

Research Report

Imaging and Analysis Center PMI PMI PRINCETON UNIVERSITY

2022



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A MESSAGE FROM THE DIRECTORS

Dear Friends of the Imaging and Analysis Center,

The Imaging and Analysis Center (IAC) in the Princeton Materials Institute (PMI) offers high-end, state-of-the-art instrumentation and expertise for characterization of hard, soft, and biological materials to stimulate research and education at Princeton University and beyond. The IAC houses and operates a full range of instruments employing visible photons, electrons, ions, X-rays, and scanning probe microscopy for the physical examination and analysis of complex materials. With ~30 years of continuous support from Princeton University, as well as the National Science Foundation, the Air Force Office of Scientific Research, the Office of Naval Research, the State of New Jersey, industrial companies, etc., the IAC has become the largest central facility at Princeton and a world leader in advanced materials characterization.

A central mission of the IAC is the education, research, and training of students at Princeton University. The IAC supports more than ten regular courses annually. The award-winning course, MSE505-Characterization of Materials is conducted at the IAC for both graduate and undergraduate students. The IAC also offers a full range of training courses, which involve direct experimental demonstrations and hands-on instruction ranging from basic sample preparation, to the operation of high-end electron microscopes. The IAC's short courses have drawn over 4,500 student enrollments. Additionally, over 700 industrial scientists from more than 140 companies and 40 institutions have utilized instruments in the IAC. Our efforts have helped build bridges between Princeton and Industry that have fostered many innovations and new product developments.

Recent IAC internal users include over 350 students and researchers from more than 90 research groups. The IAC supports ~240 current research contracts worth a total of ~\$450M. In the IAC, undergraduate students are provided with the opportunity to operate various electron microscopes during class and later utilize these instruments in research for their senior thesis. The research experience provided by the IAC has helped students win many national awards including the Fannie and John Hertz Foundation Fellowship, Rhodes Scholarship, Barry M. Goldwater National Scholarship, Fulbright Scholarship, National Science Foundation Graduate Research Fellowship, etc.

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

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

Olla

Nan Yao, Director, Imaging and Analysis Center

Chilur G. high

Richard A. Register, Director, Princeton Materials Institute

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.

Imaging and Analysis Center

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

Ceramics and Glasses

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

Polymers

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

Metal Alloys

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

Pharmaceutical Materials

drug coating, toothpaste, molecular crystals, etc.

Imaging and Analysis Center (IAC)

IAC Background: 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.





IAC team members:





John Schreiber



Paul Shac







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Electrical & Computer Eng.

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School of Architecture Forrest Meggers IAC outside users from industry and other universities:



IAC hosted the 2nd Princeton-Nature Conference "Frontiers in Electron Microscopy for the Physical and Life Sciences", partnered with the scientific publisher – *Nature*. (IAC created this program with *Nature* and hosted its first conference in 2018)



IAC new instrumentation highlights:

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



(2) Xenocs Xeuss 3.0 Small-angle X-ray Scattering System (SAXS) (funds from Princeton Center for Complex Materials (PCCM), a National Science Foundation (NSF) Materials Research Science and Engineering Center (MRSEC; DMR-2011750).



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.

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Andlinger Center for Energy and Environment

A data-driven ray tracing simulation for mean radiant temperature and spatial variations in the indoor radiant field with experimental validation

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A data-driven simulation technique is proposed for the calculation of the 3-dimensional radiant temperature distribution across a room with the aid of a ray tracing method. The proposed simulation accounts for interreflections of radiant heat fluxes from surfaces reflective in the longwave range within the indoor environment. The simulation provides results which include high-resolution spatial radiant field maps for indoor spaces as well as human body mapping for radiant heat fluxes received by different body segments, depending on the bodily position of a person in space. The simulation technique is validated with a physical experiment in a controlled climate chamber, where a heat-flux sensor array is used to measure the mean radiant temperature (MRT) by measuring the average plane radiant temperature in 6 directions at multiple points in space. The results for the experiment show excellent agreement between the simulated and measured results. The simulation allows one to resolve and visualize spatial variations of the radiant field, identify impact of radiant asymmetry and surface materials on the room's irradiation distribution as well as the variations on the human body in different positions and orientations.

Status: published work in Energy Buildings 2022, 254, 111585

Design of UV-Absorbing Donor Molecules for Nearly Imperceptible Organic Solar Cells

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Transparent photovoltaic cells are an emerging technology that can provide point-of-use electricity generation for building-integrated applications. While most transparent solar cells to date target absorption of the photon-rich near-infrared portion of the solar spectrum, these devices compromise color neutrality and transparency because of parasitic absorption of long-wavelength visible light. One solution to eliminate parasitic absorption is to employ materials that absorb near-ultraviolet light with sharper absorption cutoffs. Herein, we demonstrate organic donor materials based on N,N'-diaryl-diamines that incorporate a series of aryl linkers to systematically tune their absorption profiles. When paired with acceptor 4,6-bis(3,5-di-4-pyridinylphenyl)-2-methylpyrimidine in an inverted architecture with an indium tin oxide top electrode and an organic optical outcoupling layer, the three best-performing transparent solar cells exhibit average photopic-response-weighted transmittances of 80.3–82.0% and color-rendering indices of 95.0–97.1, both of which are records for organic photovoltaics, with power-conversion efficiencies of 0.43–0.70%.

Status: published work in ACS Energy Letters 2022, 7, 180

The Emerging Role of Halogen Bonding in Hybrid Perovskite Photovoltaics

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The ongoing effort toward stabilizing hybrid perovskite solar cells and enhancing their performance has stimulated the community to pursue a number of strategies. Over the recent years, these efforts have focused on perovskite materials design, which increasingly relies on molecular modulators that engage in halogen bonding, a uniquely directional noncovalent (supramolecular) interaction. Halogen bonding in hybrid perovskites is reported to drive perovskite assembly, increase its stability against moisture and ion migration, passivate defects, and tune interfacial energetics. The resulting perovskites are shown to exhibit superior mechanical properties, and devices incorporating these materials have seen drastic improvements in their performance, all of which have been ascribed to halogen bonding. While most of these developments have so far relied on the incorporation of off-the-shelf molecular modulators that interact with the perovskite surface to effect interfacial properties, further advancements will require careful consideration of the nature of halogen bonding and rigorous structural assessments in order to aid development of nextgeneration materials. Here, we provide a critical overview of the recent developments in the use of halogen bonding agents in hybrid perovskite photovoltaics with a perspective on their utility in the future.

Status: published work in Chemistry of Materials 2022, 34, 2495

Chemotactic smoothing of collective migration

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Collective migration—the directed, coordinated motion of many self-propelled agents—is a fascinating emergent behavior exhibited by active matter with functional implications for biological systems. However, how migration can persist when a population is confronted with perturbations is poorly understood. Here, we address this gap in knowledge through studies of bacteria that migrate via directed motion, or chemotaxis, in response to a self-generated nutrient gradient. We find that bacterial populations autonomously smooth out large-scale perturbations in their overall morphology, enabling the cells to continue to migrate together. This smoothing process arises from spatial variations in the ability of cells to sense and respond to the local nutrient gradient—revealing a population-scale consequence of the manner in which individual cells transduce external signals. Altogether, our work provides insights to predict, and potentially control, the collective migration and morphology of cellular populations and diverse other forms of active matter.

Status: published work in eLife 2022, 11, e71226

Persistent iodine contamination resulting from thermal evaporation of inorganic perovskites

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Thermal evaporation is a promising technique for the fabrication of uniform perovskite films over large areas that forgo the use of hazardous solvents. However, evaporation equipment, particularly at the laboratory scale, is often shared between different materials systems and it is, thus, important to understand the potential impact that halide perovskite evaporation can have on other films and devices processed in the same chamber. Here, we observe that evaporation of perovskite precursors such as PbI₂ and CsI results in significant iodine contamination that is not efficiently removed by conventional decontamination procedures such as solvent cleaning, chamber bakeout, and foil replacement. X-ray photoelectron spectra show that this iodine contamination can incorporate itself into organic and metal films grown in the same chamber, which degrades the performance of thermally evaporated organic photovoltaic cells by ~90%. To remove the contamination and restore the performance of other optoelectronic devices grown in the same chamber, a total resurfacing/replacement of all interior evaporator surfaces was required.

Status: published work in J. Vac. Sci. Technol B 2022, 40, 060601

Molecular Dynamics Simulations of Reverse Osmosis in Silica Nanopores

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Selective transport of water, salt, and ionic current across water-filled nanopores is a key feature in a variety of natural and engineered systems including geologic media, biological channels, and water treatment membranes. This feature has been extensively observed at the macroscale, but its relation to nanoscale material properties (pore shape, surface charge density, and the behavior of water and ions in individual nanopores) remains incompletely understood. Here, we use nonequilibrium molecular dynamics simulations to examine reverse osmosis during pressure-driven flow of NaCl aqueous solutions across individual silica nanopores separating two bulk-liquid-like water reservoirs as a function of salinity (0.07 or 0.7 M) and pore wall surface charge density (0 or -0.1 Cm^{-2}). We quantify the fluxes of water, salt, and ionic current both within the pore and through the pore as well as the thermodynamic gradients that develop between the pore entrance and exit. Finally, we characterize the selective transport properties of the nanopores. We find that fluid flow in our nanopores is consistent with classical theories but with a hydraulic permeability that decreases as the streaming potential increases as expected based on nonequilibrium thermodynamics. Furthermore, we predict a preferential transport of anions (vs cations) through both uncharged and negatively charged pores. Our results support emerging efforts to incorporate molecular-scale phenomena and coupled fluxes into continuum scale models of transport in nanoporous materials in the geosciences, engineering, and biology.

Status: published work in J. Phys. Chem. C 2022, 126, 9161

Department of Chemical and Biological Engineering,

Determination of the characteristic magnetic pre-sheath length at divertor surfaces using micro-engineered targets on DiMES at DIII-D

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The magnetic pre-sheath (MPS) length, LMPS, is a critical parameter to define the sheath potential, which controls the ion trajectory of low-Z species (D, T, He, and C), as well as the prompt re-deposition of high-Z species. To determine LMPS, we fabricated micro-trenches ($30 \times 30 \times 4 \mu m$) via focused ion beam milling on a silicon surface and exposed them to L-mode deuterium plasmas in DIII-D via the divertor material evaluation system (DiMES) removable sample exposure probe. The areal distribution of impurity depositions, mainly consisting of carbon, was measured by energy-dispersive x-ray spectroscopy (EDS) to reveal the deuterium ion shadowing effect on the trench floors. The carbon deposition profiles showed that the erosion was maximized for the azimuthal direction of $\phi = -40^{\circ}$ as well as the polar angle of $\theta = 80^{\circ}$. A Monte Carlo equation-of-motion (EOM) model, based on a collisionless MPS, was used to calculate the azimuthal and polar deuterium ion angle distributions (IADs) at the surface. Good agreement with the experimental C deposition profiles was obtained for the case k = 2.5–3.5. A validation of theoretical sheath models supports its applicability to ITER and pilot plant divertors to successfully predict plasma–materials interactions.

Status: published work in Nuclear Fusion 2022, 62, 066001

Development of an In Vitro Release Assay for Low-Density Cannabidiol Nanoparticles Prepared by Flash NanoPrecipitation

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Nanoparticle encapsulation is an attractive approach to improve the oral bioavailability of hydrophobic therapeutics. However, the physicochemical properties of the hydrophobic therapeutic can present obstacles to in vitro characterization of nanoparticle formulations. Namely, drugs with low density and high membrane binding affinity frustrate traditional analytical methods to monitor release kinetics from nanoparticles. In this work, cannabidiol (CBD) was encapsulated into nanoparticles with low polydispersity and high drug loading via Flash NanoPrecipitation (FNP), a scalable self-assembly process. Hydroxypropyl methylcellulose acetate succinate (HPMCAS) and lecithin were employed as amphiphilic particle stabilizers during the FNP process. However, the low density and high membrane binding affinity of the amorphous CBD nanoparticle core prevented the characterization of in vitro release kinetics by conventional methods. To address this challenge, an alternative approach is described to coencapsulate 6 nm hydrophobic Fe₃O₄ colloids with CBD during FNP. This densification enabled the centrifugal separation of dissolved (released) CBD from unreleased CBD during the in vitro assay while avoiding the losses associated with a filtration step. The resulting nanoparticle formulations provided more rapid and complete in vitro dissolution kinetics than bulk CBD, representing a 6-fold improvement in dissolution compared to crystalline CBD. The coencapsulation of high-density Fe₃O₄ colloids to enable the separation of nanoparticles from release media is a novel approach to measuring in vitro release kinetics of nanoencapsulated low-density, hydrophobic drug molecules.

Status: published work in Mol. Pharmaceutics 2022, 19, 1515

Design of soft matter for additive processing

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Digital assembly via extrusion-based additive manufacturing, or three-dimensional (3D) printing, grants the opportunity to attain exquisite control over material structure and composition at the local ('voxel') level. The synthetic incorporation of a diverse array of chemistries into 3D-printed soft materials has expanded its use into many application areas. However, substantial opportunity exists for synthesizing materials in which the functional microstructure (at both filler and molecular levels) interacts with the processing flows of extrusion-based manufacturing to achieve unique and enhanced properties. Here we articulate principles for designing and synthesizing soft materials with the potential to generate printed structures with superlative mechanical and stimuli-responsive properties. Specifically, we consider the rheological requirements of printing via direct ink writing and materials extrusion, and examine materials that show printing-directed alignment or trapping of tailored non-equilibrium structures. Finally, we discuss characterization approaches that connect filament-level microstructure with macroscopic behaviour, thus 'closing the loop' of material development. Collectively, these create the potential for additive manufacturing to achieve voxel-level control of composition, microstructure and properties.

Status: published work in Nature Synthesis 2022, 1, 592

Effect of Porous Catalyst Support on Plasma-Assisted Catalysis for Ammonia Synthesis

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We report on the effect of catalyst support particle porosity on the conversion of NH₃ synthesis from N₂ and H₂ in a coaxial dielectric barrier discharge (DBD) plasma reactor. The discharge was created using an AC applied voltage with the reactor at room temperature and near atmospheric pressure (550 Torr). Two different particles of almost equal diameter (~1.5 mm) porous silica (SiO₂) ceramic beads (average pore size: 8 nm) and smooth, nonporous soda lime glass beads - were compared in the DBD reactor. As the pore size in the SiO₂ particles was smaller than the Debye length, penetration of the plasma into the pores of the particles was unlikely; however, reactive species generated in the plasma outside the particles could diffuse into the pores. The N₂ conversion and energy yield of NH₃ increased with applied voltage for both particle types, and these values were consistently higher when using the SiO₂ beads. Discharge and plasma properties were estimated from Lissajous plots and using calculations with the BOLSIG+ software. High resolution optical emission spectra revealed that the concentrations of N_2^+ , atomic N, and atomic H (H $_{\alpha}$, H $_{\beta}$) in the plasma discharge were lower with the porous SiO₂ beads than with the glass beads at every applied voltage tested. This indicates that these active species participate in heterogeneous reactions at support particle surfaces and that the larger surface area presented by the porous particles led to higher rates of depletion of these intermediates and a higher rate of ammonia synthesis.

Status: published work in J. Phys. Chem. A 2022, 126, 8741

Minimum Molecular Weight and Tie Molecule Content for Ductility in Polyethylenes of Varying Crystallinity

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Semicrystalline polymers of low glass transition temperature, such as polyethylene (PE), can be either brittle or ductile depending on their content of intercrystallite stress transmitters - such as tie molecules (TMs), chains that directly bridge the intercrystalline amorphous layer. TM content will increase with increasing molecular weight (M) or with the fraction of high-M chains in a disperse polymer and with decreasing intercrystallite repeat spacing d, which can be manipulated through thermal history and the incorporation of comonomer. The present work examines the failure mode of model narrow-distribution linear PEs (LPEs) of high crystallinity, where d is varied through crystallization history, and ethylenebutene copolymers (hydrogenated polybutadienes (hPBs)) of moderate crystallinity, where d is limited by the short-branch content. For each series, a rather sharp brittle-to-ductile transition (BDT) is observed with increasing M. However, across the three series, the value of MBDT does not depend solely on the value of d; indeed, a higher M is required to achieve ductility in quenched samples of hPB than in LPE, despite the much lower values of d for hPB. Consequently, the calculated value of TM fraction at the BDT increases strongly as crystallinity decreases, by a factor of ~50 from slow-cooled LPE to quenched hPB. This strong dependence is explained by considering the influence of TMs on the brittle fracture stress (σ_b), with the BDT occurring when there are sufficient TMs for σ_b to exceed the yield stress (σ_v), which is strongly dependent on crystallinity but independent of TM content.

Status: published work in Macromolecules 2022, 55, 3249

Decoupling of Glassy Dynamics from Viscosity in Thin Supported Poly(n-butyl methacrylate) Films

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We utilized fast scanning calorimetry to characterize the glass transition temperature (Tg) and intrinsic molecular mobility of low-molecular weight poly(n-butyl methacrylate) thin films of varying thicknesses. We found that the Tg and intrinsic molecular mobility were coupled, showing no film thickness dependent variation. We further employed a unique noncontact capillary nanoshearing technique to directly probe layer-resolved gradients in the rheological response of these films. We found that layer-resolved shear mobility was enhanced with a reduction in film thickness, whereas the effective viscosity decreased. Our results highlight the importance of polymer–substrate attractive interactions and free surface-promoted enhanced mobility, establishing a competitive nanoconfinement effect in poly(n-butyl methacrylate) thin films. Moreover, the findings indicate a decoupling in the thickness-dependent variation of Tg and intrinsic molecular mobility with the mechanical responses (shear mobility and effective viscosity).

Status: published work in ACS Polymers Au 2022, 2, 333

Untying the Cesium "Not": Cesium–Iodoplumbate Complexation in Perovskite Solution-Processing Inks Has Implications for Crystallization

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We illustrate the critical importance of the energetics of cation–solvent versus cation–iodoplumbate interactions in determining the stability of ABX₃ perovskite precursors in a dimethylformamide (DMF) solvent medium. We have shown, through a complementary suite of nuclear magnetic resonance (NMR) and computational studies, that Cs+ exhibits significantly different solvent vs iodoplumbate interactions compared to organic A+-site cations such as CH₃NH₃⁺ (MA⁺). Two NMR studies were conducted: ¹³³Cs NMR analysis shows that Cs⁺ and MA⁺ compete for coordination with PbI₃ – in DMF. ²⁰⁷Pb NMR studies of PbI₂ with cationic iodides show that perovskite-forming Cs⁺ (and, somewhat, Rb⁺) do not comport with the ²⁰⁷Pb chemical shift trend found for Li⁺, Na⁺, and K⁺. Three independent computational approaches yielded strikingly similar results: Cs⁺ interacts more strongly with the PbI₃ –iodoplumbate than does MA⁺ in a polar solvent environment like DMF. The stronger energy preference for PbI₃ – coordination of Cs⁺ vs MA⁺ in DMF demonstrates that Cs⁺ is not simply a postcrystallization cation "fit" for the perovskite A⁺-site. Instead, it may facilitate preorganization of the framework precursor that eventually transforms into the crystalline perovskite structure.

Status: published work in J. Phys. Chem. Lett. 2022, 13, 6130

Capillary forces generated by biomolecular condensates

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Liquid–liquid phase separation and related phase transitions have emerged as generic mechanisms in living cells for the formation of membraneless compartments or biomolecular condensates. The surface between two immiscible phases has an interfacial tension, generating capillary forces that can perform work on the surrounding environment. Here we present the physical principles of capillarity, including examples of how capillary forces structure multiphase condensates and remodel biological substrates. As with other mechanisms of intracellular force generation, for example, molecular motors, capillary forces can influence biological processes. Identifying the biomolecular determinants of condensate capillarity represents an exciting frontier, bridging soft matter physics and cell biology.

Status: published work in Nature 2022, 609, 255

Improved Absorber Phase Stability, Performance, and Lifetime in Inorganic Perovskite Solar Cells with Alkyltrimethoxysilane Strain-Release Layers at the Perovskite/TiO₂ Interface

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All-inorganic β -CsPbI₃ has superior chemical and thermal stability compared to its hybrid counterparts, but the stability of state-of-the-art β -CsPbI₃ perovskite solar cells (PSCs) under normal operating conditions (i.e., under illumination in an inert atmosphere) remains inferior to their hybrid counterparts. Here, we found that the lattice distortion in CsPbI₃ near the perovskite/electron transport layer (ETL) interface can induce polymorphic transformation in encapsulated CsPbI₃ films aged under illumination. To suppress this lattice distortion, we introduced alkyltrimethoxysilane strain-release layers (SRLs) at the perovskite/ETL interface. We found the SRL with the longest alkyl chain is the most effective at reducing interfacial lattice distortion, leading to enhanced charge transfer at the perovskite/ETL interface and improved phase/device stability. Its incorporation in β -CsPbI₃ solar cells resulted in a power-conversion efficiency of 20.1% and an operational lifetime with an extrapolated T₈₀ of >3000 h for encapsulated devices tested under continuous illumination under maximum power point tracking conditions.

Status: published work in ACS Energy Lett. 2022, 7, 3531

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

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Transparent photovoltaics (TPVs) can be integrated into the surfaces of buildings and vehicles to provide point-of-use power without impacting aesthetics. Unlike TPVs that target the photon-rich near-infrared portion of the solar spectrum, TPVs that harvest ultraviolet (UV) photons can have significantly higher transparency and color neutrality, offering a superior solution for low-power electronics with stringent aesthetic tolerance. In addition to being highly transparent and colorless, an ideal UV-absorbing TPV should also be operationally stable and scalable over large areas while still outputting sufficient power for its specified application. None of today's TPVs meet all these criteria simultaneously. Here, the first UV-absorbing TPV is demonstrated that satisfies all four criteria by using CsPbCl_{2.5}Br_{0.5} as the absorber. By precisely tuning the halide ratio during thermal co-evaporation, high-quality large-area perovskite films can be accessed with an ideal absorption cutoff for aesthetic performance. The resulting TPVs exhibit a record average visible transmittance of 84.6% and a color rendering index of 96.5, while maintaining an output power density of 11 W m⁻² under one-sun illumination. Further, the large-area prototypes up to 25 cm² are demonstrated, that are operationally stable with extrapolated lifetimes of >20 yrs under outdoor conditions.

Status: published work in Advanced Energy Materials 2022, 2200402

Morphological instability and roughening of growing 3D bacterial colonies

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While colony morphogenesis is well studied in two dimensions, many bacteria grow as large colonies in three-dimensional (3D) environments, such as gels and tissues in the body or subsurface soils and sediments. Here, we describe the morphodynamics of large colonies of bacteria growing in three dimensions. Using experiments in transparent 3D granular hydrogel matrices, we show that dense colonies of four different species of bacteria generically become morphologically unstable and roughen as they consume nutrients and grow beyond a critical size— eventually adopting a characteristic branched, broccoli-like morphology independent of variations in the cell type and environmental conditions. This behavior reflects a key difference between two-dimensional (2D) and 3D colonies; while a 2D colony may access the nutrients needed for growth from the third dimension, a 3D colony inevitably becomes nutrient limited in its interior. We elucidate the onset of the instability using linear stability analysis and numerical simulations of a continuum model that treats the colony as an "active fluid" whose dynamics are driven by nutrient-dependent cellular growth. We find that when all dimensions of the colony substantially exceed the nutrient penetration length, nutrient-limited growth drives a 3D morphological instability that recapitulates essential features of the experimental observations.

Status: published work in PNAS 2022, 119, e2208019119

A biophysical threshold for biofilm formation

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Bacteria are ubiquitous in our daily lives, either as motile planktonic cells or as immobilized surface-attached biofilms. These different phenotypic states play key roles in agriculture, environment, industry, and medicine; hence, it is critically important to be able to predict the conditions under which bacteria transition from one state to the other. Unfortunately, these transitions depend on a dizzyingly complex array of factors that are determined by the intrinsic properties of the individual cells as well as those of their surrounding environments, and are thus challenging to describe. To address this issue, here, we develop a generally-applicable biophysical model of the interplay between motility-mediated dispersal and biofilm formation under positive quorum sensing control. Using this model, we establish a universal rule predicting how the onset and extent of biofilm formation depend collectively on cell concentration and motility, nutrient diffusion and consumption, chemotactic sensing, and autoinducer production. Our work thus provides a key step toward quantitatively predicting and controlling biofilm formation in diverse and complex settings.

Status: published work in eLife 2022, 11, e76380

Tuning Morphologies and Reactivities of Hybrid Organic–Inorganic Nanoparticles

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Hybrid nanoparticles (hNPs), or nanoparticles composed of both organic and inorganic components, hold promise for diverse energy and environmental applications due to their ability to stabilize reactive nanomaterials against aggregation, enhancing their ability to pervade tortuous spaces and travel long distances to degrade contaminants in situ. Past studies have investigated the use of polymer or surfactant coatings to stabilize nanomaterials against aggregation. However, fabrication of these materials often requires multiple steps. Here, we demonstrated a method of producing stable hNPs with tunable morphologies by incubating polystyrene nanoparticles formed via Flash NanoPrecipitation with citrate-stabilized gold nanocatalysts. We found that gold adsorption to polystyrene nanoparticles was enabled by the presence of a good solvent for polystyrene. Furthermore, changing process and molecular parameters provided control over the resultant nanocatalyst loading and dispersal atop hNPs. We classified these morphologies into three distinct regimes – aggregated, dispersed, or internalized – and we showed that the emergence of these regimes has key implications for controlling reaction rates in heterogeneous catalysis or groundwater remediation: hNPs with gold nanocatalysts embedded below the surfaces of polystyrene nanoparticles exhibited slower bulk catalytic reduction capacity than their disperse, surface-decorated counterparts. Our work demonstrates a simple way by which hNPs can be fabricated and presents a method to control catalytic reactions using reactive nanomaterials.

Status: published work in ACS Nano 2022, 16, 16133
Physical aging of hydroxypropyl methylcellulose acetate succinate via enthalpy recovery

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Amorphous solid dispersions (ASDs) utilize the kinetic stability of the amorphous state to stabilize drug molecules within a glassy polymer matrix. Therefore, understanding the glassy-state stability of the polymer excipient is critical to ASD design and performance. Here, we investigated the physical aging of hydroxypropyl methylcellulose acetate succinate (HPMCAS), a commonly used polymer in ASD formulations. We found that HPMCAS exhibited conventional physical aging behavior when annealed near the glass transition temperature (Tg). In this scenario, structural recovery was facilitated by a-relaxation dynamics. However, when annealed well below Tg, a sub- α -relaxation process facilitated low-temperature physical aging in HPMCAS. Nevertheless, the physical aging rate exhibited no significant change up to 40 K below Tg, below which it exhibited a near monotonic decrease with decreasing temperature. Finally, infrared spectroscopy was employed to assess any effect of physical aging on the chemical structure of HPMCAS, which is known to be susceptible to degradation at temperatures 30 K above its Tg. Our results provide critical insights necessary to understand better the link between the stability of ASDs and physical aging of the glassy polymer matrix.

Status: published work in Soft Matter 2022, 18, 8331

Insights into Metal–Organic Framework-Derived Copper Clusters for CO₂ Electroreduction

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The unique material properties of metal-organic frameworks (MOFs) have highlighted their potential as a next-generation electrocatalyst candidate. However, utilizing MOFs as electrocatalysts necessitates investigations into the changes to the MOF structure under electrochemical bias and subsequent identification and benchmarking of structure-function relationships. Herein, we demonstrate the synthesis of a Cu-based MOF (HKUST-1) film from an in situ nucleation and film growth procedure and the morphological and structural transformation of the said film under electrochemical bias. Additionally, we benchmark the resulting MOFderived (MOF-d) Cu-based material for electrochemical CO₂ reduction (CO₂R) applications. Both ex situ and in situ characterization methods highlight substantial morphological and structural changes to the HKUST-1 film during electrochemical CO₂R in CO₂-saturated 0.1 M KHCO₃ aqueous supporting electrolytes. We found that a MOF-d film containing Cu clusters was formed during the electrolysis under a cathodic bias. These results demonstrate the utility of in situ spectroscopic techniques to examine the morphological and structural changes to the HKUST-1 film under electrochemical bias and provide insights into the electrochemical CO₂R activity of the MOF-d Cu film by critically benchmarking its intrinsic reactivity against known materials using established activity descriptors.

Status: published work in J. Phys. Chem. C 2022, 126, 13649

Epitaxially crystallized polyethylene exhibiting near-equilibrium melting temperatures

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The morphology and orientation of polymer crystals are important factors which determine the performance of thin-film, polymer-based technologies such as organic electronic devices and gas separation membranes. Here, we utilize polymer-substrate epitaxy to achieve a highly oriented crystalline morphology during thin-film processing. To accomplish this, we employ matrixassisted pulsed laser evaporation (MAPLE), a slow physical vapor deposition process, to deposit linear polyethylene epitaxially atop a graphene substrate. Via MAPLE, we demonstrate the ability to achieve a film morphology comprised of well-aligned, edge-on crystalline lamellae. Furthermore, we show that MAPLE can be exploited to grow crystalline lamellae composed entirely of extended polymer chains which exhibit a near-equilibrium melting temperature. Our study demonstrates that MAPLE, as a bottom-up approach, can deposit polymer thin films with improved control over crystalline morphology.

Status: published work in Polymer Engineering and Science 2022, 62, 841

All-Polymer Bulk-Heterojunction Organic Electrochemical Transistors with Balanced Ionic and Electronic Transport

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The rapid development of organic electrochemical transistor (OECTs)-based circuits brings new opportunities for next-generation integrated bioelectronics. The all-polymer bulkheterojunction (BHJ) offers an attractive, inexpensive alternative to achieve efficient ambipolar OECTs, and building blocks of logic circuits constructed from them, but have not been investigated to date. Here, the first all-polymer BHJ-based OECTs are reported, consisting of a blend of new p-type ladder conjugated polymer and a state-of-the-art n-type ladder polymer. The whole ladder-type polymer BHJ also proves that side chains are not necessary for good ion transport. Instead, the polymer nanostructures play a critical role in the ion penetration and transportation and thus in the device performance. It also provides a facile strategy and simplifies the fabrication process, forgoing the need to pattern multiple active layers. In addition, the development of complementary metal–oxide–semiconductor (CMOS)-like OECTs allows the pursuit of advanced functional logic circuitry, as well as for amplifying electrophysiology signals. This work opens a new approach to the design of new materials for OECTs.

Status: published work in Advanced Materials 2022, 34, 2206118

Thermoresponsive Polymers for Water Treatment and Collection

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To overcome the current scarcity of fresh water sustainably, new technologies will be required that produce potable water from a range of sources, including seawater and moisture from the atmosphere. Moreover, we must recover and reuse water from wastewater streams to reduce our global water footprint. To date, there remain significant concerns about the environmental/ecological impact, high energy consumption, and extensive maintenance costs of current technologies that might prevent their transition to more sustainable routes of potable water generation. One class of material that can enable low-energy water production is thermoresponsive polymers. Due to their unique phase behavior, production flexibility, and biocompatibility, these materials may allow for sustainable routes to fresh water in current and new technologies. In this Perspective, we specifically summarize the design and application of poly(N-isopropylacrylamide) -(PNIPAm-) based thermoresponsive microgels and hydrogels. In particular, we show how these materials have been used for water purification, including wastewater treatment, seawater desalination, and moisture harvesting. Finally, we discuss the opportunities and challenges of transforming current thermoresponsive materials into practical water-related technologies.

Status: published work in Macromolecules 2022, 55, 1894

Mechanistic Impacts of Metal Site and Solvent Identities for Alkene Oxidation over Carboxylate Fe and Cr Metal–Organic Frameworks

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Isolated Fe(III) and Cr(III) sites contained in nanoporous voids of isoreticular carboxylate MIL-101(Fe) and MIL-101(Cr) are interrogated for their reactivity and selectivity of liquid-phase styrene oxidation by hydrogen peroxide (H₂O₂). Batch kinetic measurements in acetonitrile (MeCN) at 323 K showcase that both metal-normalized oxygenate production and H₂O₂ consumption rates are $O(10^1)$ higher for MIL-101(Fe) than MIL-101(Cr). Thermodynamically consistent reaction pathways, constructed through spiking experiments, reveal complex interconnectivities between primary (styrene oxide, benzaldehyde) and secondary (styrene glycol, benzoic acid, phenylacetaldehyde) oxygenates. Though benzaldehyde is the majority product for both MIL-101(Fe) and MIL-101(Cr), isoconversion ($X_{styrene} = 7\%$) product distributions suggest intrinsic differences in preferred reaction pathways. Apparent energy barriers for all pathways are lower over MIL-101(Fe) than for MIL-101(Cr), conferred by metal electron affinity differences for primary oxygenate selectivity, while secondary (inter)conversion rates trend with acid site densities. Fitted rate laws, radical trapping, adsorption experiments, and complementary DFT calculations indicate surface-mediated reactions by H2O2-derived surface species that outcompete bound styrene, product oxygenate, solvent, and water molecules for both MIL-101(Fe) and MIL-101(Cr) in MeCN. Overall, this work combines kinetic, spectroscopic, numerical, and computational approaches to rigorously define reaction and deactivation mechanisms for styrene oxidation by H₂O₂ over isoreticular MIL-101(Fe) and MIL-101(Cr).

Status: published work in ACS Catalysis 2022, 12, 14476

A charge transfer framework that describes supramolecular interactions governing structure and properties of 2D perovskites

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The elucidation of structure-to-function relationships for two-dimensional (2D) hybrid perovskites remains a primary challenge for engineering efficient perovskite-based devices. By combining insights from theory and experiment, we describe the introduction of bifunctional ligands that are capable of making strong hydrogen bonds within the organic bilayer. We find that stronger intermolecular interactions draw charge away from the perovskite layers, and we have formulated a simple and intuitive computational descriptor, the charge separation descriptor (CSD), that accurately describes the relationship between the Pb-I-Pb angle, band gap, and inplane charge transport with the strength of these interactions. A higher CSD value correlates to less distortion of the Pb-I-Pb angle, a reduced band gap, and higher in-plane mobility of the perovskite. These improved material properties result in improved device characteristics of the resulting solar cells.

Status: published work in Nature Communications 2022, 13, 3970

Accelerated aging of all-inorganic, interface-stabilized perovskite solar cells

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To understand degradation routes and improve the stability of perovskite solar cells (PSCs), accelerated aging tests are needed. Here, we use elevated temperatures (up to 110 Celsius) to quantify the accelerated degradation of encapsulated CsPbI₃ PSCs under constant illumination. Incorporating a 2D Cs₂PbI₂Cl₂ capping layer between the perovskite active layer and hole-transport layer stabilizes the interface while increasing power conversion efficiency of the all-inorganic PSCs from 14.9% to 17.4%. Devices with this 2D capping layer did not degrade at 35 Celsius and required >2100 hours at 110 Celsius under constant illumination to degrade by 20% of their initial efficiency. Degradation acceleration factors based on the observed Arrhenius temperature dependence predict intrinsic lifetimes of 51,000 \pm 7,000 hours (>5 years) operating continuously at 35 Celsius.

Status: published work in Science 2022, 377, 307

Department of Civil and Environmental Engineering

The effects of calcium hydroxide and activator chemistry on alkali-activated metakaolin pastes exposed to high temperatures

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Having a detailed understanding of the high temperature behavior of alkali-activated metakaolin (AAMK) is important for use of this material in fire resistance applications. Here, we assess the impact of a small amount of calcium hydroxide (10 wt% replacement for metakaolin) on the phase formation, pore structure and microstructure of AAMK exposed to temperatures of up to 900 °C. 5 and 10 M NaOH-activated pastes, and equivalent molarity Na₂SiO₃-activated pastes, with and without calcium hydroxide are characterized using Fourier transform infrared spectroscopy and X-ray diffraction to identify the crystalline phases that form on heating and the likely location of calcium within the material. Mercury intrusion porosimetry and scanning electron microscopy provide a detailed understanding of the evolution of the pore network on heating and degree of densification of the samples. It is found that the calcium addition enhances the formation of nepheline on heating and reduces the concentration-dependent differences seen between the 5 and 10 M Na₂SiO₃-activated systems.

Status: published work in Cement and Concrete Research 2022, 154, 106742

Synthesis and Growth of Green graphene from Biochar Revealed by Magnetic Properties of Iron Catalyst

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Understanding the mechanism of iron-catalyzed graphitization of biomass is an important step for the large-scale synthesis of green graphene. Although iron is known to be the most active transition metal for the catalytic graphitization of cellulose-derived biochar, the direct effect of the iron molecular structure on the formation of highly graphitic carbon remains elusive. Here, biochar has been produced from pyrolysis of iron-impregnated cellulose at three different temperatures 1000°C, 1400°C, and 1800°C. X-ray diffraction, X-ray photoelectron spectroscopy and magnetic measurements are used to probe changes in biochar nanostructure that is catalyzed by the inclusion of iron. We find that an increase of pyrolysis temperature leads to an increase in the iron particle size and the degree of iron reduction, as well as the formation of larger graphitic carbon crystallite sizes, and these two attributes of iron are seen to positively affect the biochar graphitization usually challenging under 2000°C.

Status: published work in ChemSusChem 2022, e202201864

Sealing fractures to increase underground storage security: Lessons learned from a multiscale multimodal imaging study of a syntaxial vein in a mudrock

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Veins recovered from deep sedimentary formations offer insights into mineral precipitates and processes that lead to sealing of underground fractures. In this study, we characterized the mineralogy and porosity of a syntaxial vein in a mudrock sample from the Wolfcamp formation in Texas. The original fracture had an aperture of 5 mm and is now filled with distinct zones of minerals and vuggy regions. Thin sections from cuts across the vein were examined at micron scale resolution using scanning electron microscopy, EDS, QEMSCAN, and polarized light microscopy. Larger-scale analyses were done using synchrotron X-ray fluorescence. Collectively, these methods reveal elongated crystals of dolomite as large as 900 µm, overlain with a mixture of smaller crystals including calcite and ferroan dolomite. Quantitative analysis of a 3D X-ray CTimage indicates that the vein volume contains 62% elongate dolomite crystals, 33% mixed ferroan dolomite and calcite, 1% silica, and 4% vuggy void space. Synchrotron small and ultra-small angle X-ray scattering reveals that the vein mineral precipitates have ~1% porosity. This is much smaller than the porosity of the mudrock matrix. The findings in this study suggest that fracture fluids migrated vertically and experienced pressure reduction causing exsolution of CO₂. A geochemical simulation demonstrated how this could have led to carbonate precipitation in the veins.

Status: published work in Chemical Geology 2022, 614, 121164

Cell-Free CO₂ Valorization to C6 Pharmaceutical Precursors via a Novel Electro-Enzymatic Process

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CO₂ valorization

The healthcare industry emits significant amounts of CO₂ and has an imperative need for decarbonization. This study demonstrated a new hybrid electro-enzymatic process that converts waste CO₂ into high-value C6 pharmaceutical precursor compounds. A novel three-chamber electrolyzer equipped with a Cu-based gas diffusion electrode converted gaseous CO₂ into ethanol at a high current density (40–60 mA/cm²), high selectivity (43–81 mol %), and production rate (368–428 mg/L/h). Purified ethanol from the electrolyzer was then sent to an enzymatic bioreactor where ADH and DERA enzymes upgraded ethanol into C6 statin precursor molecules at high yields (29–35%) via acetaldehyde. Competitive C6 lactol synthesis rates (4.7–5.7 mM/day) and titers (712–752 mg/L) were achieved, demonstrating the potential of the end-to-end process. The C6 lactol product can seamlessly be converted to statins, a class of lipid-lowering medication that is among the largest selling class of drugs in the world. This hybrid process provides a new pathway for CO₂ valorization to high-value products and accelerates healthcare sector decarbonization.

Status: published work in ACS Sustainable Chem. Eng. 2022, 10, 4114.

Upscaling 3D Engineered Trees for Off-Grid Desalination

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More than 70% of the population without access to safe drinking water lives in remote and off-grid areas. Inspired by natural plant transpiration, we designed and tested in this study an array of scalable three-dimensional (3D) engineered trees made of natural wood for continuous water desalination to provide affordable and clean drinking water. The trees took advantage of capillary action in the wood xylems and lifted water more than 1 foot off the ground with or without solar irradiation. This process overcame some major challenges of popular solar-driven water evaporation and water harvesting, such as intermittent operation, low water production rate, and system scaling. The scaled system has a ratio of surface area (vapor generation) to project area (water transport) up to 118, significantly higher than the prevailing flat-sheet design. The total energy for evaporation reached over 300% of the one-sun irradiance, enabling a freshwater production rate of 4.8 L m⁻² h⁻¹ from an array of 16 trees in an enclosed room and 14 L m⁻² h⁻¹ under a 3 m/s airflow. During long-term desalination tests, the engineered trees demonstrated a self-cleaning mechanism with daily cycles of salt accumulation and dissolution. Combining the quantification from an evaporation model and meteorology data covering the globe, we also demonstrated that the 3D engineered trees can be of particular interest for sustainable desalination in the Middle East and North Africa (MENA) regions.

Status: published work in Environ. Sci. Technol. 2022, 56, 1289

Department of Chemistry

Photoinduced band renormalization effects in the topological nodal-line semimetal ZrSiS

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Out-of-equilibrium effects provide an elegant pathway for probing and understanding the underlying physics of topological materials. In particular, controlling electronic band structure properties using ultrafast optical pulses has shown promise for creating exotic states of matter. Of recent interest is band renormalization in Dirac and Weyl semimetals as it leads to direct physical observables through the enhancement of the effective mass or in the shift of resonant energies. Here we provide experimental and theoretical signatures of photoinduced renormalization of the electronic band structure in the topological nodal-line semimetal ZrSiS. Specifically, we show how the change in the transient reflectivity spectra under femtosecond optical excitations is induced by out-of-equilibrium effects that renormalize the kinetic energy of electrons. We associate the observed spectral features with an enhancement of the effective mass and to a redshift of the resonant frequency as a function of pump field strength. Finally, we show that the transient relaxation dynamics of the reflectivity is primarily an electronic effect with a negligible phononic contribution. Our study presents conclusive modifications of electronic properties in ZrSiS using ultrashort pulses and demonstrates the potential of this approach in creating photoinduced phases in topological quantum matter through an all-optical route.

Status: published work in Physical Reviews B 2022, 106, 134303

Annealing Controls Ultrafast Dynamics of Carrier Production in Organic Photovoltaics Incorporating a Nonfullerene Acceptor

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Nonfullerene acceptors have emerged as leading candidates in organic photovoltaics pushing past some of the limitations of their fullerene counterparts with absorption extending in the visible and NIR, decreased air-sensitivity, and tunable energy levels. Significant progress has been made in demonstrating the potential of nonfullerene acceptor-based devices to reach high efficiencies; however, a photophysical and mechanistic understanding of charge generation in these nonfullerene acceptors lags behind. In particular, the effects of annealing on carrier production have not been previously examined. Here, we use transient absorption spectroscopy and atomic force microscopy to examine the effect of solvent vapor annealing on a perylene diimide-based nonfullerene acceptor, PDI-DPP-PDI. We find that when mixed with the donor PTB7-Th, the effect of solvent vapor annealing on PDI-DPP-PDI is to reduce geminate recombination, leading to balanced exciton generation and charge separation.

Status: published work in J. Phys. Chem. C 2022, 126, 17187

Chemically exfoliated nanosheets of β-Bi₂O₃

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Exploring two dimensional (2D) materials is important for further developing the field of quantum materials. However, progress in 2D material development is limited by difficulties with their production. Specifically, freestanding 2D materials with bulk non-layered structures remain particularly challenging to prepare. Traditionally, chemical or mechanical exfoliation is employed for obtaining freestanding 2D materials, but these methods typically require layered starting materials. Here we put forth a method for obtaining thin layers of β -Bi₂O₃, which has a three-dimensional covalent structure, by using chemical exfoliation. In this research, Na₃Ni₂BiO₆ was exfoliated with acid and water to obtain β -Bi₂O₃ nanosheets less than 10 nm in height and over 1 µm in lateral size. Our results open the possibility for further exploring β -Bi₂O₃ nanosheets to determine whether their properties change from the bulk to the nanoscale. Furthermore, this research may facilitate further progress in obtaining nanosheets of non-layered bulk materials using chemical exfoliation.

Status: published work in Journal of Physics: Materials 2022, 5, 044004

Ferromagnetic Double Perovskite Semiconductors with Tunable Properties

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The authors successfully dope the magnetically silent double perovskite semiconductor Sr_2GaSbO_6 to induce ferromagnetism and tune its bandgap, with Ga^{3+} partially substituted by the magnetic trivalent cation Mn^{3+} , in a rigid cation ordering with Sb^{5+} . The new ferromagnetic semiconducting $Sr_2Ga_{1-x}Mn_xSbO_6$ double perovskite, which crystallizes in tetragonal symmetry (space group I4/m) and has tunable ferromagnetic ordering temperature and bandgap, suggests that magnetic ion doping of double perovskites is a productive avenue toward obtaining materials for application in next-generation oxide-based spintronic devices.

Status: published work in Advanced Science 2022, 2104319

Magnetic cations doped into a double perovskite semiconductor

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We report two solid solutions based on the magnetic ion doping of the double perovskite oxide Sr_2GaSbO_6 : $Sr_2Ga_{1-x}Cr_xSbO_6$ ($0.1 \le x \le 0.4$) and $Sr_2Ga_{1-x}Fe_xSbO_6$ ($0.1 \le x \le 0.4$). All compositions crystallize in the same space group (I4/m) as their undoped parent phase Sr_2GaSbO_6 , with the trivalent magnetic cations Cr^{3+} or Fe^{3+} partially substituting for non-magnetic Ga^{3+} in one of the B-cation sites. The Cr- and Fe-doped phases display dominant antiferromagnetic coupling among the dopant magnetic moments, and exhibit decreasing band gaps with increasing substitution level.

Status: published work in J. Mater. Chem. C, 2022, 10, 3232

Ln₃MBi₅ (Ln=Pr, Nd, Sm; M=Zr, Hf): Intermetallics with Hypervalent Bismuth Chains

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We report five new isostructural compounds in the Ln₃MBi₅ (Ln=Pr, Nd, Sm; M=Zr, Hf) family, and compare them to the recently reported Sm₃ZrBi₅ analogue. Ln₃MBi₅ crystallizes in the P63/mcm space group, hosting the anti-Hf₅Sn₃Cu structure type. The one-dimensional structure consists of hypervalent Bi²⁻ chains and face-sharing MBi₆ octahedra that form chains along the c axis. A framework of Ln³⁺ cations charge balances and separates the two motifs. The Bi-Bi and M-Bi bond lengths decrease as the Ln cation becomes smaller across the period, but there is almost no difference in either bond length when the identity of M changes, as expected because Zr and Hf have the exact same radii due to lanthanide contraction. We present a structural stability map showing the limits of cation stability in the structure, with La³⁺ and U³⁺ as the largest cations and Sm³⁺ as the smallest cation. X-ray photoelectron spectra suggest ambiguous valence states in the Ln₃MBi₅ family and sheds new light on how their bonding behavior may vary based on chemical composition.

Status: published work in Z. Anorg. Allg. Chem. 2022, 648, e202200123

A Class of Magnetic Topological Material Candidates with Hypervalent Bi Chains

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The link between crystal and electronic structure is crucial for understanding structure–property relations in solid-state chemistry. In particular, it has been instrumental in understanding topological materials, where electrons behave differently than they would in conventional solids. Herein, we identify 1D Bi chains as a structural motif of interest for topological materials. We focus on Sm₃ZrBi₅, a new quasione-dimensional (1D) compound in the Ln₃MPn₅ (Ln = lanthanide; M = metal; Pn = pnictide) family that crystallizes in the P6₃/mcm space group. Density functional theory calculations indicate a complex, topologically nontrivial electronic structure that changes significantly in the presence of spin–orbit coupling. Magnetic measurements show a quasi-1D antiferromagnetic structure with two magnetically frustrated spins. Heat capacity, electrical, and thermoelectric measurements support this claim and suggest complex scattering behavior in Sm₃ZrBi₅. This work highlights 1D chains as an unexplored structural motif for identifying topological materials, as well as the potential for rich physical phenomena in the Ln₃MPn₅ family.

Status: published work in J. Am. Chem. Soc. 2022, 144, 9785

Square-Net Topological Semimetals: How Spectroscopy Furthers Understanding and Control

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Square-net materials are well positioned to lead optical spectroscopic explorations into the electronic structure, photoinduced dynamics, and phase transitions in topological semimetals. Hundreds of square-net topological semimetals can be prepared that have remarkably different electronic and optical properties despite having similar structures. Here we present what has been gleaned recently from these materials with the whole gamut of optical spectroscopies, ranging from steady-state reflectance and Raman investigations into topological band structures, electronic correlations, and equilibrium phase transitions to time-resolved techniques used to decipher ultrafast relaxation dynamics and nonequilibrium photoinduced phase transitions. We end with a discussion of some major remaining questions and possible future research directions.

Status: published work in J. Phys. Chem. Lett. 2022, 13, 838

Honeycomb-Structure Rul₃, A New Quantum Material Related to α-RuCl₃

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The layered honeycomb lattice material α -RuCl₃ has emerged as a prime candidate for displaying the Kitaev quantum spin liquid state, and as such has attracted much research interest. Here a new layered honeycomb lattice polymorph of RuI₃, a material that is strongly chemically and structurally related to α -RuCl₃ is described. The material is synthesized at moderately elevated pressures and is stable under ambient conditions. Preliminary characterization reveals that it is a metallic conductor, with the absence of long-range magnetic order down to 0.35 K and an unusually large T-linear contribution to the heat capacity. It is proposed that this phase, with a layered honeycomb lattice and strong spin–orbit coupling, provides a new route for the characterization of quantum materials.

Status: published work in Advanced Materials 2022, 34, 2106831

The non-centrosymmetric layered compounds IrTe₂I and RhTe₂I

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The previously unreported layered compounds IrTe₂I and RhTe₂I were prepared by a highpressure synthesis method. Single crystal X-ray and powder X-ray diffraction studies find that the compounds are isostructural, crystallizing in a layered orthorhombic structure in the noncentrosymmetric, non-symmorphic space group Pca2₁ (#29). Characterization reveals diamagnetic, high resistivity, semiconducting behavior for both compounds, consistent with the +3 chemical valence and d⁶ electronic configurations for both iridium and rhodium and the Te–Te dimers seen in the structural study. Electronic band structures are calculated for both compounds, showing good agreement with the experimental results.

Status: published work in Dalton Transaction 2022, 51, 8688

The honeycomb and hyperhoneycomb polymorphs of Irl₃

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The synthesis of IrI₃ at high pressure in its layered honeycomb polymorph is reported. Its crystal structure is refined by single crystal X-ray diffraction. Faults in the honeycomb layer stacking are observed by single crystal diffraction, synchrotron powder diffraction, and transmission electron microscopy. A previously unreported "hyperhoneycomb" polymorph of IrI₃ (β -IrI₃), is also reported - Its structure in space group Fddd is determined by single crystal XRD. Both materials are highly-resistive diamagnetic semiconductors, consistent with a low spin d⁶ configuration for Ir(III). The two- and three-dimensional Ir arrays in these polymorphs of IrI₃ are analogous to those found in the α - and β -polymorphs of Li₂IrO₃, although the Ir electron configurations are different. IrI₃ may be of future interest in the fabrication of new quantum materials.

Status: published work in J. Solid State Chem. 2022, 312, 123240

Structural Elucidation of Cryptic Algaecides in Marine Algal- Bacterial Symbioses by NMR Spectroscopy and MicroED

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Microbial secondary metabolite discovery is often conducted in pure monocultures. In a natural setting, however, where metabolites are constantly exchanged, biosynthetic precursors are likely provided by symbionts or hosts. In the current work, we report eight novel and architecturally unusual secondary metabolites synthesized by the bacterial symbiont Phaeobacter inhibens from precursors that, in a native context, would be provided by their algal hosts. Three of these were produced at low titres and their structures were determined de novo using the emerging microcrystal electron diffraction method. Some of the new metabolites exhibited potent algaecidal activity suggesting that the bacterial symbiont can convert algal precursors, tryptophan and sinapic acid, into complex cytotoxins. Our results have important implications for the parasitic phase of algal-bacterial symbiotic interactions.

Status: published work in Angewandte Chemie Int. Ed. 2022, 61, e202114022

Excited-State Dynamics of 5,14- vs 6,13-Bis(trialkylsilylethynyl)-Substituted Pentacenes: Implications for Singlet Fission

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Singlet fission is a process in conjugated organic materials that has the potential to considerably improve the performance of devices in many applications, including solar energy conversion. In any application involving singlet fission, efficient triplet harvesting is essential. At present, not much is known about molecular packing arrangements detrimental to singlet fission. In this work, we report a molecular packing arrangement in crystalline films of 5,14-bis(triisopropylsilylethynyl)-substituted pentacene, specifically a local (pairwise) packing arrangement, responsible for complete quenching of triplet pairs generated via singlet fission. We first demonstrate that the energetic condition necessary for singlet fission is satisfied in amorphous films of the 5,14-substituted pentacene derivative. In crystalline films, triplet pairs also form highly efficiently, although independent triplets are not observed. We assign the quenching to a rapid nonadiabatic transition directly to the ground state. Detrimental quenching is observed in crystalline films of two additional 5,14-bis(trialkylsilylethynyl)-substituted pentacenes with either ethyl or isobutyl substituents. Developing a better understanding of the and associated molecular packing, may benefit overcoming losses in solids of other singlet fission materials.

Status: published work in J. Phys. Chem. C 2022, 126, 9784

Radicals as Exceptional Electron-Withdrawing Groups: Nucleophilic Aromatic Substitution of Halophenols Via Homolysis-Enabled Electronic Activation

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While heteroatom-centered radicals are understood to be highly electrophilic, their ability to serve as transient electron-withdrawing groups and facilitate polar reactions at distal sites has not been extensively developed. Here, we report a new strategy for the electronic activation of halophenols, wherein generation of a phenoxyl radical via formal homolysis of the aryl O–H bond enables direct nucleophilic aromatic substitution of the halide with carboxylate nucleophiles under mild conditions. Pulse radiolysis and transient absorption studies reveal that the neutral oxygen radical (O•) is indeed an extraordinarily strong electron-withdrawing group [$\sigma_p^-(O•) = 2.79$ vs $\sigma_p^-(NO_2) = 1.27$]. Additional mechanistic and computational studies indicate that the key phenoxyl intermediate serves as an open-shell electron-withdrawing group in these reactions, lowering the barrier for nucleophilic substitution by more than 20 kcal/mol relative to the closed-shell phenol form of the substrate. By using radicals as transient activating groups, this homolysis-enabled electronic activation strategy provides a powerful platform to expand the scope of nucleophile–electrophile couplings and enable previously challenging transformations.

Status: published work in J. Am. Chem. Soc. 2022, 144, 21783

Colossal negative magnetoresistance in the complex charge density wave regime of an antiferromagnetic Dirac semimetal

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Colossal magnetoresistance (MR) is a well-known phenomenon, notably observed in holedoped ferromagnetic manganites. It remains a major research topic due to its potential in technological applications. Though topological semimetals also show large MR, its origin and nature are completely different. Here, we show that in the highly electron doped region, the Dirac semimetal CeSbTe demonstrates similar properties as the manganites. CeSb_{0.11}Te_{1.90} hosts multiple charge density wave (CDW) modulation-vectors and has a complex magnetic phase diagram. We confirm that this compound is an antiferromagnetic Dirac semimetal. Despite having a metallic Fermi surface, the electronic transport properties are semiconductor-like and deviate from known theoretical models. An external magnetic field induces a semiconductor-metal-like transition, which results in a colossal negative MR. Moreover, signatures of the coupling between the CDW and a spin modulation are observed in resistivity. This spin modulation also produces a giant anomalous Hall response

Status: published work in arXiv:2208.05466v1, 2021

Synthesis of an aqueous, air-stable, superconducting 1T'-WS2 monolayerink

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Liquid-phase chemical exfoliation is ideal to achieve industry scale production of twodimensional (2D) materials for a wide range of application such as printable electronics, catalysis and energy storage. However, many impactful 2D materials with potentials in quantum technologies can only be studied in lab settings due to their air-sensitivity, and loss of physical performance after chemical processing. Here, we report a simple chemical exfoliation method to create a stable, aqueous, surfactant-free, superconducting ink containing phase-pure 1T'-WS2 monolayers that are isotructural to the air-sensitive topological insulator 1T'-WTe2. We demonstrate that thin films can be cast on both hard and flexible substrates. The printed film is metallic at room temperature and superconducting below 7.3 K, shows strong anisotropic unconventional superconducting behavior with an in-plane and out-of-plane upper critical magnetic field of 30.1 T and 5.3 T, has a critical current of 44 mA, and is stable at ambient conditions for at least 30 days. Our results show that chemical processing can provide an engineering solution, which makes non-trivial 2D materials that used to be only studied in laboratories commercially accessible.

Status: published work in arXiv:2206.01648v1, 2022

Controllable Phycobilin Modification: An Alternative Photoacclimation Response in Cryptophyte Algae

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Cryptophyte algae are well-known for their ability to survive under low light conditions using their auxiliary light harvesting antennas, phycobiliproteins. Mainly acting to absorb light where chlorophyll cannot (500-650 nm), phycobiliproteins also play an instrumental role in helping cryptophyte algae respond to changes in light intensity through the process of photoacclimation. Until recently, photoacclimation in cryptophyte algae was only observed as a change in the cellular concentration of phycobiliproteins; however, an additional photoacclimation response was recently discovered that causes shifts in the phycobiliprotein absorbance peaks following growth under red, blue, or green light. Here, we reproduce this newly identified photoacclimation response in two species of cryptophyte algae and elucidate the origin of the response on the protein level. We compare isolated native and photoacclimated phycobiliproteins for these two species using spectroscopy and mass spectrometry, and we report the X-ray structures of each phycobiliprotein and the corresponding photoacclimated complex. We find that neither the protein sequences nor the protein structures are modified by photoacclimation. We conclude that cryptophyte algae change one chromophore in the phycobiliprotein β subunits in response to changes in the spectral quality of light. Ultrafast pump-probe spectroscopy shows that the energy transfer is weakly affected by photoacclimation.

Status: published work in ACS Central Science 2022, 8, 340

A de novo protein catalyzes the synthesis of semiconductor quantum dots

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De novo proteins constructed from novel amino acid sequences are distinct from proteins that evolved in nature. Construct K (ConK) is a binary-patterned de novo designed protein that rescues Escherichia coli from otherwise toxic concentrations of copper. ConK was recently found to bind the cofactor PLP (pyridoxal phosphate, the active form of vitamin B₆). Here, we show that ConK catalyzes the desulfurization of cysteine to H₂S, which can be used to synthesize CdS nanocrystals in solution. The CdS nanocrystals are approximately 3 nm, as measured by transmission electron microscope, with optical properties similar to those seen in chemically synthesized quantum dots. The CdS nanocrystals synthesized using ConK have slower growth rates and a different growth mechanism than those synthesized using natural biomineralization pathways. The slower growth rate yields CdS nanocrystals with two desirable properties not observed during biomineralization using natural proteins. First, CdS nanocrystals are predominantly of the zinc blende crystal phase. Second, in contrast to the growth and eventual precipitation observed in natural biomineralization systems, the CdS nanocrystals produced by ConK stabilize at a final size. Future optimization of CdS nanocrystal growth using ConK-or other de novo proteins-may help to overcome the limits on nanocrystal quality typically observed from natural biomineralization.

Status: published work in PNAS 2022, 119, e2204050119

Unlocking record capacity and rate capability of H_xCrS_2 by protonexchange pretreatment

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Unsustainable mining and limited availability of lithium-ion battery materials have created a driving need to develop alternatives such as sodium hosts. The development of suitable anode materials remains a major challenge facing sodium-ion battery development. Efforts into studying the charge storage of sodium in transition metal sulfides have gained traction due to improved kinetics compared with oxides. Van der Waals CrS₂ has been predicted to be a good intercalation host for Na but has not been isolated as a bulk phase. Rather, [CrS₂]⁻ layers exist in delafossiterelated materials such as NaCrS₂, which has only a moderate reversible capacity of about 100 mAh/g. Here we present a new material, "H_xCrS₂" (denotes approximate composition) formed by proton-exchange of NaCrS₂ which has a measured capacity of 728 mAh/g with significant improvements to capacity retention, sustaining over 700 mAh/g during cycling experiments. This is the highest reported capacity for a sulfide electrode and is higher than the capacity of antimony (576 mAh/g) which has been the most promising anode to date, pairing high capacity with high rates. Pretreatment by proton-exchange offers a route to materials such as H_xCrS₂ which provide fast diffusion and high capacities for sodium-ion batteries.

Status: published work in ChemRxiv 2022, DOI: 10.26434/chemrxiv-2022-9vlcf

Chemical Exfoliation toward Magnetic 2D VOCI Monolayers

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The diversification of magnetic two-dimensional (2D) materials holds the key to the further development of advanced technologies, such as spintronic devices and efficient data storage. However, the search for intrinsic magnetism down to the 2D limit is severely limited by the ability to reliably exfoliate large, air-stable nanosheets. Chemical exfoliation, a relatively underutilized method for delamination, offers many advantages, including a high degree of adaptability and higher yields of uniformly exfoliated materials. van der Waals (vdW) materials, in particular the family of transition-metal oxyhalides, are ideal candidates for chemical exfoliation due to their large interlayer spacing and the wide variety of interesting magnetic properties they exhibit. In this study, we employ a chemical exfoliation method to delaminate the layered antiferromagnet vanadium oxychloride (VOCl) down to the monolayer limit. The resulting nansoheets have lateral sizes of up to 20 µm, are air-stable, and can be easily isolated. Magnetic characterization was performed throughout the exfoliation process, tracking the changes in magnetic behavior among bulk VOCl, its lithiated intercalate, and the restacked nanosheet pellet. The results from this work demonstrate the potential of chemical exfoliation, along with illustrating the effects of low dimensionality on magnetic properties.

Status: published work in ACS Nano 2022, 16, 13814

Magnetic Nanosheets via Chemical Exfoliation of K_{2x}Mn_xSn_{1-x}S₂

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We report two chemical routes to prepare new magnetically doped two-dimensional (2D) tin sulfides, i.e., $Mn_xSn_{1-x}S_2$ (x = 0.1–0.2), as derivatives of $K_{2x}Mn_xSn_{1-x}S_2$. Initial codoping with K ensures high Mn doping in the nanosheets and is additionally aiding exfoliation. In chemical route 1, the parent compound is first reacted with a diluted HCl solution, which dissolves all K and half the Mn atoms, followed by treatment with TEAOH/methanol, which results in exfoliation. In chemical route 2, $K_{2x}Mn_xSn_{1-x}S_2$ is treated with I₂ in acetonitrile, leading to the removal of almost all K atoms, followed by dispersing the product in dimethylformamide, which results in partial exfoliation. The composition and structures are characterized using scanning electron microscopy, high-resolution scanning transmission electron microscopy, and selected area electron diffraction. Magnetic susceptibility measurements of the parent, intermediate, and restacked exfoliated products reveal that the manganese magnetic moment saturates at a moderate field, only in the exfoliated material. $Mn_xSn_{1-x}S_2$ nanosheets can be viewed as a magnetically doped derivative of SnS_2 , a material that is used as a high on/off ratio transistor, photocatalyst, and electrode material. Therefore, the new layered metal sulfides obtained here may have diverse applications in 2D magnetism, catalysis, or batteries.

Status: published work in Chemistry of Materials 2022, 34, 5084
Department of Electrical and Computer Engineering

Line-graph-lattice crystal structures of stoichiometric materials

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The origin of many quantum-material phenomena is intimately related to the presence of flat electronic bands. In quantum simulation, such bands have been realized through line-graph lattices, a class of lattices known to exhibit flat bands. Based on that work, we conduct a high-throughput screening for line-graph lattices among the crystalline structures of the Materials Flatband Database and report on new candidates for line-graph materials and lattice models. In particular, we find materials with line-graph-lattice structures beyond the two most commonly known examples, the kagome and pyrochlore lattices. We also identify materials that may exhibit flat topological bands. Finally, we examine the various line-graph lattices detected and highlight those with gapped flat bands and those most frequently represented among this set of materials. With the identification of real stoichiometric materials and theoretical lattice geometries, the results of this work may inform future studies of flat-band many-body physics in both condensed matter experiment and theory.

Status: published work in Physical Review Research 2022, 4, 023063

Understanding limits to mobility in ultrahigh-mobility GaAs two-dimensional electron systems: 100 million cm²/Vs and beyond

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For several decades now, ultrahigh-mobility GaAs two-dimensional electron systems (2DESs) have served as the hallmark platform for various branches of research in condensedmatter physics. Fundamental to this long-standing history of success for GaAs 2DESs was continuous sample quality improvement, which enabled scattering-free transport over macroscopic lengthscales as well as the emergence of a diverse range of exotic many-body phenomena. While the recent breakthrough in the quality of GaAs 2DESs grown by molecular beam epitaxy is highly commendable in this context, it is also important and timely to establish an up-to-date understanding of what obstructs us from pushing the mobility limit even further. Here, we present mobility data taken at a temperature of 0.3 K for a wide variety of state-of-the-art GaAs 2DESs, exhibiting a maximum, world-record mobility of $\mu \approx 57 \times 10^6$ cm²/Vs at a 2DES density of n = 1.55×10^{11} /cm². We also provide comprehensive analyses of the collective scattering mechanisms that can explain the results. Furthermore, based on our study, we discuss potential scenarios in which GaAs 2DES mobility values exceeding 100×10^6 cm²/Vs could be achieved.

Status: published work in Physical Review B 2022, 106, 075134

Correlated States of 2D Electrons near the Landau Level Filling v = 1/7

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The ground state of two-dimensional electron systems (2DESs) at low Landau level filling factors ($v \leq 1/6$) has long been a topic of interest and controversy in condensed matter. Following the recent breakthrough in the quality of ultrahigh-mobility GaAs 2DESs, we revisit this problem experimentally and investigate the impact of reduced disorder. In a GaAs 2DES sample with density $n = 6.1 \times 10^{10}$ =cm² and mobility $\mu = 25 \times 10^6$ cm²=Vs, we find a deep minimum in the longitudinal magnetoresistance (R_{xx}) at v = 1/7 when T $\simeq 104$ mK. There is also a clear sign of a developing minimum in R_{xx} at v = 2/13. While insulating phases are still predominant when $v \leq 1/6$, these minima strongly suggest the existence of fractional quantum Hall states at filling factors that comply with the Jain sequence $v = p/(2mp \pm 1)$ even in the very low Landau level filling limit. The magnetic-field-dependent activation energies deduced from the relation R_{xx} $\propto e^{Ea/2kT}$ corroborate this view and imply the presence of pinned Wigner solid states when $v \neq p/(2mp \pm 1)$. Similar results are seen in another sample with a lower density, further generalizing our observations.

Status: published work in Physical Review Letters 2022, 128, 026802

Record-quality GaAs two-dimensional hole systems

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The complex band structure, large spin-orbit induced band splitting, and heavy effective mass of two-dimensional (2D) hole systems hosted in GaAs quantum wells render them rich platforms to study many-body physics and ballistic transport phenomena. Here we report ultrahigh-quality (001) GaAs 2D hole systems, fabricated using molecular beam epitaxy and modulation doping, with mobility values as high as 5.8×10^6 cm²/(V s) at a hole density of p = 1.3 $\times 10^{11}$ /cm², implying a mean free path of ~27 µm. In the low-temperature magnetoresistance trace of this sample, we observe high-order fractional quantum Hall states up to the Landau level filling v = 12/25 near v = 1/2. Furthermore, we see a deep minimum develop at v = 1/5 in the magnetoresistance of a sample with a much lower hole density of p = 4.0 $\times 10^{10}$ /cm² where we measure a mobility of 3.6×10^6 cm²/(V s). These improvements in sample quality were achieved by the reduction of residual impurities both in the GaAs channel and in the AlGaAs barrier material, as well as optimization in the design of the sample structure.

Status: published work in Physical Review Materials 2022, 6, 034005

A comprehensive picture of roughness evolution in organic crystalline growth: the role of molecular aspect ratio

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Exploiting the capabilities of organic semiconductors for applications ranging from lightemitting diodes to photovoltaics to lasers relies on the creation of ordered, smooth layers for optimal charge carrier mobilities and exciton diffusion. This, in turn, creates a demand for organic small molecules that can form smooth thin film crystals via homoepitaxy. We have studied a set of small molecule organic semiconductors that serve as templates for homoepitaxy. The surface roughness of these materials is measured as a function of adlayer film thickness from which the growth exponent (β) is extracted. Notably, we find that three-dimensional molecules that have low molecular aspect ratios (AR) tend to remain smooth as thickness increases (small β). This is in contrast to planar or rod-like molecules with high AR that quickly roughen (large β). Molecular dynamics simulations find that the Ehrlich–Schwobel barrier (EES) alone is unable to fully explain this trend. Our results suggest that low AR molecules have low molecular mobility and moderate EES which creates a downward funneling effect leading to smooth crystal growth.

Status: published work in Materials Horizons 2022, 9, 2752

From Amorphous to Polycrystalline Rubrene: Charge Transport in Organic Semiconductors Paralleled with Silicon

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While progress has been made in the design of organic semiconductors (OSCs) with improved transport properties, the understanding of the mechanisms involved is still limited. In this study, the interplay between structural order and transport considering one single OSC, analogous to past research on silicon is investigated. Rubrene ($C_{42}H_{28}$) is selected as it spans transport mechanisms from thermally activated hopping in its amorphous form to band-like in highly ordered crystals in the orthorhombic polymorph. Transport characterizations including variable temperature conductivity, advanced Hall effect, and magnetoresistance measurements are performed on rubrene films with varying levels of order, crystal phase, and morphologies. A conductivity tuning range over four orders of magnitude is reported. As observed in silicon, transport in polycrystalline orthorhombic rubrene is limited by energy barriers at grain boundaries. Additionally, a gradual transition from predominantly bandlike to predominantly hopping transport with increasing disorder. Nevertheless, OSCs differ from covalently bonded silicon by their weak intermolecular interaction. This study highlights that molecular packing must be optimized in OSCs to favor advantageous π -orbital overlap and optimized transport properties.

Status: published work in Advanced Functional Materials 2022, p.2206438

Improved Charge Balance in Green Perovskite Light-Emitting Diodes with Atomic-Layer-Deposited Al₂O₃

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Perovskite light-emitting diodes (LEDs) have experienced a rapid increase in efficiency over the last several years and are now regarded as promising low-cost devices for displays and communication systems. However, it is often challenging to employ ZnO, a well-studied electron transport material, in perovskite LEDs due to chemical instability at the ZnO/perovskite interface and charge injection imbalance caused by the relatively high conductivity of ZnO. In this work, we address these problems by depositing an ultrathin Al₂O₃ interlayer at the ZnO/perovskite interface, allowing the fabrication of green-emitting perovskite LEDs with a maximum luminance of 21 815 cd/m². Using atomic layer deposition, we can precisely control the Al₂O₃ thickness and thus fine-tune the electron injection from ZnO, allowing us to enhance the efficiency and operational stability of our LEDs.

Status: published work in ACS Appl. Mater. Interfaces 2022, 14, 34247

Anisotropic Two-Dimensional Disordered Wigner Solid

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The interplay between the Fermi sea anisotropy, electron-electron interaction, and localization phenomena can give rise to exotic many-body phases. An exciting example is an anisotropic two-dimensional (2D) Wigner solid (WS), where electrons form an ordered array with an anisotropic lattice structure. Such a state has eluded experiments up to now as its realization is extremely demanding: First, a WS entails very low densities where the Coulomb interaction dominates over the kinetic (Fermi) energy. Attaining such low densities while keeping the disorder low is very challenging. Second, the low-density requirement has to be fulfilled in a material that hosts an anisotropic Fermi sea. Here, we report transport measurements in a clean (low-disorder) 2D electron system with anisotropic effective mass and Fermi sea. The data reveal that at extremely low electron densities, when the rs parameter, the ratio of the Coulomb to the Fermi energy, exceeds \approx 38, the current-voltage characteristics become strongly nonlinear at small dc biases. Several key features of the nonlinear characteristics, including their anisotropic voltage thresholds, are consistent with the formation of a disordered, anisotropic WS pinned by the ubiquitous disorder potential.

Status: published work in Physical Review Letters 2022, 129, 036601

Hybrid III-V diamond photonic platform for quantum nodes based on neutral silicon vacancy centers in diamond

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Integrating atomic quantum memories based on color centers in diamond with on-chip photonic devices would enable entanglement distribution over long distances. However, efforts towards integration have been challenging because color centers can be highly sensitive to their environment, and their properties degrade in nanofabricated structures. Here, we describe a heterogeneously integrated, on-chip, III-V diamond platform designed for neutral silicon vacancy (SiV⁰) centers in diamond that circumvents the need for etching the diamond substrate. Through evanescent coupling to SiV⁰ centers near the surface of diamond, the platform will enable Purcell enhancement of SiV⁰ emission and efficient frequency conversion to the telecommunication Cband. The proposed structures can be realized with readily available fabrication techniques.

Status: published work in Optics Express 2021, 29, 9174

Nonradiative Recombination via Charge-Transfer-Exciton to Polaron Energy Transfer Limits Photocurrent in Organic Solar Cells

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A recombination and exciton loss mechanism is reported in organic solar cells involving energy transfer between charge transfer (CT) excitons and polarons, impacting photocurrent generation, particularly in the near-infrared where polaronic transitions typically reside. This process sets a low-energy cut-off in the external quantum efficiency spectrum of an excitonic donor/acceptor interface, determined by the low-energy polaron absorption peak and the CT state reorganization energy. Furthermore, this process explains the deviation from unity and bias dependence of the CT state's internal quantum efficiency at low photon energies. This process is demonstrated in a variety of systems and it is hypothesized that CT state to polaron energy transfer recombination may be responsible for a share of nonradiative recombination in all organic photovoltaics and can explain numerous experimentally observed device trends regarding photocurrent generation and energy losses. Overall, this work enhances the understanding of photophysical processes in organic materials and allows the design of systems that can avoid this recombination pathway.

Status: published work in Advanced Energy Materials 2022, 12, 2200551

Quantifying the effect of energetic disorder on organic solar cell energy loss

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Understanding the factors affecting energy loss in organic photovoltaics (OPVs) is imperative to achieve further improvements in their efficiency and to establish design rules for the development of new materials. Here, we provide direct experimental evidence supporting correlation between charge-transfer (CT) state static disorder and energy loss. Specifically, upon studying several planar and bulk heterojunction solar cells, we demonstrate that the non-radiative energy loss component quadratically increases with increasing Gaussian CT-state disorder. We also show that by defining the total energy loss in terms of the peak of the CT-state distribution, obtained from temperature-dependent external quantum efficiency measurements, the effect of disorder on OPV performance can be unambiguously identified, offering a universal metric for quantifying energy loss across various devices.

Status: published work in Joule 2022, 6, 1

Hot-Casting-Assisted Liquid Additive Engineering for Efficient and Stable Perovskite Solar Cells

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High-performance inorganic–organic lead halide perovskite solar cells (PSCs) are often fabricated with a liquid additive such as dimethyl sulfoxide (DMSO), which retards crystallization and reduces roughness and pinholes in the perovskite layers. However, DMSO can be trapped during perovskite film formation and induce voids and undesired reaction byproducts upon later processing steps. Here, it is shown that the amount of residual DMSO can be reduced in as-spin-coated films significantly through use of preheated substrates, or a so-called hot-casting method. Hot casting increases the perovskite film thickness given the same concentration of solutions. By reducing the amount of DMSO in proportion to the concentration of perovskite precursors and using hot casting, it is possible to fabricate perovskite layers with improved perovskite–substrate interfaces by suppressing the formation of byproducts. The best-performing PSCs exhibit a power conversion efficiency (PCE) of 23.4% (23.0% stabilized efficiency) under simulated solar illumination. Furthermore, encapsulated devices show considerably reduced post-burn-in decay, retaining 75% and 90% of their initial and post-burn-in efficiencies after 3000 h of operation with maximum power point tracking (MPPT) under high power of ultraviolet (UV)-containing continuous light exposure.

Status: published work in Advanced Materials 2022, 34, 2205309

Composite fermion mass: Experimental measurements in ultrahigh quality two-dimensional electron systems

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Composite fermions (CFs), exotic quasiparticles formed by pairing an electron and an even number of magnetic flux quanta, emerge at high magnetic fields in an interacting electron system, and can explain phenomena such as the fractional quantum Hall state (FQHS) and other manybody phases. CFs possess an effective mass (m_{CF}) whose magnitude is inversely related to the most fundamental property of a FQHS, namely its energy gap. We present here experimental measurements of m_{CF} in ultrahigh quality two-dimensional electron systems confined to GaAs quantum wells of varying thickness. An advantage of measuring m_{CF} over gap measurements is that mass values are insensitive to disorder and are therefore ideal for comparison with theoretical calculations, especially for high-order FQHS. Our data reveal that m_{CF} increases with increasing well width, reflecting a decrease in the energy gap as the electron layer becomes thicker and the in-plane Coulomb energy softens. Comparing our measured masses with available theoretical results, we find significant quantitative discrepancies, highlighting that more rigorous and accurate calculations are needed to explain the experimental data.

Status: published work in Physical Review B 2022, 106, L041301

Erbium-implanted materials for quantum communication applications

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Erbium-doped materials can serve as spin-photon interfaces with optical transitions in the telecom C band, making them an exciting class of materials for long-distance quantum communication. However, the spin and optical coherence times of Er^{3+} ions are limited by currently available host materials, motivating the development of new Er^{3+} -containing materials. Here we demonstrate the use of ion implantation to efficiently screen prospective host candidates, and show that disorder introduced by ion implantation can be mitigated through post-implantation thermal processing to achieve inhomogeneous linewidths comparable to bulk linewidths in asgrown samples. We present optical spectroscopy data for each host material, which allows us to determine the level structure of each site, allowing us to compare the environments of Er^{3+} introduced via implantation and via doping during growth. We demonstrate that implantation can generate a range of local environments for Er^{3+} , including those observed in bulk-doped materials, and that the populations of these sites can be controlled with thermal processing.

Status: published work in Physical Review B 2022, 105, 224106

Even-Denominator Fractional Quantum Hall State at Filling Factor v = 3/4

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Fractional quantum Hall states (FQHSs) exemplify exotic phases of low-disorder twodimensional (2D) electron systems when electron-electron interaction dominates over the thermal and kinetic energies. Particularly intriguing among the FQHSs are those observed at evendenominator Landau level filling factors, as their quasiparticles are generally believed to obey non-Abelian statistics and be of potential use in topological quantum computing. Such states, however, are very rare and fragile, and are typically observed in the excited Landau level of 2D electron systems with the lowest amount of disorder. Here we report the observation of a new and unexpected even-denominator FQHS at filling factor v = 3/4 in a GaAs 2D hole system with an exceptionally high quality (mobility). Our magnetotransport measurements reveal a strong minimum in the longitudinal resistance at v = 3/4, accompanied by a developing Hall plateau centered at $(h/e^2)/(3/4)$. This even-denominator FQHS is very unusual as it is observed in the lowest Landau level and in a 2D hole system. While its origin is unclear, it is likely a non-Abelian state, emerging from the residual interaction between composite fermions.

Status: published work in Phys. Rev. Lett. 2022, 129, 156801

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 led to a new class of biophysical sensors and diagnostic devices that are being investigated as a platform for cancer screening and ultrasensitive immunoassays. However, a broader application in the life sciences based on nanoscale NMR spectroscopy has been hampered by the need to interface highly sensitive quantum bit (qubit) sensors with their biological targets. Here, we demonstrate an 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 the biomolecule adsorption density and results in near-surface qubit coherence approaching 100 µs. The developed architecture remains chemically stable under physiological conditions for over 5 d, making our technique compatible with most biophysical and biomedical applications.

Status: published work in PNAS 2022, 119, e2114186119

Iodine Electrochemistry Dictates Voltage-Induced Halide Segregation Thresholds in Mixed-Halide Perovskite Devices

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Owing to straightforward stoichiometry–bandgap tunability, mixed-halide perovskites are ideal for many optoelectronic devices. However, unwanted halide segregation under operational conditions, including light illumination and voltage bias, restricts practical use. Additionally, the origin of voltage-induced halide segregation is still unclear. Herein, a systematic voltage threshold study in mixed bromide/iodide perovskite devices is performed and leads to observation of three distinct voltage thresholds corresponding to the doping of the hole transport material (0.7 ± 0.1 V), halide segregation (0.95 ± 0.05 V), and degradation (1.15 ± 0.05 V) for an optically stable mixed-halide perovskite composition with a low bromide content (10%). These empirical threshold voltages are minimally affected by composition until very Br-rich compositions, which reveals the dominant role of iodide/triiodide/iodine electrochemistry in voltage-induced Br/I phase separation and transport layer doping reactions in halide perovskite devices.

Status: published work in Advanced Functional Materials 2022, 32, 2203432

Department of Geosciences

The origin of carbonate mud and implications for global climate

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Carbonate mud represents one of the most important geochemical archives for reconstructing ancient climatic, environmental, and evolutionary change from the rock record. Mud also represents a major sink in the global carbon cycle. Yet, there remains no consensus about how and where carbonate mud is formed. Here, we present stable isotope and trace-element data from carbonate constituents in the Bahamas, including ooids, corals, foraminifera, and algae. We use geochemical fingerprinting to demonstrate that carbonate mud cannot be sourced from the abrasion and mixture of any combination of these macroscopic grains. Instead, an inverse Bayesian mixing model requires the presence of an additional aragonite source. We posit that this source represents a direct seawater precipitate. We use geological and geochemical data to show that "whitings" are unlikely to be the dominant source of this precipitate. Next, we address the enigma of why mud and ooids are so abundant in the Bahamas, yet so rare in the rest of the world: Mediterranean outflow feeds the Bahamas with the most alkaline waters in the modern ocean (>99.7th-percentile). Finally, we show how shutting off and turning on the shallow carbonate factory can send ripples through the global climate system.

Status: published work in PNAS 2022, 119, e2210617119

Structure and density of silicon carbide to 1.5 TPa and implications for extrasolar planets

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There has been considerable recent interest in the high-pressure behavior of silicon carbide, a potential major constituent of carbon-rich exoplanets. In this work, the atomic-level structure of SiC was determined through in situ X-ray diffraction under laser-driven ramp compression up to 1.5 TPa; stresses more than seven times greater than previous static and shock data. Here we show that the B1-type structure persists over this stress range and we have constrained its equation of state (EOS). Using this data we have determined the first experimentally based mass-radius curves for a hypothetical pure SiC planet. Interior structure models are constructed for planets consisting of a SiC-rich mantle and iron-rich core. Carbide planets are found to be $\sim 10\%$ less dense than corresponding terrestrial planets.

Status: published work in Nature Communication 2022, 13, 2260

Lewis-Sigler Institute for Integrative Genomics

Cellular Sensing Governs the Stability of Chemotactic Fronts

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In contexts ranging from embryonic development to bacterial ecology, cell populations migrate chemotactically along self-generated chemical gradients, often forming a propagating front. Here, we theoretically show that the stability of such chemotactic fronts to morphological perturbations is determined by limitations in the ability of individual cells to sense and thereby respond to the chemical gradient. Specifically, cells at bulging parts of a front are exposed to a smaller gradient, which slows them down and promotes stability, but they also respond more strongly to the gradient, which speeds them up and promotes instability. We predict that this competition leads to chemotactic fingering when sensing is limited at too low chemical concentrations. Guided by this finding and by experimental data on E. coli chemotaxis, we suggest that the cells' sensory machinery might have evolved to avoid these limitations and ensure stable front propagation. Finally, as sensing of any stimuli is necessarily limited in living and active matter in general, the principle of sensing-induced stability may operate in other types of directed migration such as durotaxis, electrotaxis, and phototaxis.

Status: published work in Physical Review Letters 2022, 128, 148101

Department of Mechanical and Aerospace Engineering

Flow rate–pressure drop relation for shear-thinning fluids in narrow channels: approximate solutions and comparison with experiments.

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Non-Newtonian fluids are characterized by complex rheological behaviour that affects the hydrodynamic features, such as the flow rate-pressure drop relation. While flow rate-pressure drop measurements of such fluids are common in the literature, a comparison of experimental data with theory is rare, even for shear-thinning fluids at low Reynolds number, presumably due to the lack of analytical expressions for the flow rate-pressure drop relation covering the entire range of pressures and flow rates. Such a comparison, however, is of fundamental importance as it may provide insight into the adequacy of the constitutive models. In this work, we present a theoretical approach to calculating the flow rate-pressure drop relation of shear-thinning fluids in long, narrow channels that can be used for comparison with experimental measurements. We utilize the Carreau constitutive model and provide a semi-analytical expression for the flow rate-pressure drop relation. In particular, we derive three asymptotic solutions for small, intermediate and large values of the dimensionless pressures or flow rates, which agree with distinct limits previously known and allow us to approximate analytically the entire flow rate-pressure drop curve. We compare our semi-analytical and asymptotic results with the experimental and find excellent agreement. Our results rationalize the change in the slope of the flow rate-pressure drop data, when reported in log-log coordinates, at high flow rates, which cannot be explained using a simple power-law model.

Status: published work in J. Fluid Mech. 2021, 923, R5

Pressure-driven flow of the viscoelastic Oldroyd-B fluid in narrow nonuniform geometries: analytical results and comparison with simulations

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We analyse the pressure-driven flow of the Oldroyd-B fluid in slowly varying arbitrarily shaped, narrow channels and present a theoretical framework for calculating the relationship between the flow rate q and pressure drop Δp . We first identify the characteristic scales and dimensionless parameters governing the flow in the lubrication limit. Employing a perturbation expansion in powers of the Deborah number (De), we provide analytical expressions for the velocity, stress and the $q-\Delta p$ relation in the weakly viscoelastic limit up to O(De2). Furthermore, we exploit the reciprocal theorem derived by Boyko & Stone to obtain the $q - \Delta p$ relation at the next order, O(De3), using only the velocity and stress fields at the previous orders. We validate our analytical results with two-dimensional numerical simulations in the case of a hyperbolic, symmetric contracting channel and find excellent agreement. While the velocity remains approximately Newtonian in the weakly viscoelastic limit (i.e. the theorem of Tanner and Pipkin), we reveal that the pressure drop strongly depends on the viscoelastic effects and decreases with De. We elucidate the relative importance of different terms in the momentum equation contributing to the pressure drop along the symmetry line and identify that a pressure drop reduction for narrow contracting geometries is primarily due to gradients in the viscoelastic shear stresses. We further show that, although for narrow geometries the viscoelastic axial stresses are negligible along the symmetry line, they are comparable or larger than shear stresses in the rest of the domain.

Status: published work in J. Fluid Mech. 2022, 936, A23

Reciprocal theorem for calculating the flow rate-pressure drop relation for complex fluids in narrow geometries

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We study the mechanically driven flows of non-Newtonian fluids in narrow and confined configurations. Using the Lorentz reciprocal theorem, we derive a closed-form expression for the flow rate–pressure drop relation of complex fluids in such geometries, which holds for a wide class of non-Newtonian constitutive models. For the weakly non-Newtonian limit, our theory provides the first-order non-Newtonian correction for the flow rate–pressure drop relation solely using the corresponding Newtonian solution, eliminating the need to solve the non-Newtonian flow problem. In particular, for the flow-rate-controlled situation, we find that the first-order non-Newtonian pressure drop correction may increase, decrease, or not change the total pressure drop for a viscoelastic second-order fluid, depending on the geometry, but always decreases it for a shear-thinning Carreau fluid.

Status: published work in Physical Review Fluids 2021, 6, L081301

Combining Spatial and Temporal Resolution in Cryo-TEM of Device Materials

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Cryogenic transmission electron microscopy (cryo-TEM) has been instrumental to reducing the effects of electron-beam sample interactions and enabling higher spatial resolution studies of beam sensitive materials. However, the process of thinning and freezing samples for cryo-TEM characterization is often complex and frequently requires removing materials from their environment or stimuli of interest for extended times, hindering characterization of transient or active states. For a device material such as a battery electrode, techniques involve disassembling the battery post-cycling and either liberating electrode particles, depositing them onto a TEM grid, and plunge freezing or removing the entire electrode or electrode stacks and transferring to a cryofocused ion beam for thinning. Additional time is needed to protect the materials from air exposure, necessary to preserve their chemical structures akin to the original sealed battery.

Status: published work in Microscopy and Microanalysis 2022, 28, 2162

Three-Dimensional Self-Similarity of Coalescing Viscous Drops in the Thin-Film Regime

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Coalescence and breakup of drops are classic problems in fluid physics that often involve self-similarity and singularity formation. While the coalescence of suspended drops is axisymmetric, the coalescence of drops on a substrate is inherently three-dimensional. Yet, studies so far have only considered this problem in two dimensions. In this Letter, we use interferometry to reveal the three-dimensional shape of the interface as two drops coalescence on a substrate. We unify the known scaling laws in this problem within the thin-film approximation and find a three-dimensional self-similarity that enables us to describe the anisotropic shape of the dynamic interface with a universal curve.

Status: published work in Physical Review Letters 2022, 129, 144501

Enhanced Thermal Stability of Aerosol-Synthesized Ni-Rich Li-Ion Battery Cathode Materials via Concentration-Gradient Ca Doping

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High-Ni cathode materials such as Li-Ni_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) are replacing low-Ni, high-Co cathode materials in Li-ion batteries. However, the poor thermal stability and long-term cycling performance of high-Ni cathode materials are a barrier to rapid commercial application. Doping is used to optimize the fire safety and electrochemical performance of NCM811. In this work, we synthesized calcium (Ca)-doped NCM811 materials with direct control of the local dopant concentration by using an aerosol synthesis process (rapid metal salt solution aerosol pyrolysis). By identifying the appropriate precursors and controlling the ion concentration and a unique gradient structure of Ca can be controllably formed within the NCM811 cathode particles. This Ca-doping technique significantly increased the thermal stability of NCM811. In thermal decomposition tests of the delithiated materials, the oxygen release of uniform and gradient Ca-doped NCM811 decreased by 52 and 85%, respectively, as compared to that of the undoped materials. Furthermore, the thermal onset temperature was increased from 498 to 527 K. Herein, we show that rapid formation of a concentration-gradient structure in aerosol synthesis is a promising route to optimize the thermal stability of cathode materials for Li-ion batteries.

Status: published work in ACS Appl. Energy Mater. 2022, 5, 10751

Buckling of elastic fibers in a shear flow

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Three-dimensional dynamics of flexible fibers in shear flow are studied numerically, with a qualitative comparison to experiments. Initially, the fibers are straight, with different orientations with respect to the flow. By changing the rotation speed of a shear rheometer, we change the ratio A of bending to shear forces. We observe fibers in the flow-vorticity plane, which gives insight into the motion out of the shear plane. The numerical simulations of moderately flexible fibers show that they rotate along effective Jeffery orbits, and therefore the fiber orientation rapidly becomes very close to the flow-vorticity plane, on average close to the flow direction, and the fiber remains in an almost straight configuration for a long time. This 'ordering' of fibers is temporary since they alternately bend and straighten while tumbling. We observe numerically and experimentally that if the fibers are initially in the compressional region of the shear flow, they can undergo compressional buckling, which is in contrast to the typical local bending that originates over a long time from the fiber ends. We identify differences between local and compressional bending and discuss their competition. There are two main finding. First, the compressional buckling is limited to a certain small range of the initial orientations, excluding those from the flow-vorticity plane. Second, since fibers straighten in the flow-vorticity plane while tumbling, the compressional buckling is transient—it does not appear for times longer than 1/4 of the Jeffery period. For larger times, bending of fibers is always driven by their ends.

Status: published work in New Journal of Physics 2022, 24, 013013

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 Journal 2022, 18, 514

Department of Molecular Biology

Direct visualization of floppy two-dimensional DNA origami using cryogenic electron microscopy

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Two-dimensional (2D) DNA origami that is capable of self-assembling into complex 2D and 3D geometries pave the way for a bottom-up synthesis for various applications in nano/biotechnology. Here, we directly visualized the aqueous structure of 2D DNA origami cross-tiles and their assemblies using cryogenic electron microscopy. We uncovered flexible arms in cross-tile monomers and designated inter-tile folding. In addition, we observed the formation of clusters and stacks of DNA cross-tiles in solution, which could potentially affect the interaction and assembly of DNA origami. Finally, we quantitatively evaluated the flexibility of DNA origami in solution using finite element analysis. Our discovery has laid the foundation for investigating the dynamic structures of 2D DNA origami assemblies in solution, providing insights regarding the self-assembly and self-replication mechanisms of 2D DNA origami.

Status: published work in iScience 2022, 25, 104373

Structural basis for the severe adverse interaction of sofosbuvir and amiodarone on L-type Ca $_{v}$ channels

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Drug-drug interaction of the antiviral sofosbuvir and the antiarrhythmics amiodarone has been reported to cause fatal heartbeat slowing. Sofosbuvir and its analog, MNI-1, were reported to potentiate the inhibition of cardiomyocyte calcium handling by amiodarone, which functions as a multi-channel antagonist, and implicate its inhibitory effect on L-type Ca_v channels, but the molecular mechanism has remained unclear. Here we present systematic cryo-EM structural analysis of Ca_v1.1 and Ca_v1.3 treated with amiodarone or sofosbuvir alone, or sofosbuvir/MNI-1 combined with amiodarone. Whereas amiodarone alone occupies the dihydropyridine binding site, sofosbuvir is not found in the channel when applied on its own. In the presence of amiodarone, sofosbuvir/MNI-1 is anchored in the central cavity of the pore domain through specific interaction with amiodarone and directly obstructs the ion permeation path. Our study reveals the molecular basis for physical, pharmacodynamic interaction of two drugs on the scaffold of Ca_v channels.

Status: published work in Cell 2022, 185, 4801

Structural basis for pore blockade of human voltage-gated calcium channel $Ca_v 1.3$ by motion sickness drug cinnarizine

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The structure of human Cav1.3 channel bound to cinnarizine unveils a direct pore blockade of LTCC by motion sickness drugs. Local structural shifts at the cinnarizine-binding site cause an axial rotation of the ensuing helical segment. The $\alpha \rightarrow \pi$ transition of the gating residue-locating helical turn in S6III further constricts the ion-permeation pore. The structures shown here, along with our previous studies, reveal the molecular details for the MOA of diverse Ca_v channel modulators and lay the foundation for structure-aided drug discovery. Furthermore, all the reported structures of LTCC, either Ca_v1.1 from endogenous tissue or Ca_v1.3 from heterologous expression, are featured with four up VSDs and closed PD, consistent with inactivated states. In contrast, the recently reported structures of N-type Ca_v2.2 channels reveal a down VSDII. Establishment of a recombinant expression system for L-type Cav channels paves the avenue to investigate the intrinsic biophysical differences between different types of Cav channels.

Status: published work in Cell Research 2022, 32, 946
Structures of the R-type human $Ca_v 2.3$ channel reveal conformational crosstalk of the intracellular segments

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The R-type voltage-gated Ca^{2+} (Ca_v) channels $Ca_v 2.3$, widely expressed in neuronal and neuroendocrine cells, represent potential drug targets for pain, seizures, epilepsy, and Parkinson's disease. Despite their physiological importance, there have lacked selective small-molecule inhibitors targeting these channels. High-resolution structuresmay aid rational drug design. Here, we report the cryo-EM structure of human $Ca_v 2.3$ in complex with $\alpha 2\delta$ –1 and $\beta 3$ subunits at an overall resolution of 3.1 Å. The structure is nearly identical to that of $Ca_v 2.2$, with VSD_{II} in the down state and the other three VSDs up. A phosphatidylinositol 4,5-bisphosphate (PIP2) molecule binds to the interface of VSDII and the tightly closed pore domain. We also determined the cryo-EM structure of a $Ca_v 2.3$ mutant in which a $Ca_v 2$ -unique cytosolic helix in repeat II (designated the CH2_{II} helix) is deleted. This mutant, named Δ CH2, still reserves a down VSD_{II}, but PIP2 is invisible and the juxtamembrane region on the cytosolic side is barely discernible. Our structural and electrophysiological characterizations of the wild type and Δ CH₂ $Ca_v 2.3$ show that the CH2_{II} helix stabilizes the inactivated conformation of the channel by tightening the cytosolic juxtamembrane segments, while CH2_{II} helix is not necessary for locking the down state of VSD_{II}.

Status: published work in Nature Communications 2022, 13, 7358

Princeton Neuroscience Institute

In situ X-ray-assisted electron microscopy staining for large biological samples

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Electron microscopy of biological tissue has recently seen an unprecedented increase in imaging throughput moving the ultrastructural analysis of large tissue blocks such as whole brains into the realm of the feasible. However, homogeneous, high-quality electron microscopy staining of large biological samples is still a major challenge. To date, assessing the staining quality in electron microscopy requires running a sample through the entire staining protocol end-to-end, which can take weeks or even months for large samples, rendering protocol optimization for such samples to be inefficient. Here, we present an in situ time-lapsed X-ray-assisted staining procedure that opens the 'black box' of electron microscopy staining and allows observation of individual staining steps in real time. Using this novel method, we measured the accumulation of heavy metals in large tissue samples immersed in different staining solutions. We show that the measured accumulation of osmium in fixed tissue obeys empirically a quadratic dependence between the incubation time and sample size. We found that potassium ferrocyanide clears the tissue after osmium staining and that the tissue expands in osmium tetroxide solution, but shrinks in potassium ferrocyanide reduced osmium solution. X-ray-assisted staining gave access to the in situ staining kinetics and allowed us to develop a diffusion-reaction-advection model that accurately simulates the measured accumulation of osmium in tissue. These are first steps towards in silico staining experiments and simulation-guided optimization of staining protocols for large samples.

Status: published work in eLife 2022, 11, e72147

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

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We have achieved a three-fold increase in the speed of transmission electron microscopy by using a beam deflecting mechanism to enable highly efficient acquisition of multiple image tiles for each motion of the mechanical stage. For millimeter-scale areas, the duty cycle of imaging doubles and exceeds 30%, yielding a net average imaging rate of 0.3 gigapixels per second.

Status: published work in bioRxiv 2022, 2022.11.23.517701

Department of Physics

Observation of a linked-loop quantum state in a topological magnet

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Quantum phases can be classified by topological invariants, which take on discrete values capturing global information about the quantum state. Here we report an unusual linking-number (knot theory) invariant associated with loops of electronic band crossings in a mirror-symmetric ferromagnet. Using state-of-the-art spectroscopic methods, we directly observe three intertwined degeneracy loops in the material's three-torus, T3, bulk Brillouin zone. We find that each loop links each other loop twice. Through systematic spectroscopic investigation of this linked-loop quantum state, we explicitly draw its link diagram and conclude, in analogy with knot theory, that it exhibits the linking number (2, 2, 2), providing a direct determination of the invariant structure from the experimental data. We further predict and observe, on the surface of our samples, Seifert boundary states protected by the bulk linked loops, suggestive of a remarkable Seifert bulk–boundary correspondence. Our observation of a quantum loop link motivates the application of knot theory to the exploration of magnetic and superconducting quantum matter.

Status: published work in Nature 2022, 604, 647

Signatures of Weyl Fermion Annihilation in a Correlated Kagome Magnet

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The manipulation of topological states in quantum matter is an essential pursuit of fundamental physics and next-generation quantum technology. Here we report the magnetic manipulation of Weyl fermions in the kagome spin-orbit semimetal Co₃Sn₂S₂, observed by high-resolution photoemission spectroscopy. We demonstrate the exchange collapse of spin-orbit-gapped ferromagnetic Weyl loops into paramagnetic Dirac loops under suppression of the magnetic order. We further observe that topological Fermi arcs disappear in the paramagnetic phase, suggesting the annihilation of exchange-split Weyl points. Our findings indicate that magnetic exchange collapse naturally drives Weyl fermion annihilation, opening new opportunities for engineering topology under correlated order parameters.

Status: published work in Physical Reviews Letters 2022, 127, 256403

Visualization of Tunable Weyl Line in A-A Stacking Kagome Magnets

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Kagome magnets provide a fascinating platform for a plethora of topological quantum phenomena, in which the delicate interplay between frustrated crystal structure, magnetization and spin-orbit coupling (SOC) can engender highly tunable topological states. Here, utilizing angle-resolved photoemission spectroscopy, we directly visualize the Weyl lines with strong out-of-plane dispersion in the A-A stacked kagome magnet $GdMn_6Sn_6$. Remarkably, the Weyl lines exhibit a strong magnetization-direction tunable SOC gap and binding energy tunability after substituting Gd with Tb and Li, respectively. Our results not only illustrate the magnetization direction and valence counting as efficient tuning knobs for realizing and controlling distinct three-dimensional topological phases, but also demonstrate AMn_6Sn_6 (A = rare earth or Li, Mg, Ca) as a versatile material family for exploring diverse emergent topological quantum responses.

Status: published work in Advanced Materials 2022, p. 2205927

Planar thermal Hall effect of topological bosons in the Kitaev magnet $\alpha\text{-}\text{RuCl}_3$

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In the field of quantum spin liquids, the honeycomb magnet α -RuCl₃ has attracted considerable interest because it is proximate to the Kitaev Hamiltonian H_K. In 2006, Kitaev published the exact solution for the ground state of H_K, and found that the excitations are Majoranas and vortices. The thermal Hall conductivity κ_{xy} of Majorana fermions is predicted to be half-quantized. This effect has been reported in α -RuCl₃, but this observation has proven difficult to reproduce and remains highly controversial. We report detailed measurements of the Onsager-like planar thermal Hall conductivity κ_{xy} in α -RuCl₃, a spin-liquid candidate of topical interest. With the thermal current J_Q and magnetic field B || a (zigzag axis), the observed κ_{xy}/T varies strongly with temperature T (1-10 K). Using a novel fitting procedure, we show that this temperature dependence matches the distinct form expected for topological bosonic modes in a Chern insulator-like model. Our analysis yields band energies that are in agreement with earlier experiments and that the excitations evolve into increasingly magnon-like modes at high B with a Chern number ~ 1. The bosonic character is incompatible with half-quantization of κ_{xy}/T .

Status: published work in Nature Materials 2023, 22, 36

Microwave-Frequency Scanning Gate Microscopy of a Si/SiGe Double Quantum Dot

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Conventional transport methods provide quantitative information on spin, orbital, and valley states in quantum dots but lack spatial resolution. Scanning tunneling microscopy, on the other hand, provides exquisite spatial resolution at the expense of speed. Working to combine the spatial resolution and energy sensitivity of scanning probe microscopy with the speed of microwave measurements, we couple a metallic tip to a Si/SiGe double quantum dot (DQD) that is integrated with a charge detector. We first demonstrate that the dc-biased tip can be used to change the occupancy of the DQD. We then apply microwaves through the tip to drive photon-assisted tunneling (PAT). We infer the DQD level diagram from the frequency and detuning dependence of the tunneling resonances. These measurements allow the resolution of ~65 μ eV excited states, an energy consistent with valley splittings in Si/SiGe. This work demonstrates the feasibility of scanning gate experiments with Si/SiGe devices.

Status: published work in Nano Letters 2022, 22, 4807

Low-Reynolds-number, biflagellated 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 nonreciprocal 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 biflagellated sphere at low Re via Quincke rotation. These Quincke swimmers exhibit three different forms of motion, including a self-oscillatory state due to elastohydrodynamic–electrohydrodynamic interactions. Each form of motion follows a distinct trajectory in space. Our experiments and numerical results demonstrate a method to generate, and potentially control, the locomotion of artificial flagellated swimmers.

Status: published work in PNAS 2021, 118, e2022000118

Eavesdropping on competing condensates by the edge supercurrent in a Weyl superconductor.

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In a topological insulator the metallic surface states are easily distinguished from the insulating bulk states. By contrast, in a topological superconductor, much less is known about the relationship between an edge supercurrent and the bulk pair condensate. Can we force their pairing symmetries to be incompatible? In the superconducting state of the Weyl semimetal MoTe₂, an edge supercurrent is observed as oscillations in the current-voltage curves induced by fluxoid quantization. We have found that the s-wave pair field of supercurrent injected from niobium contacts is incompatible with the intrinsic pair condensate in MoTe₂. The incompatibility leads to strong stochasticity in the switching current Ic as well as other anomalous properties such as an unusual antihysteretic behavior with the wrong sign. Under the injected supercurrent, the uxoid-induced edge oscillations survive to much higher magnetic fields H. Interestingly, the oscillations are either very noisy or noise-free depending on the pair field that ends up dictating the edge pairing. Using the phase noise as a sensitive probe that eavesdrops on the competing bulk states, we uncover an underlying blockade mechanism whereby the intrinsic condensate can preemptively block proximitization by the Nb pair field depending on the history.

Status: published work in arXiv.org 2022, 2208.00933

Two-qubit silicon quantum processor with operation fidelity exceeding 99%

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Silicon spin qubits satisfy the necessary criteria for quantum information processing. However, a demonstration of high-fidelity state preparation and readout combined with high-fidelity single- and two-qubit gates, all of which must be present for quantum error correction, has been lacking. We use a two-qubit Si/SiGe quantum processor to demonstrate state preparation and readout with fidelity greater than 97%, combined with both single- and two-qubit control fidelities exceeding 99%. The operation of the quantum processor is quantitatively characterized using gate set tomography and randomized benchmarking. Our results highlight the potential of silicon spin qubits to become a dominant technology in the development of intermediate-scale quantum processors.

Status: published work in Science Advances 2022, 8, eabn5130

Singular angular magnetoresistance and sharp resonant features in a highmobility metal with open orbits, ReO₃

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We report high-resolution angular magnetoresistance (AMR) experiments performed on crystals of ReO₃ with high mobility (>100 000 cm²/V s at 2 K) and extremely low residual resistivity (5–8 n Ω cm). The Fermi surface, comprised of intersecting cylinders, supports open orbits. The resistivity ρ_{xx} in a magnetic field B = 9 T displays a singular pattern of behavior. With E || x and B initially || z, tilting B in the longitudinal k_z-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-k_z plane, ρ_{xx} increases steeply by a factor of 8. Using the Shockley-Chambers tube integral approach, we show that, in ReO₃, 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 that appear at very small tilt angles in the longitudinal AMR scans are not explained by the tube integral approach.

Status: published work in Physical Review Materials 2021, 5, 105004

Catalogue of flat-band stoichiometric materials

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Topological electronic flattened bands near or at the Fermi level are a promising route towards unconventional superconductivity and correlated insulating states. However, the related experiments are mostly limited to engineered materials, such as moiré systems. Here we present a catalogue of the naturally occurring three-dimensional stoichiometric materials with flat bands around the Fermi level. We consider 55,206 materials from the Inorganic Crystal Structure Database catalogued using the Topological Quantum Chemistry website. We combine several direct signatures and properties of band flatness with a high-throughput analysis of all crystal structures. We identify materials hosting line-graph or bipartite sublattices that probably lead to flat bands. From this trove of information, we create the Materials Flatband Database website. We use the database to extract a curated list of 2,379 high-quality flat-band materials, from which we identify 345 promising candidates that potentially host flat bands with charge centres that are not strongly localized on the atomic sites. We showcase five representative materials and provide a theoretical explanation for the origin of their flat bands close to the Fermi energy using the S-matrix method introduced in a parallel work.

Status: published work in Nature 2022, 603, 824

Evidence of a room-temperature quantum spin Hall edge state in a higherorder topological insulator

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Room-temperature realization of macroscopic quantum phases is one of the major pursuits in fundamental physics. The quantum spin Hall phase is a topological quantum phase that features a two-dimensional insulating bulk and a helical edge state. Here we use vector magnetic field and variable temperature-based scanning tunneling microscopy to provide micro-spectroscopic evidence for a room-temperature quantum spin Hall edge state on the surface of the higher-order topological insulator Bi₄Br₄. We find that the atomically resolved lattice exhibits a large insulating gap of over 200 meV, and an atomically sharp monolayer step edge hosts an in-gap gapless state, suggesting topological bulk–boundary correspondence. An external magnetic field can gap the edge state. We further identify the geometrical hybridization of such edge states, which no only supports the Z_2 topology of the quantum spin Hall state but also visualizes the building blocks of the higher-order topological insulator phase.

Status: published work in Nature Materials 2022, 21, 1111

Evidence for electronic signature of a magnetic transition in the topological magnet HoSbTe

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Topological insulators with intrinsic magnetic order are emerging as an exciting platform to realize fundamentally new excitations from topological quantum states of matter. To study these systems and their physics, people have proposed a variety of magnetic topological insulator systems, including HoSbTe, an antiferromagnetic weak topological insulator candidate. In this work, we use scanning tunneling microscopy to probe the electronic structure of HoSbTe with antiferromagnetic and ferromagnetic orders that are tuned by applying an external magnetic field. Although around the Fermi energy we find minor differences between the quasiparticle interferences under the ferromagnetic and antiferromagnetic orders, deep inside the valance region, a quasiparticle interference signal emerges with ferromagnetism. This observation is consistent with our first-principles calculations indicating the magnetism-driven transition of the electronic states in this spin-orbit coupled topological magnet.

Status: published work in Physical Review B 2022, 106, 035151

One-dimensional Luttinger liquids in a two-dimensional moiré lattice

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The Luttinger liquid (LL) model of one-dimensional (1D) electronic systems provides a powerful tool for understanding strongly correlated physics. Substantial theoretical efforts have attempted to extend the LL phenomenology to two dimensions. Such coupled-wire models have been successfully used to construct two-dimensional (2D) anisotropic non-Fermi liquids, quantum Hall states, topological phases and quantum spin liquids. However, an experimental demonstration of arrays of 1D LLs suitable for realizing these models remains absent. Here we report the experimental realization of 2D arrays of 1D LLs with crystalline quality in a moiré superlattice made of twisted bilayer tungsten ditelluride (tWTe₂). The moiré pattern of tWTe₂ hosts identical, parallel 1D electronic channels, separated by a fixed nanoscale distance, which is tunable by the twist angle. At a twist angle of approximately 5 degrees hole-doped tWTe₂ exhibits exceptionally large transport anisotropy with a resistance ratio of around 1,000 between two orthogonal in-plane directions. The across-wire conductance exhibits power-law scaling behaviours, consistent with the formation of a 2D anisotropic phase that resembles an array of LLs. Our results open the door for realizing a variety of correlated and topological quantum phases based on LL physics.

Status: published work in Nature 2022, 605, 57

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Hysteresis in the thermally induced phase transition of cellulose ethers

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Functionalized cellulosics have shown promise as naturally derived thermoresponsive gelling agents. However, the dynamics of thermally induced phase transitions of these polymers at the lower critical solution temperature (LCST) are not fully understood. Here, with experiments and theoretical considerations, we address how molecular architecture dictates the mechanisms and dynamics of phase transitions for cellulose ethers. Above the LCST, we show that hydroxypropyl substituents favor the spontaneous formation of liquid droplets, whereas methyl substituents induce fibril formation through diffusive growth. In celluloses which contain both methyl and hydroxypropyl substituents, fibrillation initiates after liquid droplet formation, suppressing the fibril growth to a sub-diffusive rate. Unlike for liquid droplets, the dissolution of fibrils back into the solvated state occurs with significant thermal hysteresis. We tune this hysteresis by altering the content of substituted hydroxypropyl moieties. This work provides a systematic study to decouple competing mechanisms during the phase transition of multifunctionalized macromolecules.

Status: published work in Soft Matter 2022, 18, 6254

Probing and Manipulating a Single Chemical Bond Using Scanning Probe Microscopy

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The ability to obtain images of organic molecules with atomic resolution using qPlus type AFM opened doors for a wide range of applications, including directly characterizing molecular structures, probing molecular properties, creating new structures, and even providing a tool for studying various types of chemical bonds. Using AFM tips to manipulate chemical bonds provided insights into the bond-forming process which is involved in many surface interactions. This is essential for obtaining insights into the physical nature of a chemical bond and its role in many chemical and catalytic mechanisms. However, the controlled breaking of a chemical bond using mechanical forces, along with accurate measurements of these forces, is extremely challenging and its detailed process has not yet been fully understood. Dative bonds are commonly found in transition metal complexes and play vital roles in catalysis, organometallic chemistry, and biochemistry. We studied the break of a single dative bond between a CO molecule and a ferrous phthalocyanine (FePc) complex using AFM together with real-space pseudopotential density functional theory (DFT) calculations. Our results reveal detailed mechanisms of bond breaking by both repulsive and attractive forces. This work advances understanding of the origins of measured forces in dative bond breaking.

Transition of Deformation Mechanism in Single Crystalline Metallic Nanowires

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Metallic nanowires (NWs) usually exhibit ultrahigh mechanical strength and are ideal candidates for studying fundamental deformation mechanisms at the nanoscale. Different from bulk materials, surface dislocation nucleation has been identified as a dominant deformation mechanism in NWs. Extensive research has been performed on defect-free, single-crystalline metallic NWs where surface-nucleated dislocations tend to slip across the NW, as a result of two competitive deformation mechanisms, twinning and localized dislocation slip. The former leads to large plasticity, while the latter results in limited plasticity. Thus, it is of interest to study how the two deformation mechanisms compete with each other in face-centered cubic (FCC) metallic NWs and what the underlying factors are. Here, using in situ transmission electron microscopy tensile tests, we report an additional factor, cross-sectional shape, that can affect the competition between the deformation mechanisms in single-crystalline FCC metallic NWs.

Magnetic Signature in a Topological Kagome Magnet

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The exploration of quantum topology under non-trivial lattice geometry and strong electron interaction is emerging as a new frontier in condensed-matter physics that not only has analogies with high-energy physics but also expands the range of quantum materials available for next-generation technology. Recently, the transition-metal-based kagome magnets have attracted great attention, as they often show correlated topological band structures. A kagome lattice, made of corner-sharing triangles, naturally has relativistic band crossings at the Brillouin zone corners. The inclusion of spin–orbit coupling and out-of-plane ferromagnetic ordering in the kagome lattice effectively realizes the spinless Haldane model by generating Chern gapped topological fermions. ReMn₆Sn₆ is a key advance in quantum materials. Unlike other members of the kagome magnet family, it consists of segregated kagome layers formed purely by manganese atoms. More crucially, its kagome lattice uniquely features both an out-of-plane magnetization ground state and the largest coercivity (1.1 T) within the RMn₆Sn₆ family. In this report, we focused on TbMn₆Sn₆ and detailed its microstructure and the magnetic signature via electron microscopy and magnetic force microscopy.

Atomic Resolution STEM Imaging of Novel Van der Waals Materials Synthesized by Soft Chemical Methods

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Van der Waals 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 Van der Waals materials has intensified in recent years, fueled by the realization of magnetism in two dimensions (2D). Cation deintercalation with soft-chemical methods provides a route to synthesize new layered compounds with emergent physical and chemical properties that are inaccessible by conventional high-temperature solid-state synthesis methods. One example is CrSe₂, a van der Waals (vdW) material that is promising as an air-stable 2D magnet. Cation deintercalation has rarely been studied mechanistically, and optimized reaction pathways to yield high-quality materials are often poorly understood. Here, we performed a detailed study of the oxidative deintercalation process of NaCrS₂ and KCrSe₂ and the final products by using high-resolution scanning transmission electron microscopy (STEM) and electron dispersive spectroscopy (EDS) (no beam damage issue).

Comparison of Different Microscopic Sample Preparation and Imaging Techniques for Visualization of Connective Tissue Components in Peripheral Nerve

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Surface structural analysis is an essential step in evaluating the morphology and structural organization of complex biological materials. Such microscopic observations predominantly rely on Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and micro-Computed Tomography (micro-CT). Hydrated tissue samples pose a significant challenge to SEM imaging. Solvent dehydration and critical point drying are used extensively to prepare biologic samples for SEM imaging. Recently, two methods have been developed that allow specimens to be prepared for SEM analysis that are structurally close or equal to their native hydrated state thereby promising potential artefact free observations, these methods are: replacing the water via ionic liquids (ILs), also called an ambient-temperature molten salt (ASTM) which possesses low vapor pressure that can be withheld in vacuum and the NanoSuit® method that coats the specimen to block liquid escape while under vacuum. In this paper, we examine which method will provide the most suitable recipe for imaging beam-sensitive, wet biological materials and provide comparison with micro-CT as a complementary technique to SEM to evaluate the quality of the sample preparation technique.

Elucidating Facet Dependent Electronic and Electrochemical Properties of Cu₂O Nanocrystals using AFM/SCEM and DFT

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Cuprous oxide (Cu₂O) has extensively been studied owing to its excellent optical, magnetic, and catalytic properties. Many of these properties are facet-dependent and have not been well elucidated. This work synthesized cubic, cuboctahedral, octahedral, and rhombic dodecahedral shaped Cu₂O nanocrystals of ~300 nm in size to evaluate the facet-dependent electrochemical activities. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were firstly used to reveal the average electrochemical activities at the assembly level. Atomic force microscopy-scanning electrochemical microscopy (AFM-SECM) was further used to assess the electrochemical activities of different Cu₂O nanocrystals at the facet level. [Ru(NH₃)₆]Cl₃ was employed as the probe molecules that reacted with four different Cu₂O nanocrystals. The tipcurrent mapping results indicate that rhombic dodecahedral Cu₂O exhibits higher electrocatalytic activity than other shaped Cu₂O, due to the presence of dominant exposed facet of [110] as indicated by the high current. Density-functional theory (DFT) calculations confirmed the facet dependence of local surface energy and electronic structure of Cu₂O nanocrystals. Besides electrochemical activity, the surface work function and adsorptive properties were both observed to vary with the shape and dominant exposed facets of Cu₂O.

Status: published work in Nanotoday 2022, 44, 101538

Egg protein derived ultralightweight hybrid monolithic aerogel for water purification

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The integration of 2D-graphitic carbon (G) with 1D-carbon nanofiber (CF) allows for the unique properties of 2D graphitic carbon to be combined with the low densities, mechanical performance, and high surface area required for applications across the energy and sustainability landscape. Through a combination of experiments and numerical modeling, we demonstrate the transformation of standard egg-white (EW) proteins into an ultralightweight G-CF aerogel with a multiscale structure. The resulting covalently-bonded hierarchical structure, derived from the complex underlying protein configuration, exhibits a density that is two orders of magnitude lower than existing state-of-the-art materials. We apply this material to the challenges of desalination and water purification, notably demonstrating that the G-CF aerogel significantly improves upon existing materials, capturing 98.2% of ionic impurities and 99.9% of nano/microplastic contamination from seawater.

Status: published work in Materials Today 2022, 59, 46

Crystal structure and magnetic properties in semiconducting $Eu_{3-\delta}Zn_xSn_yAs_3$ with Eu-Eu dimers

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Magnetic structure and crystal symmetry, which primarily determine the time-reversal and inversion symmetry, may give rise to numerous exotic quantum phenomena in magnetic semiconductors and semimetals when arranged in different patterns. In this work, a new layered magnetic semiconductor, $Eu_{3-\delta}Zn_xSn_yAs_3$, was discovered and high-quality single crystals were grown using the Sn flux. According to X-ray diffraction and atomic-resolution STEM, $Eu_{3-\delta}Zn_xSn_yAs_3$ is found to crystallize in a hexagonal symmetry with the space group P6₃/mmc (No. 194). After examining different specimens, we conclude that their stoichiometry is fixed at ~ $Eu_{2.6}Zn_{0.65}Sn_{0.85}As_3$ and is composed of septuple ($Eu_{1-\delta}Sn_yAs_2$)-Eu-(Zn_xAs)-Eu sequences. Magnetization measurement shows an antiferromagnetic ordering in $Eu_{3-\delta}Zn_xSn_yAs_3$ at $T_N \sim 12$ K, where the magnetic easy-axis is along the c-axis, and Mössbauer spectroscopy observes magnetic hyperfine splitting on Eu and Sn at 6 K. Electrical resistivity measurement indicates semiconductor behavior with a band gap of ~0.86 eV. Various Eu-based magnetic semiconductors could provide a tunable platform to study potential topological and magnetic properties.

Status: published work in Journal of Applied Physics 2022, 132, 043902

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