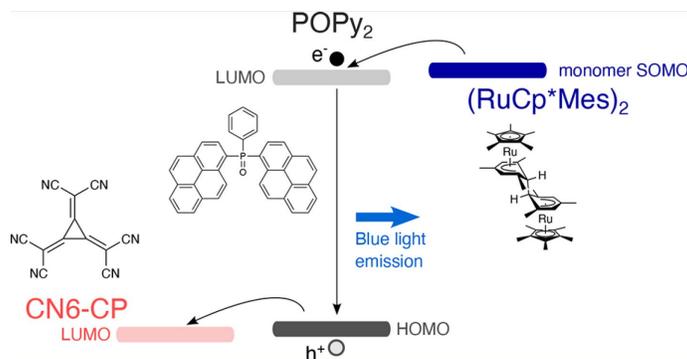
What is the fate of the ground state of a two-dimensional electron system at very low Landau level filling factors (ν) where interaction reigns supreme? An ordered array of electrons, the so-called Wigner crystal, has long been believed to be the answer. It was in fact the search for the elusive Wigner crystal that led to the discovery of an unexpected, incompressible liquid state, namely the fractional quantum Hall state at $\nu = 1/3$. Understanding the competition between the liquid and solid ground states has since remained an active field of fundamental research. Here we report experimental data for a new two-dimensional system where the electrons are confined to an AlAs quantum well. The exceptionally high quality of the samples and the large electron effective mass allow us to determine the liquid-solid phase diagram for the two-dimensional electrons in a large range of filling factors near $\sim 1/3$ and $\sim 1/5$. The data and their comparison with an available theoretical phase diagram reveal the crucial role of Landau level mixing and finite electron layer thickness in determining the prevailing ground states.

Status: published work in Phys. Rev. Research 2021, **3**, 013181

Powerful Organic Molecular Oxidants and Reductants Enable Ambipolar Injection in a Large-Gap Organic Homojunction Diode

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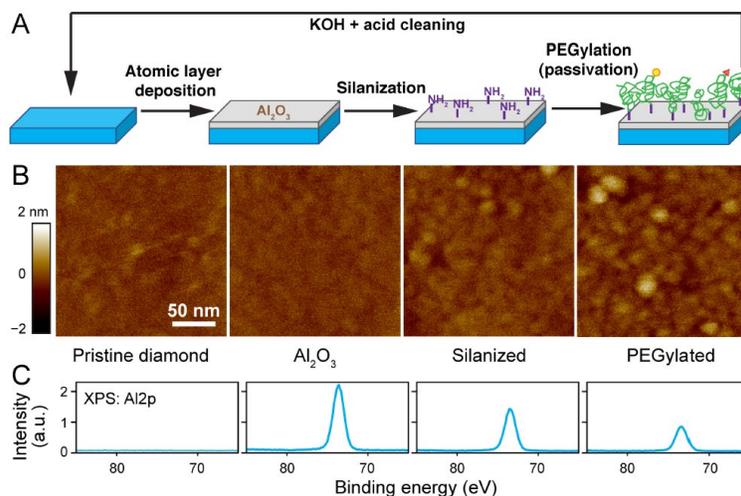
Doping has proven to be a critical tool for enhancing the performance of organic semiconductors in devices like organic light-emitting diodes. However, the challenge in working with high ionization-energy (IE) organic semiconductors is to find p-dopants with correspondingly high electron affinity (EA) that will improve the conductivity and charge carrier transport in a film. Here, we use an oxidant that has been recently recognized to be a very strong p-type dopant, hexacyano-1,2,3-trimethylene-cyclopropane (CN6-CP). We measure the frontier orbitals of CN6-CP using ultraviolet and inverse photoemission spectroscopy techniques and confirm a high EA value of 5.88 eV in the condensed phase. The introduction of CN6-CP in a film of large-band-gap, large-IE phenyldi(pyren-1-yl)phosphine oxide (POPy₂) leads to a significant shift of the Fermi level toward the highest occupied molecular orbital and a 2 orders of magnitude increase in conductivity. Using CN6-CP and n-dopant (RuCp*Mes)₂, we fabricate a POPy₂-based rectifying p-i-n homojunction diode with a 2.9 V built-in potential. Blue light emission is achieved under forward bias. This effect demonstrates the dopant-enabled hole injection from the CN6-CP-doped layer and electron injection from the (RuCp*Mes)₂-doped layer in the diode.

Status: published work in ACS Appl. Mater. Interfaces 2022, **XX**, XXX

Biocompatible surface functionalization architecture for a diamond quantum sensor

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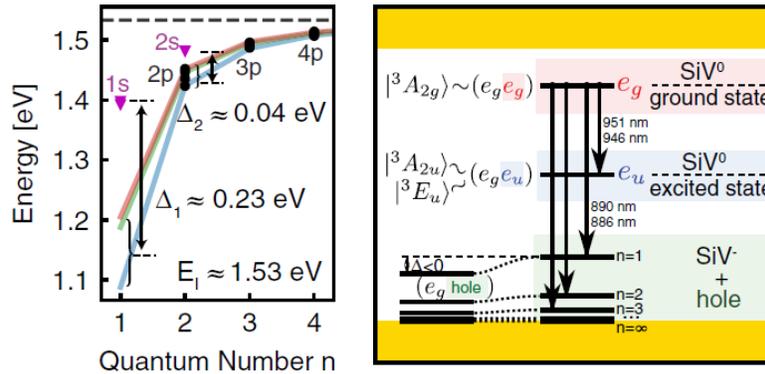


Quantum metrology enables some of the most precise measurements. In the life sciences, diamond-based quantum sensing has enabled a new class of biophysical sensors and diagnostic devices that are being investigated as a platform for cancer screening and ultra-sensitive immunoassays. However, a broader application in the life sciences based on nanoscale nuclear magnetic resonance spectroscopy has been hampered by the need to interface highly sensitive quantum bit (qubit) sensors with their biological targets. Here, we demonstrate a new approach that combines quantum engineering with single-molecule biophysics to immobilize individual proteins and DNA molecules on the surface of a bulk diamond crystal that hosts coherent nitrogen vacancy qubit sensors. Our thin (sub-5 nm) functionalization architecture provides precise control over protein adsorption density and results in near-surface qubit coherence approaching 100 μ s. The developed architecture remains chemically stable under physiological conditions for over five days, making our technique compatible with most biophysical and biomedical applications.

Status: published work at arXiv.org 2021, 2108.04843

Optically Detected Magnetic Resonance in Neutral Silicon Vacancy Centers in Diamond via Bound Exciton States

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Neutral silicon vacancy (SiV^0) centers in diamond are promising candidates for quantum networks because of their excellent optical properties and long spin coherence times. However, spin-dependent fluorescence in such defects has been elusive due to poor understanding of the excited state fine structure and limited off-resonant spin polarization. Here we report the realization of optically detected magnetic resonance and coherent control of SiV^0 centers at cryogenic temperatures, enabled by efficient optical spin polarization via previously unreported higher-lying excited states. We assign these states as bound exciton states using group theory and density functional theory. These bound exciton states enable new control schemes for SiV^0 as well as other emerging defect systems.

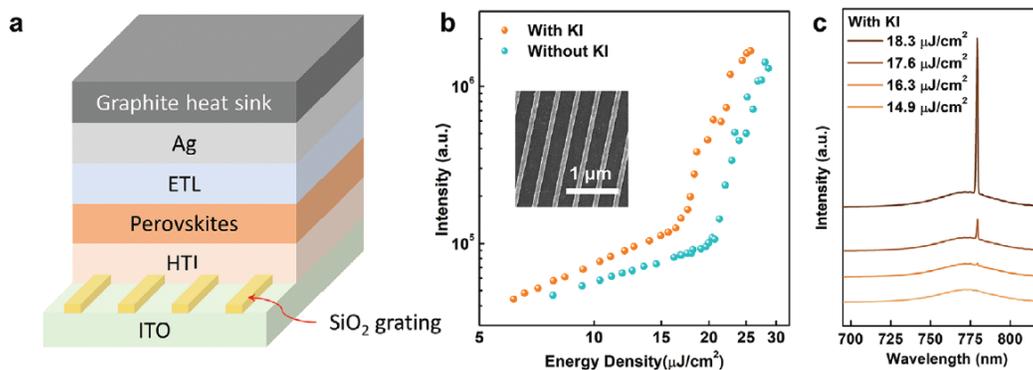
Status: published work in Phys. Rev. Lett. 2020, **125**, 237402

Nanosecond-Pulsed Perovskite Light-Emitting Diodes at High Current Density

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While metal-halide perovskite light-emitting diodes (PeLEDs) hold the potential for a new generation of display and lighting technology, their slow operation speed and response time limit their application scope. Here, high-speed PeLEDs driven by nanosecond electrical pulses with a rise time of 1.2 ns are reported with a maximum radiance of approximately $480 \text{ kW sr}^{-1} \text{ m}^{-2}$ at 8.3 kA cm^{-2} , and an external quantum efficiency (EQE) of 1% at approximately 10 kA cm^{-2} , through improved device configuration designs and material considerations. Enabled by the fast operation of PeLEDs, the temporal response provides access to transient charge carrier dynamics under electrical excitation, revealing several new electroluminescence quenching pathways. Finally, integrated distributed feedback (DFB) gratings are explored, which facilitate more directional light emission with a maximum radiance of approximately $1200 \text{ kW sr}^{-1} \text{ m}^{-2}$ at 8.5 kA cm^{-2} , a more than two-fold enhancement to forward radiation output.

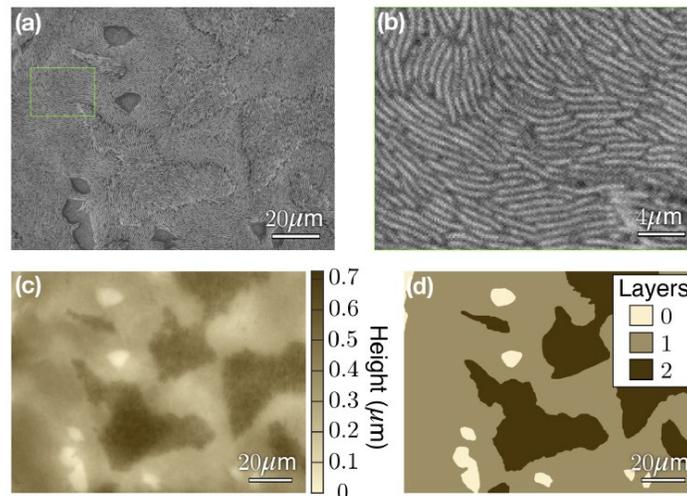
Status: published work in *Advanced Materials* 2021, **33**, 2104867

Lewis-Sigler Institute for Integrative Genomics

Topological defects promote layer formation in *Myxococcus xanthus* colonies

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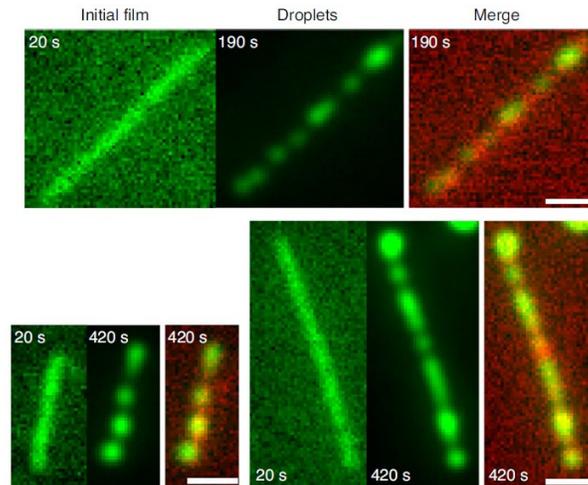
The soil bacterium *Myxococcus xanthus* lives in densely packed groups that form dynamic three-dimensional patterns in response to environmental changes, such as droplet-like fruiting bodies during starvation. The development of these multicellular structures begins with the sequential formation of cell layers in a process that is poorly understood. Using confocal three-dimensional imaging, we find that motile rod-shaped *M. xanthus* cells are densely packed and aligned in each layer, forming an active nematic liquid crystal. Cell alignment is nearly perfect throughout the population except at point defects that carry half-integer topological charge. We observe that new cell layers preferentially form at the position of $+1/2$ defects, whereas holes preferentially open at $-1/2$ defects. To explain these findings, we model the bacterial colony as an extensible active nematic fluid with anisotropic friction. In agreement with our experimental measurements, this model predicts an influx of cells toward $+1/2$ defects, and an outflux of cells from $-1/2$ defects. Our results suggest that cell motility and mechanical cell-cell interactions are sufficient to promote the formation of cell layers at topological defects, thereby seeding fruiting bodies in colonies of *M. xanthus*.

Status: published work at Nature Physics 2021, **17**, 211

A hydrodynamic instability drives protein droplet formation on microtubules to nucleate branches

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Liquid–liquid phase separation occurs not only in bulk liquid, but also on surfaces. In physiology, the nature and function of condensates on cellular structures remain unexplored. Here we study how the condensed protein TPX2 behaves on microtubules to initiate branching microtubule nucleation, which is critical for spindle assembly in eukaryotic cells. Using fluorescence, electron and atomic force microscopies and hydrodynamic theory, we show that TPX2 on a microtubule reorganizes according to the Rayleigh–Plateau instability, like dew droplets patterning a spider web. After uniformly coating microtubules, TPX2 forms regularly spaced droplets, from which branches nucleate. Droplet spacing increases with greater TPX2 concentration. A stochastic model shows that droplets make branching nucleation more efficient by confining the space along the microtubule where multiple necessary factors colocalize to nucleate a branch.

Status: published work in Nature Phys. 2021, 17, 493

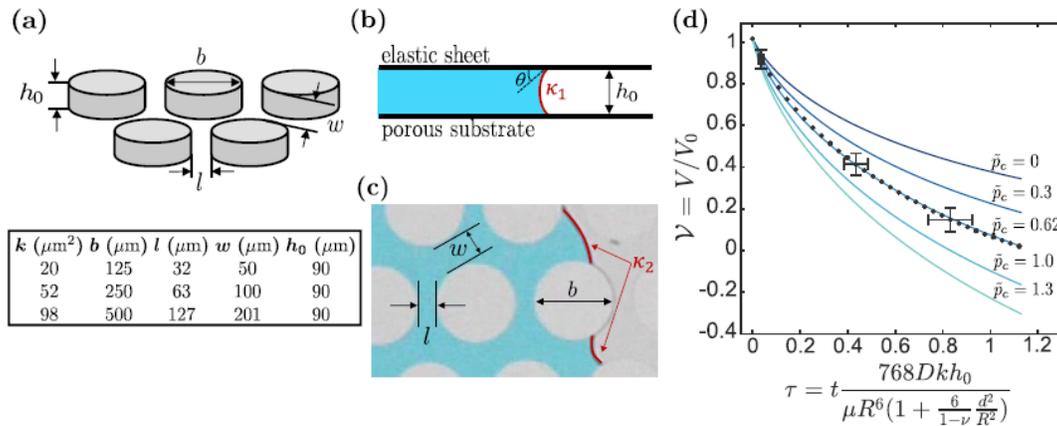
Department of Mechanical and Aerospace Engineering

Relaxation of a fluid-filled blister on a porous substrate

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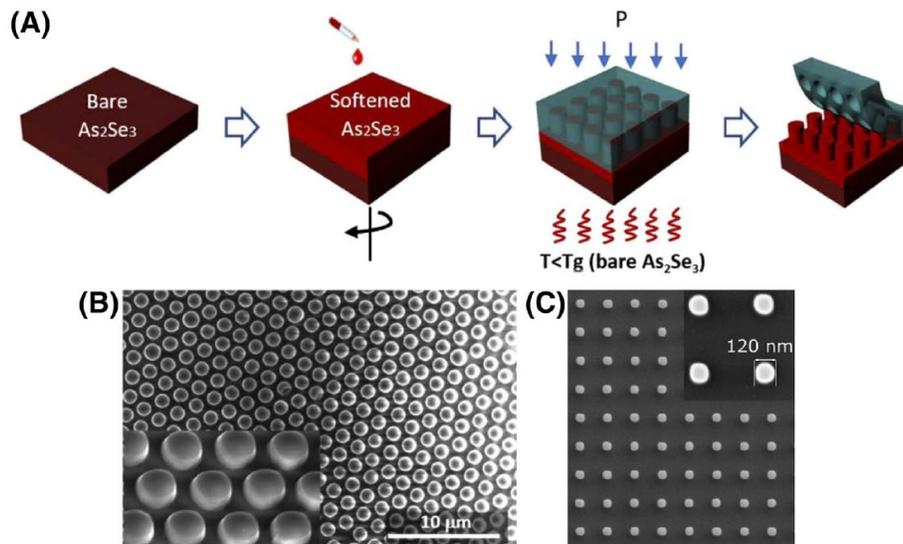
The relaxation dynamics of a fluid-filled blister between an elastic sheet and a porous substrate are controlled by the deformation of the elastic sheet, the viscous stresses in the pores, and the capillary pressure at the liquid-air interface due to imbibition. We develop a mathematical model to study the effects of varying the permeability of the porous substrate, the bending stiffness of the elastic sheet, and the blister size on the relaxation dynamics. Experiments are conducted by injecting a finite volume of viscous fluid between a porous substrate and an elastic sheet, where fluid first invades the pores, and subsequently, as the pressure in the fluid increases, the elastic sheet is peeled and uplifted from the substrate to form a fluid-filled blister. After injection is stopped, the fracture front is static, and the elastic stresses in the overlying sheet and the capillary pressure at the liquid-air interface drive the drainage of the blister into the pores. We identify two regimes of drainage. For thick sheets and more permeable substrates, drainage is primarily due to the stresses in the deformed elastic sheet. For thin sheets and less permeable substrates, drainage is driven by the imbibition of the liquid into the pore space. Our model and experiments are relevant to the drainage of fluid-driven fractures in porous media.

Status: published work at Phys. Rev. Fluids 2021, **6**, 084101

Scalable solution processing of amorphous and crystalline chalcogenide films

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Chalcogenide materials have attracted interest for diverse device applications, including thermoelectrics, phase-change memory and optoelectronics, and even solid-state batteries. Part of their appeal is solution processability, which offers a potentially inexpensive, scalable route to thin film fabrication. A number of solution-based methods have been explored with crystalline metal chalcogenides, but combining industrially practical solvents with high-throughput film deposition remains challenging. Similar issues are faced with amorphous chalcogenides, where decades of work have focused on the role of dissolution chemistry in processing high-quality films. Here, we outline recent progress in understanding dissolution and film formation in both systems. By combining wisdom from crystalline and amorphous chalcogenides, we aim to highlight fundamentals underlying scalable solution processing and map areas for future study.

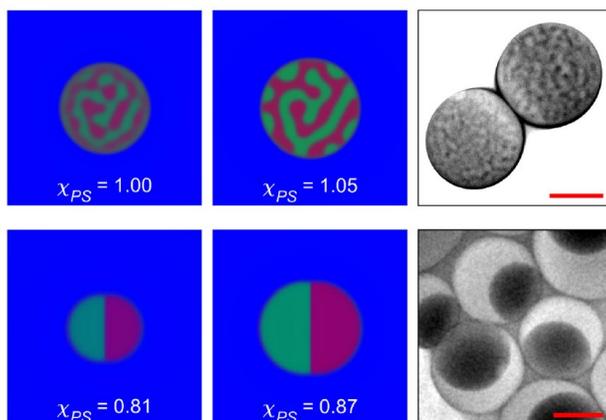
Status: published work in Trends in Chemistry 2021, **3**, 535

Evolution of Polymer Colloid Structure During Precipitation and Phase Separation

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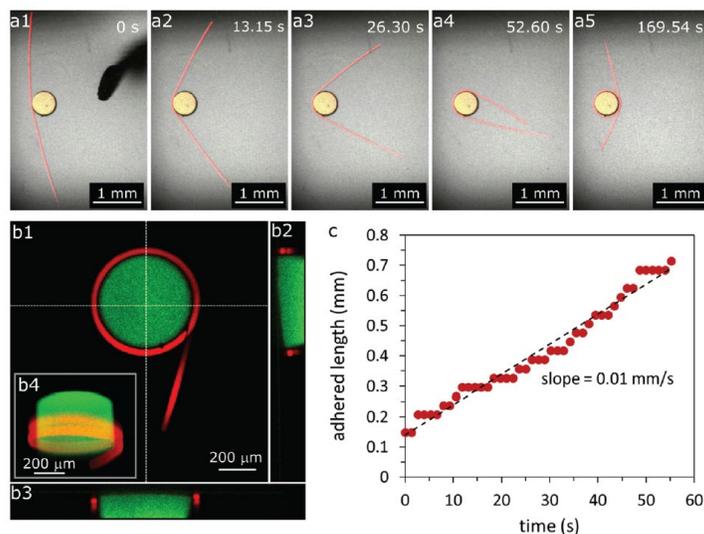
Polymer colloids arise in a variety of contexts ranging from synthetic to natural systems. The structure of polymeric colloids is crucial to their function and application. Hence, understanding the mechanism of structure formation in polymer colloids is important to enabling advances in their production and subsequent use as enabling materials in new technologies. Here, we demonstrate how the specific pathway from precipitation to vitrification dictates the resulting morphology of colloids fabricated from polymer blends. Through continuum simulations, free energy calculations, and experiments, we reveal how colloid structure changes with the trajectory taken through the phase diagram. We demonstrate that during solvent exchange, polymer-solvent phase separation of a homogeneous condensate can precede polymer-polymer phase separation for blends of polymers that possess some degree of miscibility. For less-miscible, higher molecular-weight blends, phase separation and kinetic arrest compete to determine the final morphology. Such an understanding of the pathways from precipitation to vitrification is critical to designing functional structured polymer colloids.

Status: published work at JACS Au 2021, 1, 936

Electrostatic wrapping of a microfiber around a curved particle

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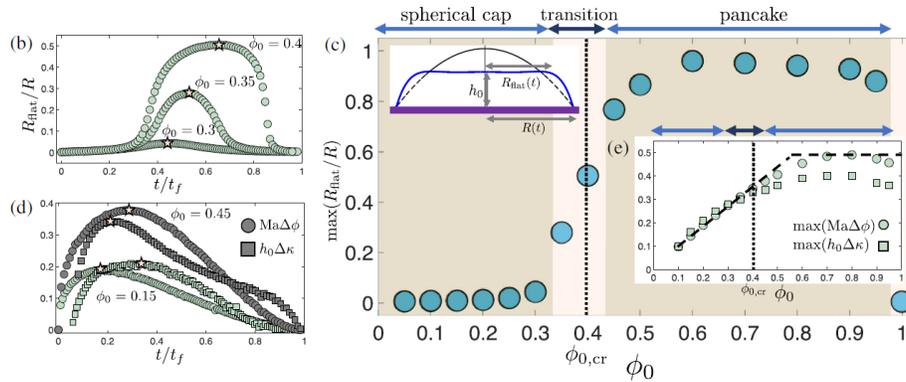
The dynamics of the wrapping of a charged flexible microfiber around an oppositely charged curved particle immersed in a viscous fluid is investigated. We observe that the wrapping behavior varies with the radius and Young's modulus of the fiber, the radius of the particle, and the ionic strength of the surrounding solution. We find that wrapping is primarily a function of the favorable interaction energy due to electrostatics and the unfavorable deformation energy needed to conform the fiber to the curvature of the particle. We perform an energy balance to predict the critical particle radius for wrapping, finding reasonably good agreement with experimental observations. In addition, we use mathematical modeling and observations of the deflected shape of the free end of the fiber during wrapping to extract a measurement of the Young's modulus of the fiber. We evaluate the accuracy and potential limitations of this in situ measurement when compared to independent mechanical tests.

Status: published work in *Soft Matter* 2021, **17**, 3609

Evaporation of Binary-Mixture Liquid Droplets: The Formation of Picoliter Pancakelike Shapes

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Small multicomponent droplets are of increasing importance in a plethora of technological applications ranging from the fabrication of self-assembled hierarchical patterns to the design of autonomous fluidic systems. While often far away from equilibrium, involving complex and even chaotic flow fields, it is commonly assumed that in these systems with small drops surface tension keeps the shapes spherical. Here, studying picoliter volatile binary-mixture droplets of isopropanol and 2-butanol, we show that the dominance of surface tension forces at small scales can play a dual role: Minute variations in surface tension along the interface can create Marangoni flows that are strong enough to significantly deform the drop, forming micron-thick pancakelike shapes that are otherwise typical of large puddles. We identify the conditions under which these flattened shapes form and explain why, universally, they relax back to a spherical-cap shape toward the end of drop lifetime. We further show that the formation of pancakelike droplets suppresses the “coffee-ring” effect and leads to uniform deposition of suspended particles. The quantitative agreement between theory and experiment provides a predictive capability to modulate the shape of tiny droplets with implications in a range of technologies from fabrication of miniature optical lenses to coating, printing, and pattern deposition.

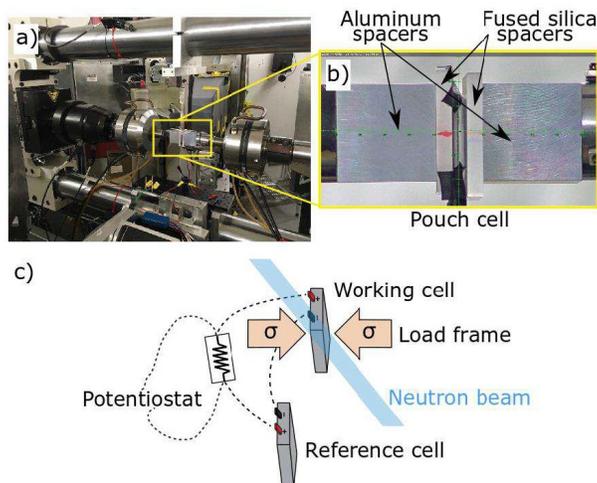
Status: published work in Phys. Rev. Lett. 2021, **127**, 024501

Investigating Mechano-Electrochemical Coupling Phenomenon in Lithium-Ion Pouch Cells Using *in-situ* Neutron Diffraction

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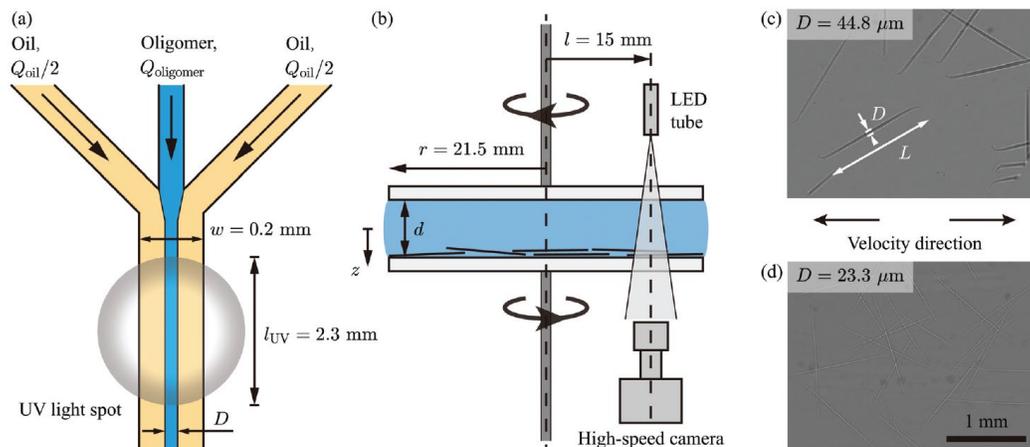
In lithium-ion battery electrode materials, internal mechanical strain is coupled to electrochemical processes. As a result, lithium-ion electrodes can be used for mechano-electrochemical energy harvesting. A promising way to investigate this mechano-electrochemical coupling is through neutron scattering, which can measure the lighter elements that compose battery anodes. In this paper, we conduct *in-situ* neutron diffraction studies on commercial lithium-ion pouch cells using the VULCAN diffractometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. By applying stress on these pouch cells, and examining the phase-specific lattice strains, Bragg peak intensities, and peak broadening, we can gain insight into the mechano-electrochemical correlation in lithium-ion electrodes. We measure a negative electrochemical lattice strain of the graphite electrode, indicating that stress causes lithium ions to leave the graphite structure.

Status: published work in ECS Transactions 2021, **104**, 75

Shear-induced migration of confined flexible fibers

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We report an experimental study of the shear-induced migration of flexible fibers in suspensions confined between two parallel plates. Non-Brownian fiber suspensions are imaged in a rheo-microscopy setup, where the top and the bottom plates counter-rotate and create a Couette flow. Initially, the fibers are near the bottom plate due to sedimentation. Under shear, the fibers move with the flow and migrate towards the center plane between the two walls. Statistical properties of the fibers, such as the mean values of the positions, orientations, and end-to-end lengths of the fibers, are used to characterize the behaviors of the fibers. A dimensionless parameter Λ_{eff} , which compares the hydrodynamic shear stress and the fiber stiffness, is used to analyze the effective flexibility of the fibers. The observations show that the fibers that are more likely to bend exhibit faster migration. As Λ_{eff} increases (softer fibers and stronger shear stresses), the fibers tend to align in the flow direction and the motions of the fibers transition from tumbling and rolling to bending. The bending fibers drift away from the walls to the center plane. Further increasing Λ_{eff} leads to more coiled fiber shapes, and the bending is more frequent and with larger magnitudes, which leads to more rapid migration towards the center. Different behaviors of the fibers are quantified with Λ_{eff} , and the structures and the dynamics of the fibers are correlated with the migration.

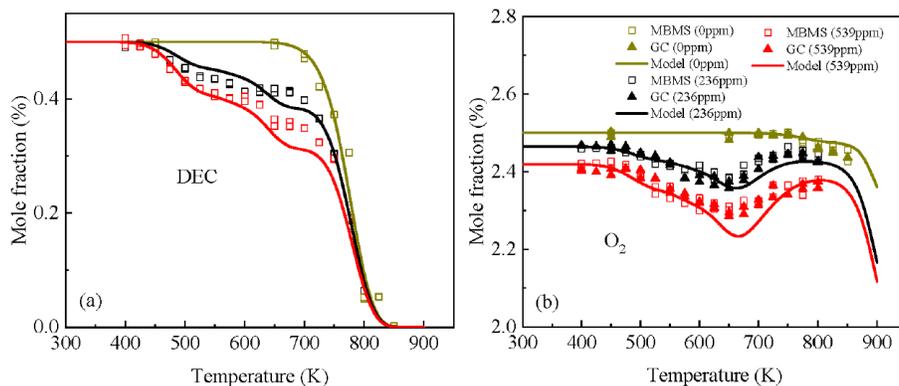
Status: published work in *Soft Matter* 2022, **18**, 514

Studies of Ozone-Sensitized Low- and High-Temperature Oxidations of Diethyl Carbonate

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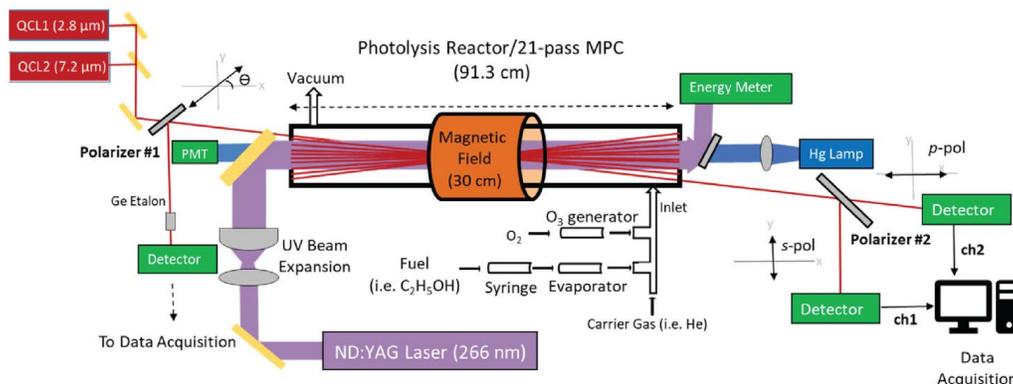


Diethyl carbonate (DEC) oxidation with different levels of O₃ addition was performed in an atmospheric laminar flow reactor from 400 to 850 K. Experimental results showed that, without O₃ addition, the oxidation of DEC began from 650 K with no low-temperature reactivity, while with O₃ addition the low temperature chemistry of DEC was observed from 450 K. A DEC/O₃ kinetic model was developed, and the model predictions agreed with the experimental data reasonably well with a slight overprediction of DEC oxidation between 550 and 750 K. The low-temperature chemistry of DEC with O₃ addition was described in the reaction pathway of DEC. It was found that O₃ assisted the low-temperature oxidation of DEC mainly through the production of the active O: atom instead of the direct reaction with the fuel molecule. The present work indicated that the Li-ion battery degradation at 400–500 K might result from the low-temperature chemistry of DEC with active oxygen supplies from the cathode metal oxide materials or from singlet O₂ during the battery discharge process. This article used O₃ to mimic the oxidizing environment in the Li-ion battery by providing active atomic oxygen. It provided insights into the chemically sensitized gas-phase low-temperature chemistry of DEC and explained the mechanism of battery degradation involving the low-temperature oxidation at the electrolyte solvent and the cathode interface from 400 to 500 K.

Status: published work in *J. Phys. Chem. A* 2021, **125**, 1760

Kinetic studies of excited singlet oxygen atom O(¹D) reactions with ethanol

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The multichannel reaction of excited singlet oxygen atom with ethanol, O(¹D) + C₂H₅OH, was studied in a photolysis flow reactor coupled with mid-infrared Faraday rotation spectroscopy (FRS) and UV-IR direct absorption spectroscopy (DAS) at 297 K with reactor pressures of 60, 120, and 150 Torr (bath He). The excited singlet oxygen atom was generated through the photolysis of O₃ at 266 nm. The photon flux and O(¹D) concentrations were determined by in situ actinometry based on O₃ depletion. Temporal profiles of OH and H₂O were monitored via DAS signals at ca. 3568.62 and 3568.29 cm⁻¹, while temporal profiles of HO₂ were measured via FRS signals at ca. 1396.90 cm⁻¹. The branching ratios of the target reaction were determined by fitting temporal profiles to simulations from an in-house reaction mechanism. Two major reaction channels were identified as CH₃CHOH + OH and CH₃O + CH₂OH, and their branching ratios were determined as 0.46 ± 0.12 and 0.42 ± 0.11, respectively. A specific HO₂ + RO₂ reaction between HO₂ and O₂CH₂CH₂OH (β-RO₂) at the low-temperature range is estimated in this work as HO₂ + O₂CH₂CH₂OH → products with a rate constant of 7 × 10⁻¹² cm³ molecule⁻¹ s⁻¹.

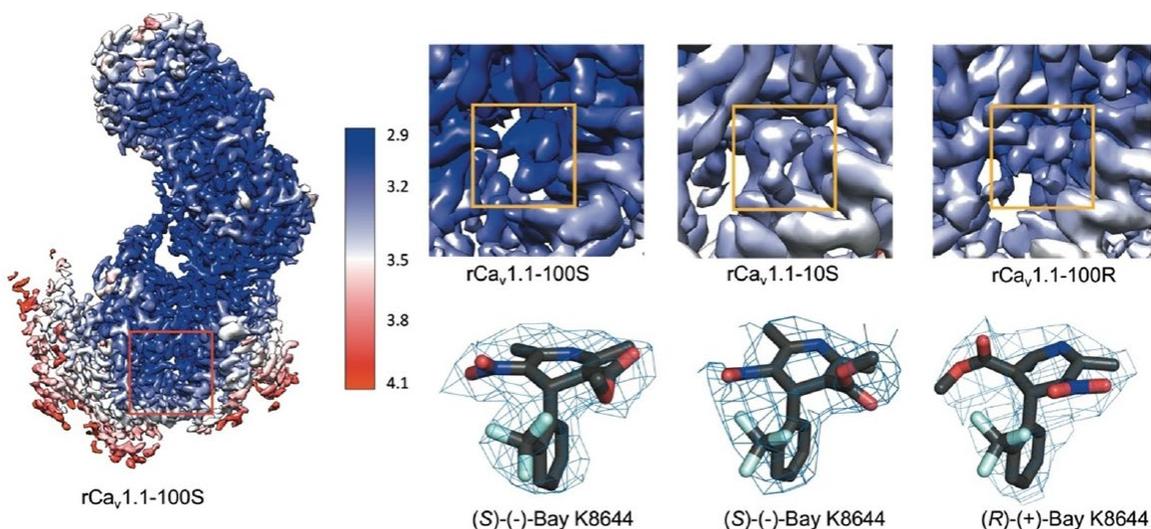
Status: published work in Int. J. Chem. Kinet. 2021, **53**, 688

Department of Molecular Biology

Structural Basis of the Modulation of the Voltage-Gated Calcium Ion Channel $\text{Ca}_v1.1$ by Dihydropyridine Compounds

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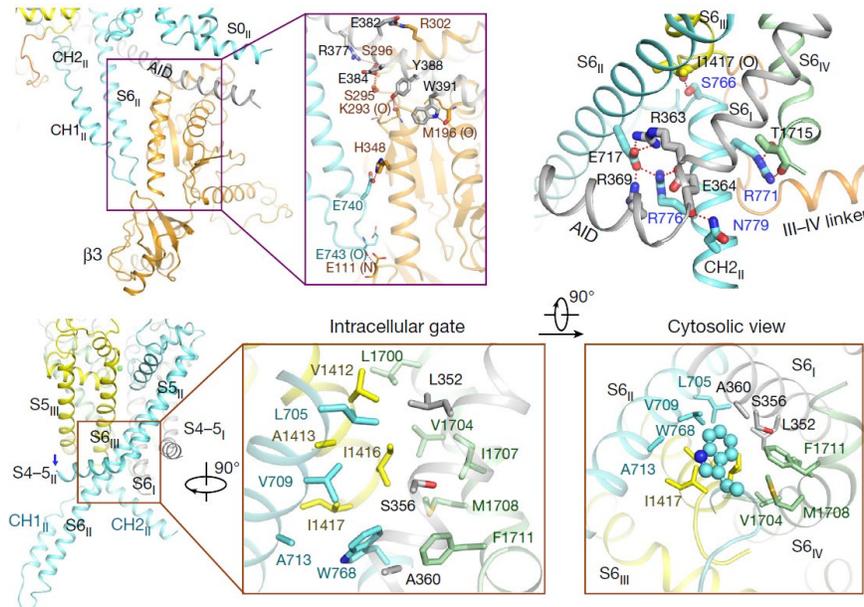
1,4-Dihydropyridines (DHP), the most commonly used antihypertensives, function by inhibiting the L-type voltage-gated Ca^{2+} (Ca_v) channels. DHP compounds exhibit chirality-specific antagonistic or agonistic effects. The structure of rabbit $\text{Ca}_v1.1$ bound to an achiral drug nifedipine reveals the general binding mode for DHP drugs, but the molecular basis for chiral specificity remained elusive. Herein, we report five cryo-EM structures of nanodisc-embedded $\text{Ca}_v1.1$ in the presence of the bestselling drug amlodipine, a DHP antagonist (R)-(+)-Bay K8644, and a titration of its agonistic enantiomer (S)-(-)-Bay K8644 at resolutions of 2.9–3.4 Å. The amlodipine-bound structure reveals the molecular basis for the high efficacy of the drug. All structures with the addition of the Bay K8644 enantiomers exhibit similar inactivated conformations, suggesting that (S)-(-)-Bay K8644, when acting as an agonist, is insufficient to lock the activated state of the channel for a prolonged duration.

Status: published work at *Angewandte Chemie* 2021, **133**, 3168

Structure of human $\text{Ca}_v2.2$ channel blocked by the painkiller ziconotide

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The neuronal-type (N-type) voltage-gated calcium (Ca_v) channels, which are designated $\text{Ca}_v2.2$, have an important role in the release of neurotransmitters. Ziconotide is a $\text{Ca}_v2.2$ -specific peptide pore blocker that has been clinically used for treating intractable pain. Here we present cryo-electron microscopy structures of human $\text{Ca}_v2.2$ (comprising the core $\alpha 1$ and the ancillary $\alpha 2\delta$ -1 and $\beta 3$ subunits) in the presence or absence of ziconotide. Ziconotide is thoroughly coordinated by helices P1 and P2, which support the selectivity filter, and the extracellular loops (ECLs) in repeats II, III and IV of $\alpha 1$. To accommodate ziconotide, the ECL of repeat III and $\alpha 2\delta$ -1 have to tilt upward concertedly. Three of the voltage-sensing domains (VSDs) are in a depolarized state, whereas the VSD of repeat II exhibits a down conformation that is stabilized by Ca_v2 -unique intracellular segments and a phosphatidylinositol 4,5-bisphosphate molecule. Our studies reveal the molecular basis for $\text{Ca}_v2.2$ -specific pore blocking by ziconotide and establish the framework for investigating electromechanical coupling in Ca_v channels.

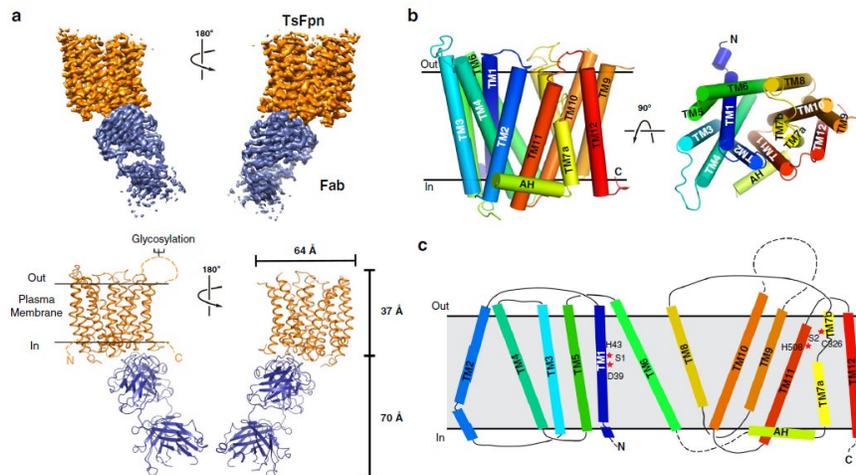
Status: published work at Nature 2021, **596**, 143

Structural basis of ion transport and inhibition in ferroportin

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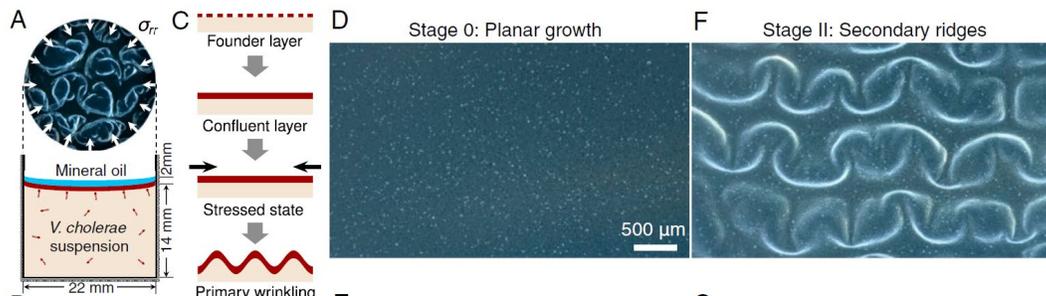
Ferroportin is an iron exporter essential for releasing cellular iron into circulation. Ferroportin is inhibited by a peptide hormone, hepcidin. In humans, mutations in ferroportin lead to ferroportin diseases that are often associated with accumulation of iron in macrophages and symptoms of iron deficiency anemia. Here we present the structures of the ferroportin from the primate Philippine tarsier (TsFpn) in the presence and absence of hepcidin solved by cryo-electron microscopy. TsFpn is composed of two domains resembling a clamshell and the structure defines two metal ion binding sites, one in each domain. Both structures are in an outward-facing conformation, and hepcidin binds between the two domains and reaches one of the ion binding sites. Functional studies show that TsFpn is an electroneutral H^+/Fe^{2+} antiporter so that transport of each Fe^{2+} is coupled to transport of two H^+ in the opposite direction. Perturbing either of the ion binding sites compromises the coupled transport of H^+ and Fe^{2+} . These results establish the structural basis of metal ion binding, transport and inhibition in ferroportin and provide a blueprint for targeting ferroportin in pharmacological intervention of ferroportin diseases.

Status: published work at Nature Communications 2020, **11**, 5686

Hierarchical transitions and fractal wrinkling drive bacterial pellicle morphogenesis

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Bacterial cells can self-organize into structured communities at fluid–fluid interfaces. These soft, living materials composed of cells and extracellular matrix are called pellicles. Cells residing in pellicles garner group-level survival advantages such as increased antibiotic resistance. The dynamics of pellicle formation and, more generally, how complex morphologies arise from active biomaterials confined at interfaces are not well understood. Here, using *Vibrio cholerae* as our model organism, a custom-built adaptive stereo microscope, fluorescence imaging, mechanical theory, and simulations, we report a fractal wrinkling morphogenesis program that differs radically from the well-known coalescence of wrinkles into folds that occurs in passive thin films at fluid–fluid interfaces. Four stages occur: growth of founding colonies, onset of primary wrinkles, development of secondary curved ridge instabilities, and finally the emergence of a cascade of finer structures with fractallike scaling in wavelength. The time evolution of pellicle formation depends on the initial heterogeneity of the film microstructure. Changing the starting bacterial seeding density produces three variations in the sequence of morphogenic stages, which we term the bypass, crystalline, and incomplete modes. Despite these global architectural transitions, individual microcolonies remain spatially segregated, and thus, the community maintains spatial and genetic heterogeneity. Our results suggest that the memory of the original microstructure is critical in setting the morphogenic dynamics of a pellicle as an active biomaterial.

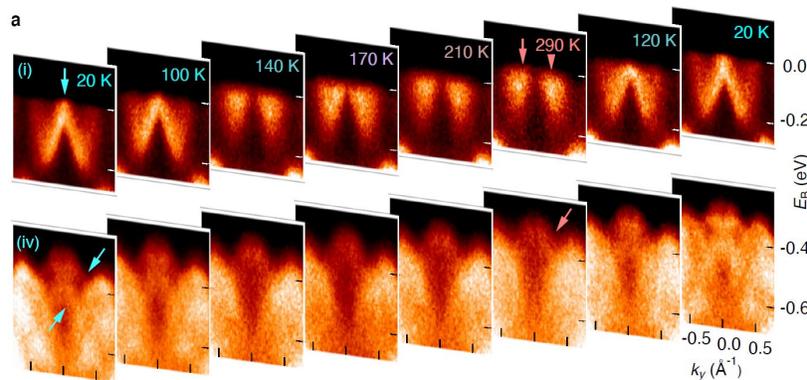
Status: published work in PNAS 2021, **118**, e2023504118

Department of Physics

Signatures of magnetic Weyl fermion annihilation

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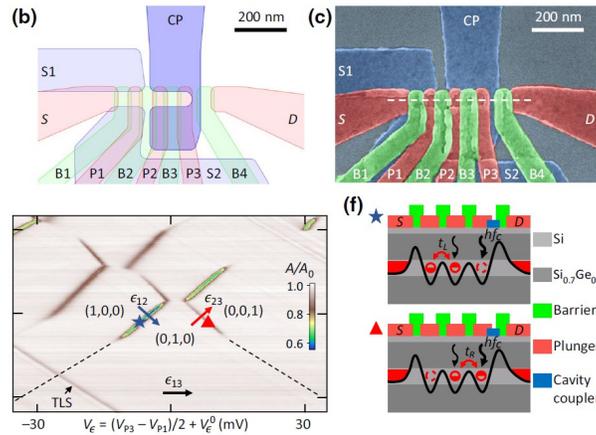
Correlated topological magnets are emerging as a new class of quantum materials, exhibiting exotic interacting fermions and unconventional phase transitions. Despite considerable interest, direct observation of the magnetic manipulation of topological quasiparticles remains limited. Here we report a correlated topological phase transition in a kagome spin-orbit semimetal, examined by high-resolution photoemission spectroscopy. By modulating the magnetic order, we observe a clear exchange gap collapse in our spectra, associated with a large renormalization of a spin-orbit-gapped Weyl loop at the Fermi level. This unexpected response suggests the collapse of opposite-spin partner ferromagnetic Weyl loops into a paramagnetic Dirac loop. Taken together with *ab initio* calculation, our results further indicate that oppositely-charged Weyl points pair up and annihilate under collapse, and the Fermi arc surface states are removed. Our findings suggest a novel topological phase transition driven by magnetic interactions, guiding future exploration of renormalized topology under correlated order parameters.

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Probing the Variation of the Intervalley Tunnel Coupling in a Silicon Triple Quantum Dot

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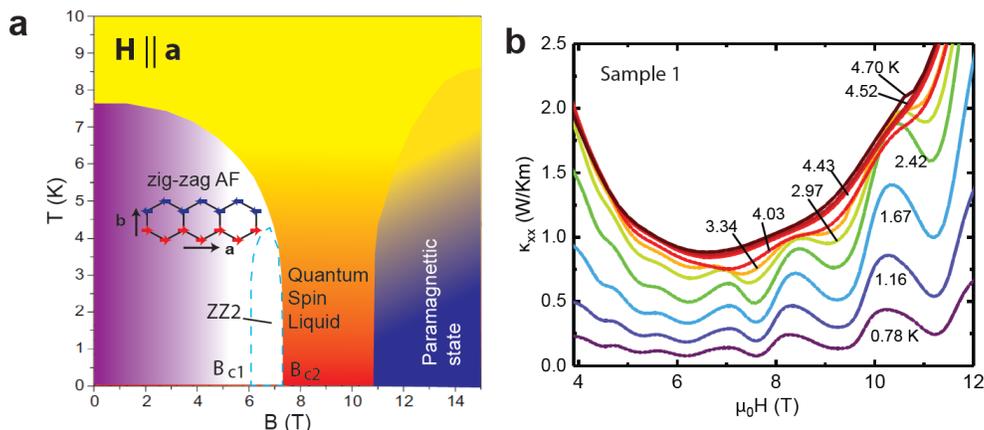
Electrons confined in silicon quantum dots exhibit orbital, spin, and valley degrees of freedom. The valley degree of freedom originates from the bulk band structure of silicon, which has six degenerate electronic minima. The degeneracy can be lifted in silicon quantum wells due to strain and electronic confinement, but the “valley splitting” of the two lowest-lying valleys is known to be sensitive to atomic scale disorder. Large valley splittings are desirable to have a well-defined spin qubit. In addition, an understanding of the intervalley tunnel coupling that couples different valleys in adjacent quantum dots is important, as the resulting gaps in the energy-level diagram may affect the fidelity of charge and spin-transfer protocols in silicon quantum-dot arrays. Here we use microwave spectroscopy to probe variations in the valley splitting, and the intra- and intervalley tunnel couplings that couple dots i and j in a triple quantum dot. We uncover large variations in the ratio of intervalley to intravalley tunnel couplings $t'_{12}/t_{12} = 0.90$ and $t'_{23}/t_{23} = 0.56$. By tuning the interdot tunnel barrier we also show that t'_{ij} scales linearly with t_{ij} , as expected from theory. The results indicate strong interactions between different valley states on neighboring dots, which we attribute to local inhomogeneities in the silicon quantum well.

Status: published work at PRX Quantum 2021, **2**, 020309

Oscillations of the thermal conductivity observed in the spin-liquid state of α -RuCl₃

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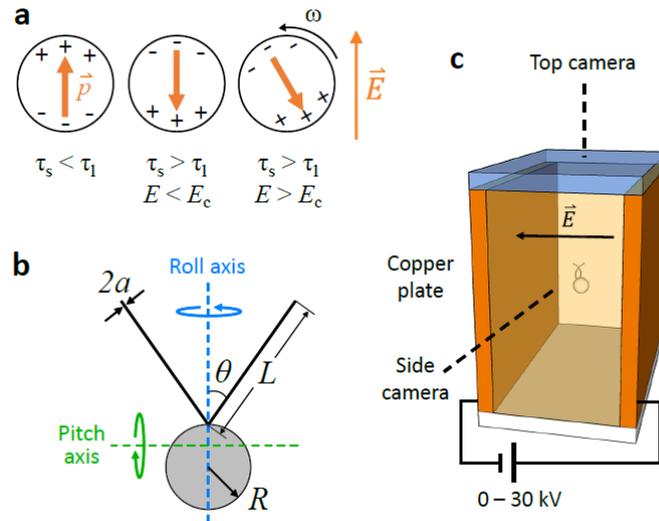
In the class of materials called spin liquids, a magnetically ordered state cannot be attained even at milliKelvin temperatures because of conflicting constraints on each spin. The resulting quantum spin-liquid (QSL) state is currently of intense interest because it exhibits novel excitations as well as wave-function entanglement. The layered insulator α -RuCl₃ orders as a zigzag antiferromagnet below ~ 7 K in zero magnetic field. The zigzag order is destroyed when a magnetic field H is applied parallel to the zigzag axis a . Within the field interval (7.3, 11) Tesla, there is growing evidence that a QSL state exists. Here we report the observation of oscillations in its thermal conductivity below 4 K. The oscillation amplitude is very large within the interval (7.3, 11) T and strongly suppressed on either side. Paradoxically, the oscillations are periodic in $1/H$, analogous to quantum oscillations in metals, even though α -RuCl₃ is an excellent insulator with a gap of 1.9 eV. By tilting H out of the plane, we find that the oscillation period is determined by the in-plane component H_a . As the temperature is raised above 0.5 K, the oscillation amplitude decreases exponentially. The decrease anticorrelates with the emergence above ~ 2 K of an anomalous planar thermal Hall conductivity measured with $H \parallel a$. To exclude extrinsic artifacts, we carried out several tests. The implications of the oscillations are discussed.

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Low-Reynolds-number, bi-flagellated Quincke swimmers with multiple forms of motion

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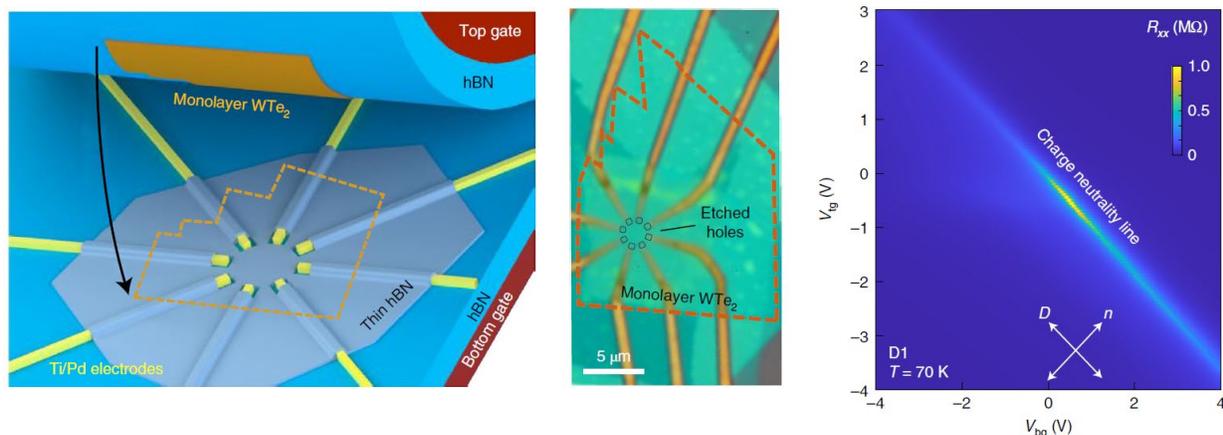
In the limit of zero Reynolds number (Re), swimmers propel themselves exploiting a series of non-reciprocal body motions. For an artificial swimmer, a proper selection of the power source is required to drive its motion, in cooperation with its geometric and mechanical properties. Although various external fields (magnetic, acoustic, optical, etc.) have been introduced, electric fields are rarely utilized to actuate such swimmers experimentally in unbounded space. Here we use uniform and static electric fields to demonstrate locomotion of a bi-flagellated sphere at low Re via Quincke rotation. These Quincke swimmers exhibit three different forms of motion, including a self-oscillatory state due to elasto-electro-hydrodynamic interactions. Each form of motion follows a distinct trajectory in space. Our experiments and numerical results demonstrate a new method to generate, and potentially control, the locomotion of artificial flagellated swimmers.

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Evidence for a monolayer excitonic insulator

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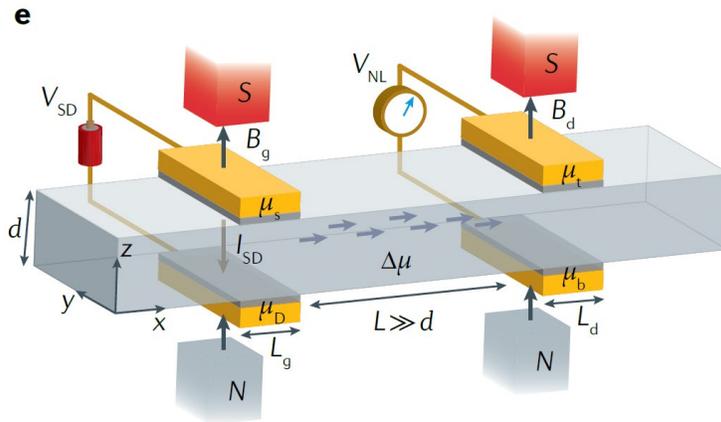
The interplay between topology and correlations can generate a variety of quantum phases, many of which remain to be explored. Recent advances have identified monolayer WTe_2 as a promising material for doing so in a highly tunable fashion. The ground state of this two-dimensional crystal can be electrostatically tuned from a quantum spin Hall insulator to a superconductor. However, much remains unknown about the gap-opening mechanism of the insulating state. Here we report evidence that the quantum spin Hall insulator is also an excitonic insulator, arising from the spontaneous formation of electron–hole bound states, namely excitons. We reveal the presence of an intrinsic insulating state at the charge neutrality point in clean samples and confirm the correlated nature of this charge-neutral insulator by tunnelling spectroscopy. We provide evidence against alternative scenarios of a band insulator or a localized insulator and support the existence of an excitonic insulator phase in the clean limit. These observations lay the foundation for understanding a new class of correlated insulators with nontrivial topology and identify monolayer WTe_2 as a promising candidate for exploring quantum phases of ground-state excitons.

Status: published work in Nature Physics 2021, **XX**, XXX

Experimental signatures of the chiral anomaly in Dirac–Weyl semimetals

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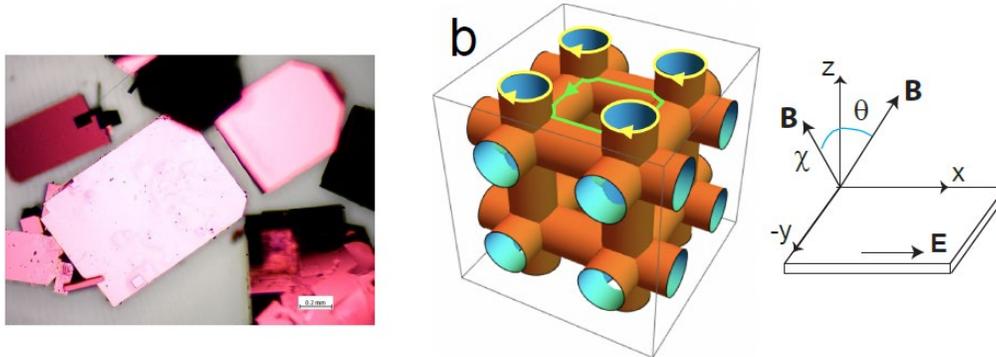
In condensed matter, the chiral anomaly describes the conversion of left- moving Dirac–Weyl fermions to right- moving ones in parallel electric and magnetic fields. The resulting axial current leads to an unusual negative longitudinal magnetoresistance (LMR). Five years ago, the discovery of Dirac and Weyl semimetals led to many experiments investigating this phenomenon. In this Review, we critically assess LMR experiments in the Dirac–Weyl semimetals Na_3Bi , GdPtBi , ZrTe_5 , Cd_3As_2 and TaAs , which have shown signatures of the chiral anomaly, and discuss possible current- jetting artefacts. The focus is on Dirac and Weyl nodes that are rigorously symmetry protected. Other experiments, such as non- local transport, thermopower, thermal conductivity and optical pump–probe response, are also reviewed. Looking ahead, we anticipate what can be gleaned from improved LMR experiments and new experiments on the thermal conductivity and optical response.

Status: published work in *Nature Rev. Phys.* 2021, **3**, 394

Singular angular magnetoresistance and sharp resonant features in a high-mobility metal with open orbits, ReO_3

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We report high-resolution angular magnetoresistance (AMR) experiments performed on crystals of ReO_3 with high mobility ($90,000 \text{ cm}^2/\text{Vs}$ at 2 K) and extremely low residual resistivity ($5\text{-}8 \text{ n}\Omega\text{cm}$). The Fermi surface, comprised of intersecting cylinders, supports open orbits. The resistivity ρ_{xx} in a magnetic field $B = 9 \text{ T}$ displays a singular pattern of behavior. With $E \parallel x$ and B initially $\parallel z$, tilting B in the longitudinal $k_z\text{-}k_x$ plane leads to a steep decrease in ρ_{xx} by a factor of 40. However, if B is tilted in the transverse $k_y\text{-}k_z$ plane, ρ_{xx} increases steeply by a factor of 8. Using the Shockley tube integral approach, we show that, in ReO_3 , the singular behavior results from the rapid conversion of closed to open orbits, resulting in opposite signs for AMR in orthogonal planes. The floor values of ρ_{xx} in both AMR scans are identified with specific sets of open and closed orbits. Also, the “completion angle” γ_c detected in the AMR is shown to be an intrinsic geometric feature that provides a new way to measure the Fermi radius k_F . However, additional sharp resonant features which appear at very small tilt angles in the longitudinal AMR scans are not explained by the tube integral approach.

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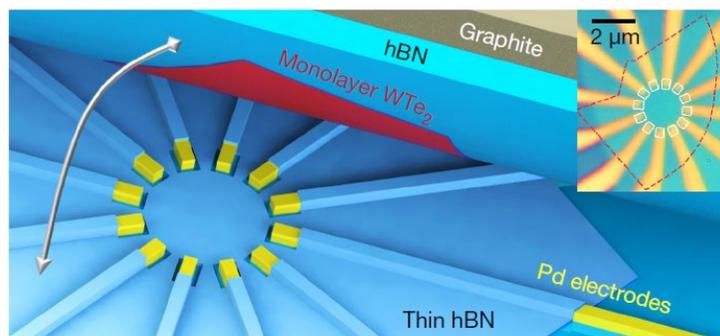
Landau quantization and highly mobile fermions in an insulator

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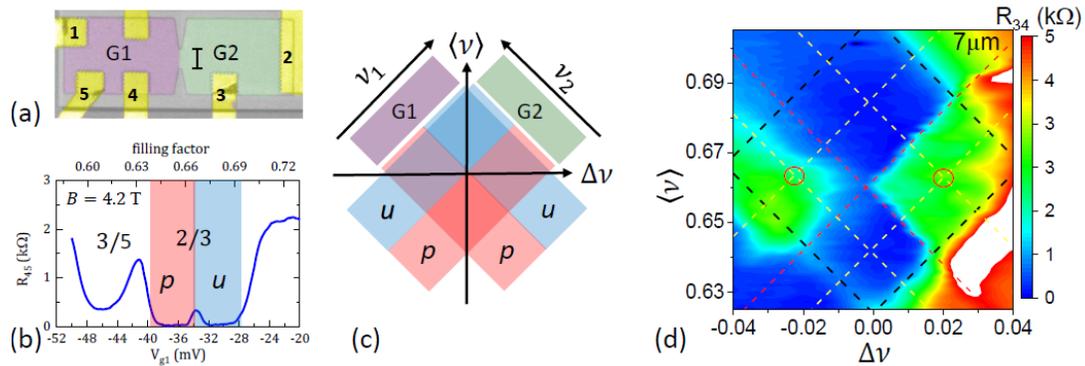
In strongly correlated materials, quasiparticle excitations can carry fractional quantum numbers. An intriguing possibility is the formation of fractionalized, charge-neutral fermions—for example, spinons and fermionic excitons—that result in neutral Fermi surfaces and Landau quantization in an insulator. Although previous experiments in quantum spin liquids, topological Kondo insulators and quantum Hall systems have hinted at charge-neutral Fermi surfaces, evidence for their existence remains inconclusive. Here we report experimental observation of Landau quantization in a two-dimensional insulator, monolayer tungsten ditelluride (WTe_2), a large-gap topological insulator. Using a detection scheme that avoids edge contributions, we find large quantum oscillations in the material's magnetoresistance, with an onset field as small as about 0.5 tesla. Despite the huge resistance, the oscillation profile, which exhibits many periods, mimics the Shubnikov–de Haas oscillations in metals. At ultralow temperatures, the observed oscillations evolve into discrete peaks near 1.6 tesla, above which the Landau quantized regime is fully developed. Such a low onset field of quantization is comparable to the behaviour of high-mobility conventional two-dimensional electron gases. Our experiments call for further investigation of the unusual ground state of the WTe_2 monolayer, including the influence of device components and the possible existence of mobile fermions and charge-neutral Fermi surfaces inside its insulating gap.

Status: published work in Nature 2021, **589**, 225

Transport in helical Luttinger liquids in the fractional quantum Hall regime

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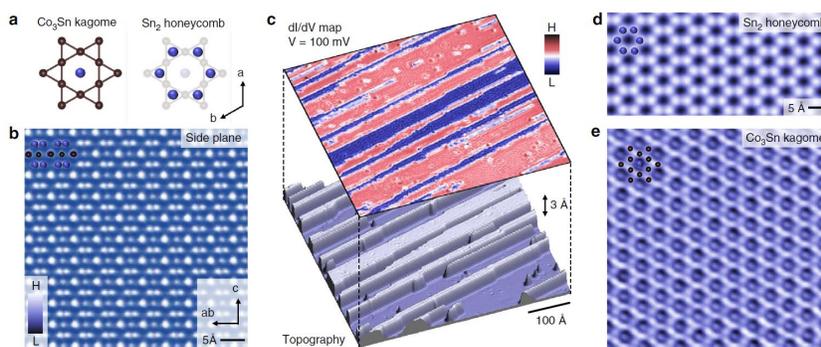
Domain walls in fractional quantum Hall ferromagnets are gapless helical one-dimensional channels formed at the boundaries of topologically distinct quantum Hall (QH) liquids. Naively, these helical domain walls (hDWs) constitute two counter-propagating chiral states with opposite spins. Coupled to an s-wave superconductor, helical channels are expected to lead to topological superconductivity with high order non-Abelian excitations. Here we investigate transport properties of hDWs in the $\nu = 2/3$ fractional QH regime. Experimentally we found that current carried by hDWs is substantially smaller than the prediction of the naive model. Luttinger liquid theory of the system reveals redistribution of currents between quasiparticle charge, spin and neutral modes, and predicts the reduction of the hDW current. Inclusion of spin-non-conserving tunneling processes reconciles theory with experiment. The theory confirms emergence of spin modes required for the formation of fractional topological superconductivity.

Status: published work in Nature Communications 2021, **12**, 5312

Fermion–boson many-body interplay in a frustrated kagome paramagnet

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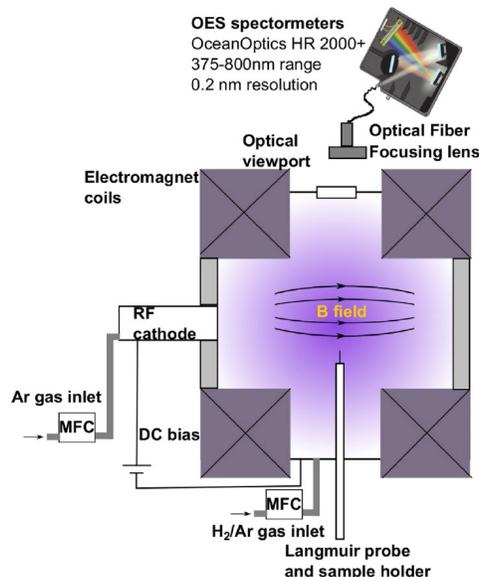
Kagome-nets, appearing in electronic, photonic and cold-atom systems, host frustrated fermionic and bosonic excitations. However, it is rare to find a system to study their fermion–boson many-body interplay. Here we use scanning tunneling microscopy/spectroscopy to discover unusual electronic coupling to flat-band phonons in a layered kagome paramagnet, CoSn. We image the kagome structure with atomic resolution and observe the bosonic mode interacting with dispersive kagome electrons near the Fermi surface. The fermionic quasi-particle dispersion exhibits a pronounced renormalization, signaling a giant coupling to bosons. Through the selfenergy analysis, first-principles calculation, and a lattice vibration model, we present evidence that this mode arises from the geometrically frustrated phonon flat-band. Our findings provide the first example of kagome bosonic mode (flat-band phonon) in electronic excitations and its strong interaction with fermionic degrees of freedom in kagome-net materials.

Status: published work at Nature Communications 2020, **11**, 4003

High hydrogen coverage on graphene via low temperature plasma with applied magnetic field

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The chemical functionalization of two-dimensional materials is an effective method for tailoring their chemical and electronic properties with applications in energy, catalysis, and electronics. One exemplary 2D material, graphene, can be exploited for hydrogen storage and large on/off ratio devices by hydrogen termination. In this work, we describe a promising plasma-based method to provide high hydrogen coverage on graphene. A low pressure (~ 10 mtorr) discharge generates a fine-tunable low-temperature hydrogen-rich plasma in the applied radial electric and axial magnetic fields. Post-run characterization of these samples using Raman and X-ray photoelectron spectroscopy demonstrates a higher hydrogen coverage, 35.8%, than the previously reported results using plasmas. Plasma measurements indicate that with the applied magnetic field, the density of hydrogen atoms can be more than 10 times larger than the density without the magnetic field. With the applied electric field directed away from the graphene substrate, the flux of plasma ions towards this substrate and the ion energy are insufficient to cause measurable damage to the treated 2D material. The low damage allows a relatively long treatment time of the graphene samples that contributes to the high coverage obtained in these experiments.

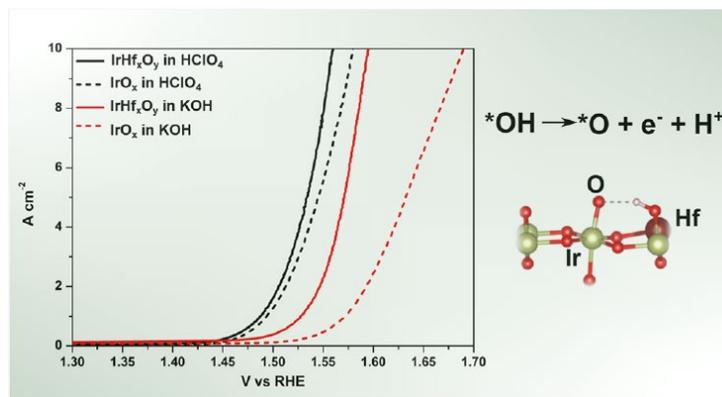
Status: published work at Carbon 2021, **177**, 244

Increasing Iridium Oxide Activity for the Oxygen Evolution Reaction with Hafnium Modification

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Synthesis and implementation of highly active, stable, and affordable electrocatalysts for the oxygen evolution reaction (OER) is a major challenge in developing energy efficient and economically viable energy conversion devices such as electrolyzers, rechargeable metal-air batteries, and regenerative fuel cells. The current benchmark electrocatalyst for OER is based on iridium oxide (IrO_x) due to its superior performance and excellent stability. However, large scale applications using IrO_x are impractical due to its low abundance and high cost. Herein, we report a highly active hafnium-modified iridium oxide (IrHf_xO_y) electrocatalyst for OER. The IrHf_xO_y electrocatalyst demonstrated ten times higher activity in alkaline conditions ($\text{pH} = 11$) and four times higher activity in acid conditions ($\text{pH} = 1$) than a IrO_x electrocatalyst. The highest intrinsic mass activity of the IrHf_xO_y catalyst in acid conditions was calculated as $6950\text{ A g}_{\text{IrO}_x}^{-1}$ at an overpotential (η) of 0.3 V. Combined studies utilizing operando surface enhanced Raman spectroscopy (SERS) and DFT calculations revealed that the active sites for OER are the Ir–O species for both IrO_x and IrHf_xO_y catalysts. The presence of Hf sites leads to more negative charge states on nearby O sites, shortening of the bond lengths of Ir–O, and lowers free energies for OER intermediates that accelerate the OER process.

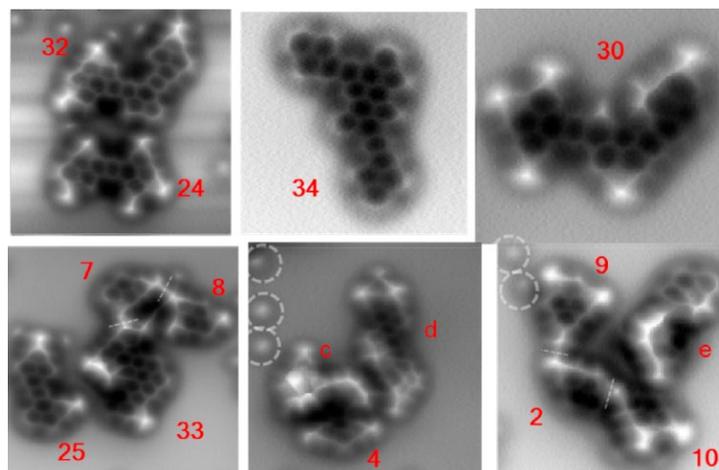
Status: published work at JACS 2021, **143**, 15616

**Princeton Institute for the Science and Technology of
Materials (PRISM)**

The Role of Methyl Groups in the Early Stage of Thermal Polymerization of Polycyclic Aromatic Hydrocarbons Revealed by Molecular Imaging

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The initial thermal reactions of aromatic hydrocarbons are relevant to many industrial applications. However, tracking the growing number of heavy polycyclic aromatic hydrocarbon (PAH) products is extremely challenging because many reactions are unfolding in parallel from a mixture of molecules. Herein, we studied the reactions of 2,7-dimethylpyrene (DMPY) to decipher the roles of methyl substituents during mild thermal treatment. We found that the presence of methyl substituents is key for reducing the thermal severity required to initiate chemical reactions in natural molecular mixtures. A complex mixture of thermal products including monomers, dimers, and trimers was characterized by NMR, mass spectrometry, and noncontact atomic force microscopy (nc-AFM). A wide range of structural transformations including methyl transfer and polymerization reactions were identified. A detailed mechanistic understanding on the roles of H radicals during the polymerization of polycyclic aromatic hydrocarbons was obtained.

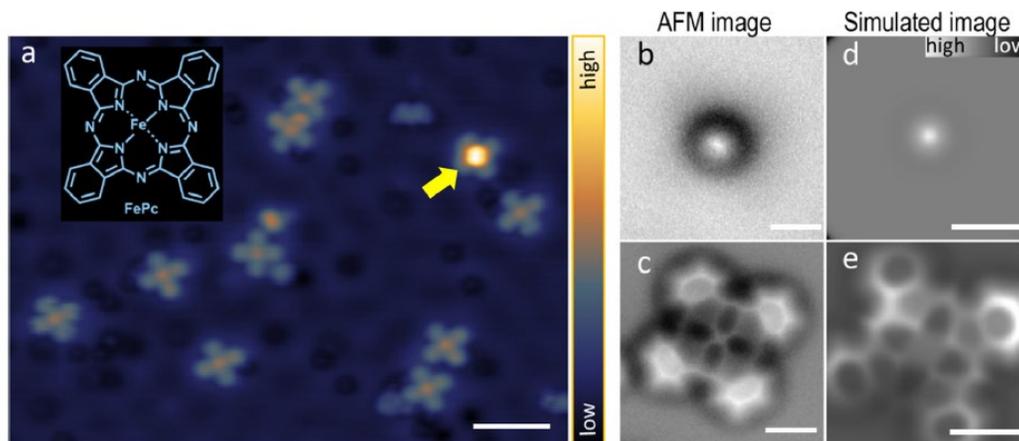
Status: published work at Energy and Fuels 2021, **35**, 2224

Breaking a dative bond with mechanical forces

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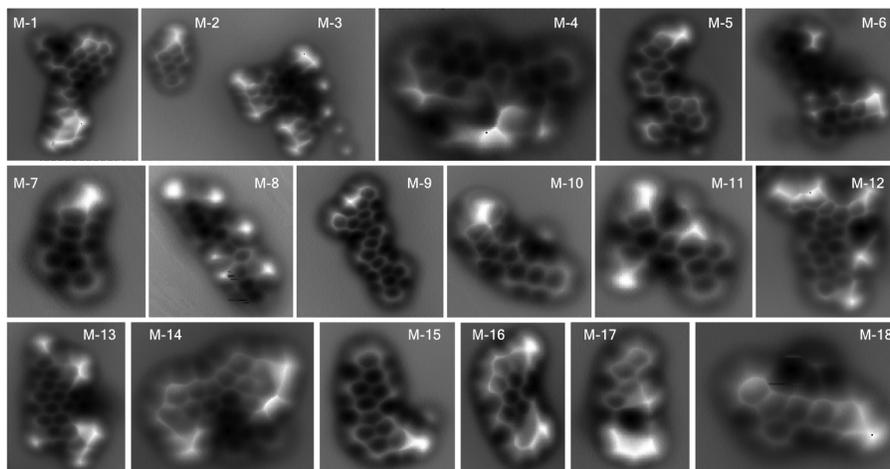
Bond breaking and forming are essential components of chemical reactions. Recently, the structure and formation of covalent bonds in single molecules have been studied by noncontact atomic force microscopy (AFM). Here, we report the details of a single dative bond breaking process using non-contact AFM. The dative bond between carbon monoxide and ferrous phthalocyanine was ruptured via mechanical forces applied by atomic force microscope tips; the process was quantitatively measured and characterized both experimentally and via quantum-based simulations. Our results show that the bond can be ruptured either by applying an attractive force of ~ 150 pN or by a repulsive force of ~ 220 pN with a significant contribution of shear forces, accompanied by changes of the spin state of the system. Our combined experimental and computational studies provide a deeper understanding of the chemical bond breaking process.

Status: published work in Nature Comms. 2021, **12**, 5635

Ex Situ and In Situ Thermal Transformations of M-50 Pitch Revealed by Non-contact Atomic Force Microscopy

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Petroleum pitch M-50 (or A-240) has been well-known in making valuable carbon materials through thermal treatments. How these molecules react to produce carbon materials and the mechanisms of thermal polymerization and molecular weight growth under thermal conditions are of great significance and yet still unclear. Structures produced by thermal reactions of M-50 pitch were characterized with noncontact atomic force microscopy and compared to the structures in M-50 pitch previously characterized. Reaction products were generated from M-50 pitch by two different approaches: an ex situ approach via thermal treatment at 400 °C under N₂ and an in situ approach via reaction directly on a Cu(111) surface. Polycyclic aromatic hydrocarbons (PAHs) from the ex situ reaction are larger than those in the starting M-50 pitch and with fewer methyl groups. Both types of five membered rings, conjugated and non-conjugated, are observed. Very large PAHs are formed under the *in situ* surface conditions as a result of reactions catalyzed by the Cu surface, with five-membered rings preserved as planar moieties in the product. The data suggest that methyl groups play important roles in initiating the polymerization and molecular weight growth of M-50 pitch molecules, but the reactivities of five-membered rings remain unclear.

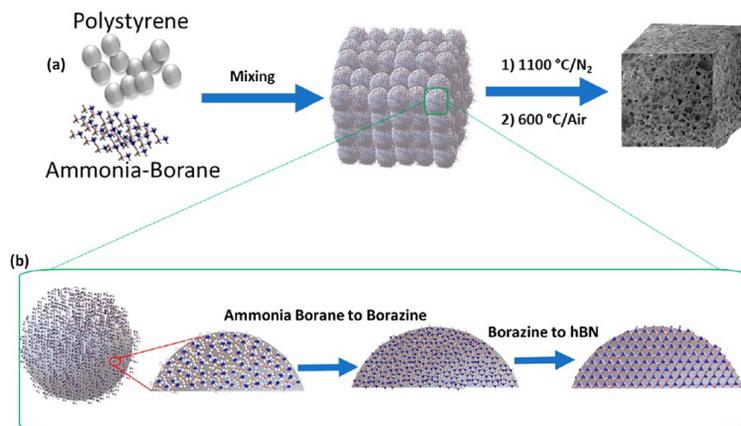
Status: published work in Energy and Fuels 2021, **35**, 18210

Interfacial Engineering to Tailor the Properties of Multifunctional Ultralight Weight hBN-Polymer Composite Aerogels

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A common feature of aerogels is that they are brittle and suffer from poor mechanical properties. The development of high-performance, lightweight, and mechanically robust polymer composite aerogels may find use in a broad range of applications such as packaging, transportation, construction, electronics, and aerospace. Most aerogels are made of ceramic materials, such as silica, alumina, and carbide. These aerogels are dense and brittle. Two-dimensional (2D) layered nanostructures such as graphene, graphene oxide and hexagonal boron nitride (hBN) have promising potential in emerging technologies. Here, we report the development of highly porous, ultralightweight, and flexible aerogel composites made by the infiltration of various polymers into 2D hBN aerogels. The 2D hBN aerogels in which pore size could be controlled were fabricated using a unique self-assembly approach involving polystyrene nanoparticles as templates for ammonia borane into desired structures. We have shown that the physical, mechanical, and thermal properties of hBN-polymer composite aerogels can be tuned by the infiltration of different additives. We also performed theoretical calculations to gain insight into the interfacial interactions between the hBN-polymer structure, as the interface is critical in determining key material properties.

Status: published work at ACS Appl. Mater. Interfaces 2021, **13**, 13620

Graphene-based catalyst for CO₂ reduction: The critical role of solvents in materials design

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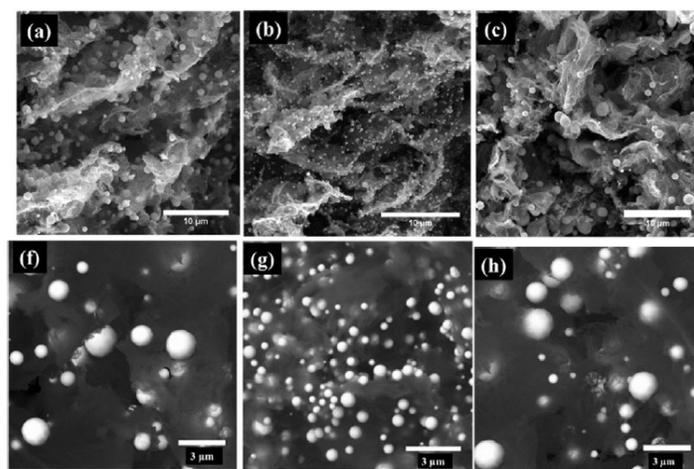
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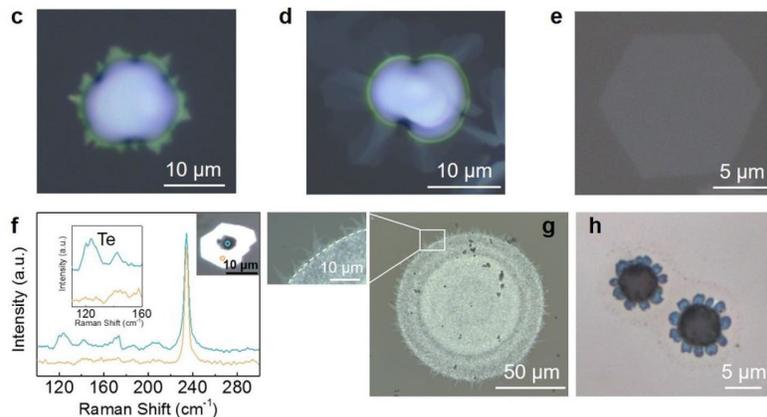
The catalytic reduction of carbon dioxide (CO₂) to hydrocarbon fuels offers a tremendous opportunity for a transformational impact on both global energy and environmental sustainability. To enhance the CO₂ reduction process, the design and synthesis of novel and catalytic materials. The solvent used in the synthesis of these materials can play a crucial role in tailoring the material properties resulting in changes to their catalytic performance. However, the field still lacks a systematic analysis of the specific effect for different solvents. Here, we report the role of water, ethanol (EtOH), ethylene glycol (EG), Dimethylformamide (DMF), and *c*-Butyrolactone (GBL) on the synthesis of reduced graphene oxide (rGO)-copper nanoparticles (CuNP) electrocatalysts used in CO₂ reduction reactions (CO₂RR). As these solvents contain different terminal groups, we observed a variation in the d-spacing of the rGO, surface area, nanoparticle yield, and defect density, and characterized the corresponding change in the CO₂RR activity. The use of DMF results in higher porosity, d-spacing, yield of CuNP, surface area and defect density which lead to higher efficiency and selectivity of 19.5% and 28.4% for formate and CO, respectively.

Status: published work at Journal of Catalysis 2021, **404**, 512

Liquid-vapor Growth of Atomically Thin Metal Tellurides with Controllable Polymorphism

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Atomically thin transition metal dichalcogenides (TMDs), together with their polymorphism, provide promising alternatives for next generation electronic devices and a platform to explore exotic quantum phenomena. However, a large-scale synthesis method that can reliably produce high-quality two-dimensional (2D) TMDs with controlled phase is still lacking. Instead, TMDs with high concentration of defects and defect-stabilized metastable crystalline phases are often obtained via conventional chemical vapor deposition. Here we developed a liquid-vapor (LV) technique to exploit liquid precursors to suppress the equilibrium shift to the decomposition direction and successfully synthesized high-quality TMDs. We highlight the importance of exploiting the synergism of equilibrium and kinetics to facilitate the synthesis reaction (forward) and to impede decomposition (reverse). We demonstrated the advantages of LV method by synthesizing diverse high-quality 2D metal tellurides with controllable polymorphs, which would be challenging, if not impossible, to realize by using conventional methods due to weak metal-tellurium bonds, thermal instability and the co-existence of mixed crystalline phases. In particular, we successfully synthesized high-quality monolayer 2H MoTe₂, which is only possible when Te defect level is suppressed. Our approach provides a new paradigm in high-quality and largescale materials synthesis and can be readily extended to a variety of quantum materials.

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