Letters to a Pre-Scientist: A Middle School Pen-Pal Program Inspiring Students to Explore a Future in STEM

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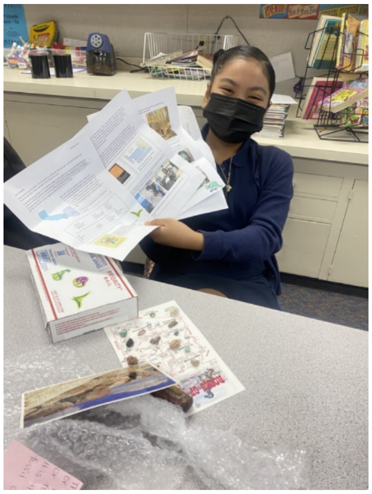
Letters to a Pre-Scientist (LPS) is a national, non-profit organization that works to broaden students' awareness of what STEM professionals look like and do at work and inspire them to explore a career in STEM by connecting them with STEM professionals via snail mail. LPS works in low-income middle schools where >60% of the students qualify for free or reduced-price lunch. Students in these communities often lack access to high-quality science education; moreover, often the only scientist they have come across in their lives thus far is their science teacher. Since it is hard to aspire to a career you do not know exists, LPS works to broaden their awareness of what careers exist. Furthermore, media portrayals of scientists are typically riddled with stereotypes and are not representative of both the diverse career types and individuals that actually compose the STEM workforce. Measures of the impact of stereotypes in science, such as the Draw-a-Scientist Test, show that 79% of US students draw a white, male scientist when asked to draw a picture of what they think a scientist looks like; most students draw chemists wearing lab coats.

It is clear that without intervention, many students from low-income communities are excluded from the economic opportunities and career prospects that STEM careers offer. At LPS, we're working to break down harmful stereotypes about what scientists look like and do at work because we believe that every student, no matter where they were born or live, what they look like, or how much money their family has, deserves to feel like they are valued and belong in STEM. Our program is facilitated by 5th – 10th grade science teachers and boasts a no-opt out approach; every student, no matter their initial interest in STEM, is matched with a STEM professional based on their science interests and general hobbies. Throughout the year, the pair exchanges four sets of letters, touching broadly on the topics of: (1) STEM career pathways; (2) higher education journeys; (3) overcoming obstacles; (4) reflect and inspire. By the end of the year, students and pen pals have fostered a unique connection that has helped demonstrate that scientists are just like them and that they, too, can become a scientist should they have the desire to do so.



A student in the LPS program showing off one of her letters.

Experimental Modeling of Battery Recycling

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The adoption of renewable sources of energy and the electrification of cars have been proposed to reduce CO2 emissions, but both rely on Li-ion batteries (LIBs). At present, only about 58% of the 300,000 tonnes of LIBs reaching end-of-life every year are recycled.[1] LIB recycling remains a challenge because of the wide variety of elements and compounds found within each battery. This leads to a feedstock that, while concentrated with many valuable elements, is chemically challenging to separate.

While many different recycling methods have been proposed, researchers are now showing that the transition metal oxides found within the active materials of the LIB can be carbothermally reduced, after which the valuable metals can be easily separated. Lombardo et al. surveyed the interactions of a wide range of active materials with graphite and showed that carbothermal reduction was possible at 700 °C in 90 minutes.[2] This carbothermal reduction method represents an exciting possibility to recycle LIBs in milder conditions.

'Black Mass' is the complex mix of compounds resulting from carbothermal reduction of LIBs

However, past studies have neglected to examine the extended wealth of battery components that can participate in these carbothermal reduction reactions. Polymer separators and binders can act as reducing agents and metallic current collectors form complex oxides. To date, nobody has systematically surveyed the reactions and products possible. This work will be essential to responding to future changes in LIB feedstocks.

This research has in part been supported by BASF SE under the CARA program.

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Rapid and reversible lithium insertion with multielectron redox in the WadsleyRoth compound NaNb13033

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Developing high-performing battery materials is critical to meet the ever-increasing demand for portable energy storage for electronics and electric vehicles. Owing to their exceptionally high-rate capabilities, high volumetric capacities and long lifetimes, Wadsley-Roth compounds are promising lithium anode materials for fast-charging and high-powered devices. This study comprises an in-depth structural and initial electrochemical investigation of the Wadsley-Roth phase NaNb13O33 phase. Here, we report structural insights obtained from combined neutron and synchrotron diffraction as well as solid-state nuclear magnetic resonance (ss-NMR). We find that a variety of simple, solid-state methods reliably produce a ReO6-like base structure with periodic, ”shear” planes of edge-sharing NbO6 octahedra separating 5 x 3 octahedral blocks with square-planar Na+ occupying block corners. Through ss-NMR, we reveal a new defect structure, with a fraction of sodium cations occupying lithium intercalation sites within block interiors. Through combined experimental and computational studies, we demonstrate and rationalize the high-rate performance of this new anode material in lithium-ion half cells. Using X-ray photoelectron spectroscopy (XPS), we show the multielectron redox of Nb, which enables capacities of 225 mA h g–1 at slow rates and anodic potentials. Without down-sizing or nano-scaling, 100 mA h g–1 of this capacity is retained at 20 C in micrometer-scale particles. Through bond-valence mapping and DFT, we show that such excellent rate performance results from facile, multi-channel lithium diffusion down octahedral block interiors and from high electronic conductivity within shear planes. Finally, we use differential capacity analysis to identify optimal long-term cycling rates and achieve 80% capacity retention over 600 cycles with 30-minute charging and discharging intervals. Without optimization, these results place NaNb13O33 in the ranks of promising new highrate lithium anode materials and warrant further research.

This research made use of shared facilities of the National Science Foundation (NSF) Materials Research Science and Engineering Center (MRSEC) at UC Santa Barbara, NSF DMR 1720256, a member of the Materials Research Facilities Network. ARP also acknowledges the NSF for a Graduate Research Fellowship, grant number 2139319.

Modeling magnetic interactions in battery electrode materials using first-principles statistical mechanics simulations.

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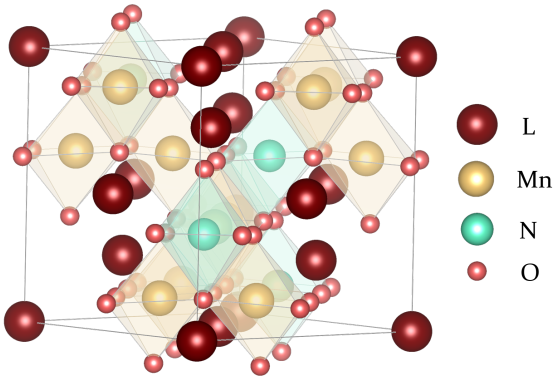

The spinel structure of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ ordered ground state (space group P4$_3$32) is pictured above.

Computational models of magnetic interactions of battery materials enable us to further understand the driving forces leading to certain preferred spin states and the influence that these configurations can have on battery redox processes. With a more thorough understanding of the battery redox reactions, these simulations can then be a powerful tool in the interpretation of experimental data, such as EPR.

In this work, first principles and statistical mechanical methods, such as cluster expansions, were implemented via the CASM software package to model magnetic and spin interactions in the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel battery material. DFT calculations of several distinct Ni-Mn configurations, including the ordered ground state (space group P4$_3$32), suggest that an antiferromagnetic arrangement of the Ni and Mn sublattices is favored due to the strong superexchange interactions between Mn^{4+} and Ni^{2+} ions. Magnetic cluster expansions of these structures confirm these findings, with strong antiferromagnetic Ni-Mn J coupling constants and ferromagnetic Mn-Mn and Ni-Ni J values for nearest neighbor transition metals. These cluster expansions also reveal a strong Ni-Mn interaction within second nearest neighbor pair clusters.

In addition to the studies mentioned above, we have also carried out some DFT calculations on a primitive Ni-Mn configuration at different Li compositions. Preliminary results from these studies indicate that Mn ions tend to be ferromagnetic in the presence of Li (when there are Ni unpaired electrons), presumably due to the superexchange interaction mentioned above, but these results also suggest that Mn prefers an antiferromagnetic configuration in the absence of Li and Ni unpaired electrons, due to the delocalization of electrons that can be achieved in such configurations through a direct exchange mechanism.

Investigating Polymorphism in $Na_2Fe_2F_7$ & its Effect on Electrochemical Properties

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With the present materials supply crunch caused by the burgeoning Li-ion battery-based electric vehicle market, more sustainable battery chemistries are needed. When considering possible chemistries, sodium (Na) and iron (Fe) stand out as promising candidates for the intercalant ions and redox centers, respectively. Recently, weberite-type sodium metal fluorides ($\mathrm{Na_2}M^{2+}M^{3+}\mathrm{F_7}$) have emerged as potential high performance Na cathode materials[1–4] with predicted energy densities in the 600 to 800 Wh/kg range (higher than any known Na cathode material) and high ionic conductivity and structural stability. One of the few weberites that has been electrochemically tested so far is $Na_2Fe_2F_7$ and while one study has shown it to have great, high-rate performance,[2] there have been inconsistent reports regarding the structure and electrochemical properties of $Na_2Fe_2F_7$.

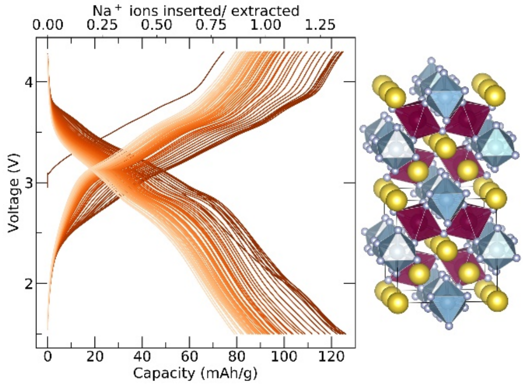

Fig. 1, Charge- discharge curve for $Na_2Fe_2F_7$ and the weberite structure.

In this study, we endeavor to reconcile these characteristics using a combined experimental-computational approach. Density functional theory calculations reveal the inherent metastability of the weberite phase and the close energetics of several $Na_2Fe_2F_7$ polymorphic forms, as well as the predicted (de)intercalation behavior for each $Na_2Fe_2F_7$ polymorph. Experimentally, we find that $Na_2Fe_2F_7$ samples inevitably contain a mixture of weberite polymorphs as characterized using a broad suite of long-range and local probes sensitive to both amorphous and crystalline phases. Notably, we present the first ever ^{23}Na nuclear magnetic resonance (NMR) investigation into weberites and showcase NMR's ability to parse out different local environments despite the presence of polymorphism. Electrochemically, our $Na_2Fe_2F_7$ material shows respectable early capacities yet exhibits steady capacity fade, which *ex situ* synchrotron X-ray diffraction and ^{23}Na NMR reveal to be associated with transformation of the weberite phase upon cycling. However, fine tuning of electrode composition and design appears to be effective at reducing this effect.

Overall, this study presents an in-depth characterization of $Na_2Fe_2F_7$ and provides key insights that pave the way to unlocking weberites as high energy density Na-ion cathode materials.

This work made use of the shared facilities of the UC Santa Barbara MRSEC (DMR 1720256) and Center for Scientific Computing (CNS 1725797, DMR 1720256). E. E. Foley and V. C. Wu were supported by the NSF Graduate Research Fellowship Program under Grant No. DGE 1650114. This work is supported by an NSF CAREER award under Grant No. DMR 2141754.

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Inorganic and Hybrid Vacancy-Ordered Double Perovskites A_2WCl_6

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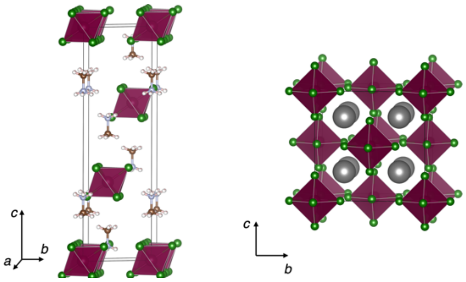
Vacancy-ordered double perovskites are an attractive set of compounds due to their promise as optoelectronic materials and because their properties can be systematically altered by substitutions on the three lattice sites available. In this work we report the optical and magnetic characterization of both inorganic and hybrid vacancy-ordered double perovskites with the formulas A_2WCl_6 (A = $CH_3NH_3^+$, Cs, and Rb). Although some previous literature exists on these compounds, the reports contain contradictory information and unanswered questions regarding the properties of these materials. We demonstrate that the A_2WCl_6 compounds can be synthesized from solution-process methods under anhydrous and anaerobic conditions. These are distinct from similar compounds which have been reported to be synthesized by hydrothemal methods, which have the formula $Cs_2WO_xCl_{6-x}$. Areas of future study include developing an understanding the magnetism of these compounds, which can not be adequately modeled using the Kotani equations for d^2 ions.



Representative crystal structures of the A_2WCl_6 compounds.

High-strength Ti-Nb alloys via oxygen-induced structural transformations

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Refractory multi-principal element (RMPE) BCC alloys are gaining popularity as thermostructural materials, yet their wider use is limited by processing challenges and poor ductility at low temperatures. Notwithstanding the challenges, their vast compositional space opens a window of opportunities for new alloy design strategies. Recently, instabilities of the BCC phase of Ti-containing alloys with oxygen incorporation have been reported to promote nano-scale structures with unprecedented mechanical properties [1,2]; however, key mechanisms are not properly understood. The high affinity of oxygen to group IV elements (the so-called HCP formers) makes them appealing to pursue investigations on phase instabilities and the ensuing deformation mechanisms.

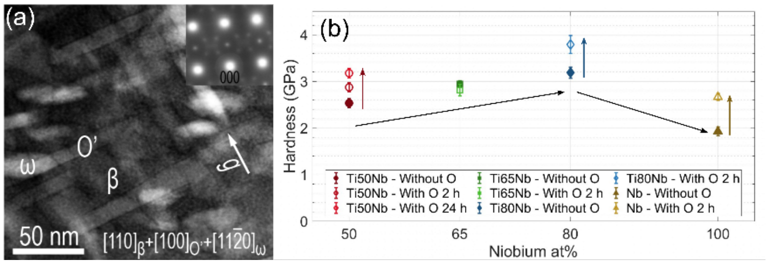

Figure 1: Ti50at%Nb alloy with ~1at%O promoting spinodal decomposition with (a) compositional induced transformations (via O'-Burgers path and ω path) and (b) a comparison of TiNb hardness values. (unpublished data)

In the present study, a series of $Ti_{1-x}Nb_x$ BCC alloys (x ranges from 0.5 to 0.8) were synthesized and enriched with ~1 at% O via arc-melting/splat-quenching/homogenizing at low pO2/oxygen enrichment. Varying Ti/Nb concentrations (including 50 at%Nb, 65 at%Nb, and 80 at%Nb) were used to probe the contribution of Nb to the evolution of microstructures and the emerging strengthening mechanisms.

All oxygen-infused Ti-Nb alloys demonstrate phase separation, resulting in Ti-rich and Nb-rich regions, with a primary transformation mechanism to HCP via a transient orthorhombic (O') phase following the Burgers path. A secondary path through an intermediate omega phase is also observed. Nanoindentation tests revealed a significant increment in hardness for the oxygen-enriched alloys. Additionally, in-situ microtensile tests of the Ti-50Nb alloy with ~1 at% O reveal a very high strength (~3 GPa) that approaches the theoretical limit. A comparison with unexposed samples is made and the implications of oxygen-induced phase transformations for the mechanical properties will be discussed.

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Halide perovskites of the lanthanides and actinides

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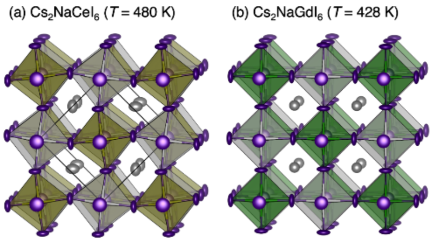
Double perovskites and vacancy ordered double perovskites are two families of compounds that have attracted significant attention as lead-free alternatives to typical $APbI_3$ perovskite semiconductors.[1] Following the general formulas $A_2B^{I}B^{III}X_6$ and $A_2B^{IV}X_6$, the double perovskite and vacancy ordered double perovskite, respectively, offer significant chemical diversity of the B site and, where X= iodide, are expected to have band gap energies similar to $APbI_3$ materials. Here, we will discuss the use of reported predictive models to aid in the solid-state synthesis and characterization of a new family of lanthanide iodide-double perovskites with a general formula of Cs_2NaLnI_6 (Ln = Ce, Nd, Gd, Tb, Dy).[2] The solution synthesis and characterization of some uranium vacancy ordered double perovskites, with the general formula A_2UX_6 (A = methylammonium, X = Cl, Br; A = tetraethylammonium, X = Cl, Br, I) will also be described. The optical properties of both families will be discussed and the photoluminescent properties of $Cs_2B^{I}LnI_6$ (Ln = Ce, Tb, Dy) will be compared to related compounds. The results suggest that due to their large ionic radii the *f*-elements can incorporate a wide range of halides into the perovskite phase, thereby permitting controlled tunability over their electronic properties.



Solid-state structures of Cs_2NaCeI_6 (a) and Cs_2NaGdI_6 (b) as representatives of the lanthanide iodide double perovskites Cs_2NaLnI_6.

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Aging processes in LiNiO2 cathodes probed by NMR and magnetism

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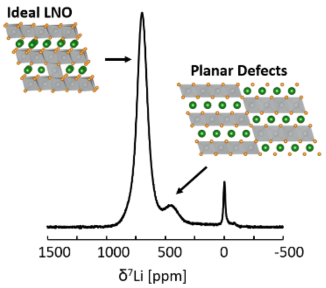
Improvements in the design of layered lithium transition metal oxide cathodes, LiMO2, offer a promising avenue for short-term gains in energy densities of Li-ion batteries. Researchers in the field are trending towards Ni-rich compositions to replace low abundance (e.g. Co) and stabilizing, but electrochemically inactive, (e.g. Mn and Al) elements that are typically used. LiNiO2 has the highest Ni content in this compositional space and while it has very large energy densities, it suffers from poor cyclability due to structural transformations, high reactivity, and thermal instability in the charged state. In this study, we use synchrotron X-ray diffraction (sXRD), nuclear magnetic resonance (NMR), and magnetometry to probe the degradation processes occurring in $LiNiO_2$ as it is cycled.



^{7}Li NMR identifies defects present in as-synthesized $LiNiO_2$, which is the main contributor to first cycle irreversibility

O*perando* magnetometry was used to accurately determine the first cycle irreversibility in $LiNiO_2$. The source of this irreversibility is defects present in the pristine material identified by ^{7}Li NMR, which we hypothesize are Li near planar defects (e.g. twin or antiphase boundaries) that have been observed in layered type cathodes.[1] After the initial cycle, the operating voltage range plays a key role in the performance degradation. At high operating voltages and high states of delithiation, the surface layer is unstable and restructures into a Li_xNi_yO rock salt structure, which limits the accessible Li content during cycling.[2] Here we characterized and identified these fatigued phases in the $LiNiO_2$ system. While lower operating voltages prevents these fatigued phases from forming, the limited cycling range will also lead to losses in energy densities. To mitigate oxygen loss and Ni migration that lead to these structural rearrangements, defect/dopant engineering of $LiNiO_2$ is needed to maintain the high energy density of this system over hundreds of cycles.

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Asymmetric miktoarm star polymers for thermoplastic elastomers

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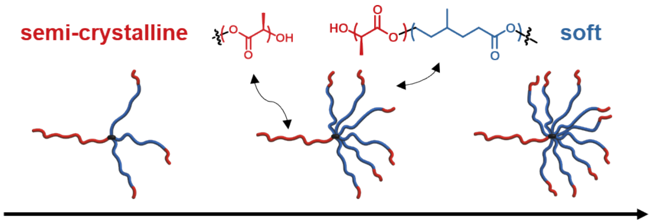
Thermoplastic elastomers (TPEs) are arguably the most industrially successful block copolymers due to a synergistic combination of robust mechanical properties and processability. The prototypical example is a linear ABA triblock copolymer with glassy A blocks flanking a rubbery B. However, morphological constraints impose an upper limit on the A-block volume fraction, $f_A \approx 0.3$, beyond which a cylinder-to-gyroid phase transition renders the material plastic, not elastic. Asymmetric miktoarm star polymers ($A(BA')_n$) can significantly deflect this transition,[1–3] which could result in stiffer TPEs. Moreover, like most commercial block copolymer TPEs, $A(BA')_n$ asymmetric miktoarm star polymers studied to date have been derived from petroleum resources.[1,4]



Increasing *n* — improved strength, toughness, and recovery

A library of polyester-based $A(BA')_n$ asymmetric miktoarm star polymers with A, A′ = poly(L-lactide) (PLLA) as the semi-crystalline hard blocks and B = poly(4-methylcaprolactone) (PMCL) as the soft segment were synthesized using a grafting-through synthetic platform known as μSTAR. Architectural manipulation of the number of BA′ arms (*n*) were systematically investigated, while holding the A, A′, and B block lengths constant. The value of *n* has a pronounced impact on the mechanical properties. Tensile toughness increases with *n*, an effect likely related to bridging, as the modulus drops because the hard-block volume fraction decreases. These insights expand our understanding of architecture effects in sustainable thermoplastic elastomers.

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Compatibilization of immiscible polymer blends through ionic interactions

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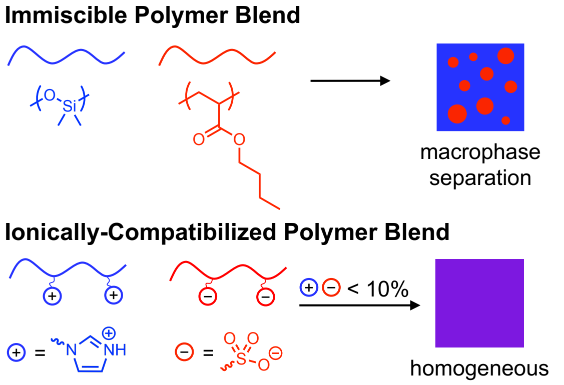
Polymer blending provides an attractive and sustainable platform to obtain materials with desirable physicochemical properties, but often results in immiscible blends exhibiting poor mechanical and optical properties that limits applicability. To address this challenge, we demonstrate that ionic interactions are a powerful tool for polymer compatibilization, recycling, and upcycling.[1] In this work, ionic bonds efficiently compatibilized a highly immiscible blend of poly(n-butyl acrylate) P(nBA) and poly(dimethylsiloxane) (PDMS). At 10 mol% or less incorporation, pendant acidic moieties were introduced in P(nBA) through reversible addition–fragmentation chain-transfer copolymerization, and pendant basic moieties were tethered along the PDMS backbone through a facile thiol-ene click reaction. Stoichiometric acid-base polymer blends exhibited optical clarity and single glass transition temperatures. In addition, oscillatory shear rheology is utilized to probe the blend dynamics as a function of temperature. The combined synthetic and characterization strategy is opening significant opportunities for understanding and exploiting low levels of ionic functionalization in commercially important polymeric systems.



Installation of oppositely charged pendant groups along the polymer backbones suppresses macrophase separation upon blending.

This work is supported by the National Science Foundation through the Materials Research Science and Engineering Center, DMR-1720256 (IRG-2), and the Institute for Collaborative Biotechnologies, an Army-sponsored University Affiliated Research Center.

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Controlling Composite Microstructure Through Applied Acoustic Fields

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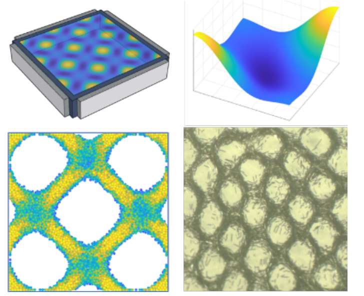
There are a wide range of composite systems whose properties can by enhanced by controlling the arrangement of the functional particles within them. An emerging method of controlling composite microstructure is acoustophoresis which utilizes sound waves to position particles during processing. This work demonstrates two model frameworks for determining what microstructures are achievable using this technique, and what processing conditions are necessary to achieve those microstructures. The first is an energy minimization approach, and the second is a discrete particle simulation of all components in the system. Experimental validation of these models is shown for a wide range of acoustic fields and interactions. These validated models are then leveraged to facilitate the design of flexible electrically conductive composites which demonstrate significantly higher conductivity and flexibility than unstructured composites of the same composition.



A grid of microparticles arranged using acoustic fields.

Ion-mediated polymer assemblies with tunable structures

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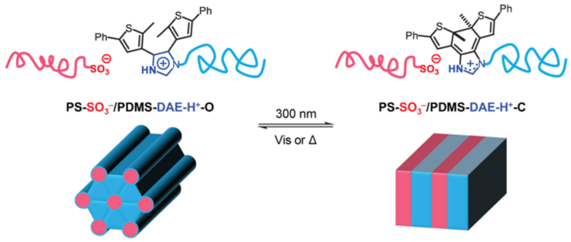
Phase separation of immiscible polymers is a critical obstacle facing plastics recycling. One strategy to prevent macroscopic phase separation is by chain-end functionalization of dissimilar polymers with reacting cation/anion groups.[1] This non-covalent interaction leads to the formation of supramolecular block copolymers (SBCPs) via "reactive blending", which can self-assemble and form various microstructures. To further study their self-assembly and dynamics, we have synthesized a library of new ionic-bonded polystyrene/polydimethylsiloxane (PS/PDMS) SBCP blends by attaching compact ions with different degrees of charge delocalization and pKa values onto the chain ends. Moreover, using X-ray scattering and microscopy techniques, we have demonstrated the formation of lamellar microstructures produced by stronger cation-anion interactions and more swollen microphases with no long-range order by weaker interactions.



Photoinduced phase transition in ionic supramolecular block copolymer melt

To further demonstrate the tunablity of this approach, we also show that self-assembly can be modified on-demand with UV light. By incorporating a photochromic diarylethene end-group (PDMS-DAE) bearing an appropriate base unit, we enable control of the localization of positive charge upon irradiation and, therefore, the strength of ionic interactions in functionalized polydimethylsiloxane with a sulfonic acid end-functionalized polystyrene (PS-SO3H) blend. Specifically, the proton transfer between the acid and base units in the melt state yields contact ion pairs that self-assemble into a cylindrical microstructure. By shining 300 nm light, we can induce photoisomerization of the diarylethene unit from ring-open form (DAE-O) to ring-closed state (DAE-C). Formation of the DAE-C structure, which has a more localized positive charge and stronger ionic bonds, induces a phase transition to a lamellar microstructure. Compatibilization of immiscible polymer blends by introducing ionic bonds and understanding the parameters that influence the tunability of microphases in such SBCPs can significantly expand the types of polymers that can be recycled.

This work was supported by the MRSEC Program of the National Science Foundation under award no. DMR 1720256 (IRG-2).

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1. G. H. Fredrickson, S. Xie, J. Edmund, M. L. Le, D. Sun, D. J. Grzetic, D. L. Vigil, K. T. Delaney, M. L. Chabinyc, and R. A. Segalman, Ionic compatibilization of polymers, *ACS Polym. Au* **2** (2022) 299–312. DOI: 10.1021/acspolymersau.2c00026

Neighboring group participation in ionic covalent adaptable networks

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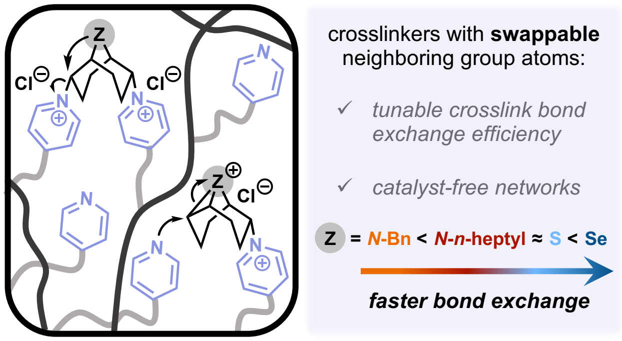

Covalent adaptable networks (CANs) contain reversible chemical crosslinks that can interchange (thereby rearranging the network topology) when subjected to a stimulus such as heat. As a result, CANs are a reprocessable and recyclable alternative to traditional thermosets. Incorporating neighboring group participation (NGP) into CANs can increase the rate of crosslinker exchange in the bulk network and remove the need for external catalysts. This work describes a modular synthetic platform to generate ionic CANs from thia-, aza-, and selena-bicyclo[3.3.1]nonane (BCN) crosslinkers with NGP and pyridine-functionalized polymers. Through stress relaxation experiments, we demonstrate that these CANs undergo transalkylation in response to temperature, the rate of which can be controlled by the identity of the intra-nucleophile [sulfur, selenium, or nitrogen] within the NGP-active BCN crosslinker. The temperature-dependent reversibility of these crosslinks allows the ionic CANs to be thermally reprocessed without significantly reducing crosslink density. In addition, when treated with an excess of a competing external nucleophile, the networks can be uncrosslinked. As a result, the linear polymer starting material (composing > 90 weight percent of the network) can be chemically recycled. This catalyst-free CAN platform's dual thermal and chemical recyclability addresses critical criteria for designing thermosets with extended lifecycles.

Incommensurate charge-stripe correlations in the kagome superconductor $CsV_3Sb_{5-x}Sn_x$

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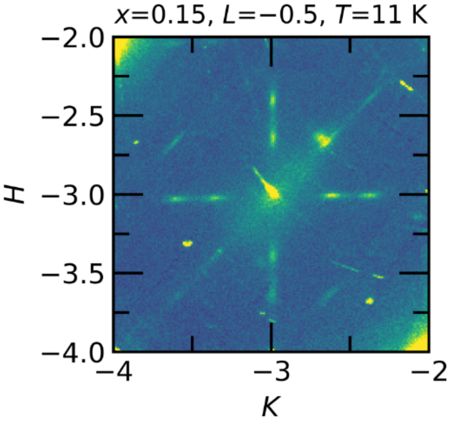
The recently discovered family of kagome superconductors AV_3Sb_5 (A = K, Rb, Cs) exhibits a variety of anomalous properties arising from a parent charge density wave (CDW) state. The CDW state manifests as a 2 x 2 reconstruction of the kagome planes into either a Star-of-David (SoD) or tri-hexagonal (TrH) distortion in combination with an out-of-plane modulation of either one or both distortion types.[1,2] In CsV_3Sb_5, CDW order is suppressed rapidly when applying moderate pressures or via small levels of hole-substitution, suggesting a nearby competing electronic state. In this work, we use bulk x-ray scattering measurements and scanning tunneling microscopy to track the charge correlations in $CsV_3Sb_{5-x}Sn_x$ upon the introduction of holes. Light hole doping (x = 0.025) weakens the out-of-plane correlations and suppresses 2 x 2 x 4 correlations. Continued hole doping further weakens out-of-plane correlations and, eventually, at x = 0.15 suppresses the in-plane 2 x 2 charge order. At this doping level, our x-ray scattering measurements reveal incommensurate quasi-1D charge correlations that form in the bulk. These charge correlations are also observed in parallel STM measurements and manifest as charge stripes pinned to commensurate positions on the surface. Our data directly reveal the existence of competing bulk charge correlations in CsV_3Sb_5 that form as the double superconducting domes are traversed via hole-doping in this family of kagome materials.



Map of x-ray scattering intensities for x = 0.15 at T = 11 K plotted about (H, K, - 0.5) showing incommensurate charge stripes.

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Transient grating spectroscopy characterization of hydrogels

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Our research investigates using transient grating spectroscopy, a method that employs acoustic wave signatures, to mechanically characterize hydrogels and other inhomogeneous materials. Previously, transient grating has been used to study dynamics of self-assembly in globular proteins with the results showing damping rate and speed of sound changes over varying temperature and protein concentration. Similarly, we provide a systematic approach across a range of polymer groups, to decompose the effects of crosslinking, swelling, and/or entanglements on Rayleigh wave speeds, which can then be related to a material's elastic modulus. Transient grating also presents a method for dynamic response measurements of hydrogels. Traditional characterization methods, such as indentation, result in large discrepancies in measurements, which indicates that mechanical properties of hydrogels differ significantly in dynamic and static conditions. These differences are the first step to developing models for the direct contribution of poroelasticity and viscoelasticity on hydrogel behavior. This project will show how we can model and subsequently develop hydrogels with the mechanical properties necessary for our desired applications.

This work was supported by the UCSB Materials Research Science and Engineering Center (MRSEC) of the National Science Foundation under award No. DMR-1720256 (IRG-3). The development of the transient grating spectroscopy at UCSB is supported by a DURIP grant from the U.S. Army Research Office under the award number W911NF-20-1-0161. Allison Chau acknowledges support from the NSF Graduate Research Fellowship Program under Grant No. 1650114. Angela Pitenis acknowledges funding support from the NSF CAREER award (CMMI-CAREER-2048043).

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Influence of Network Connectivity on Pressure Sensitive Adhesive Performance

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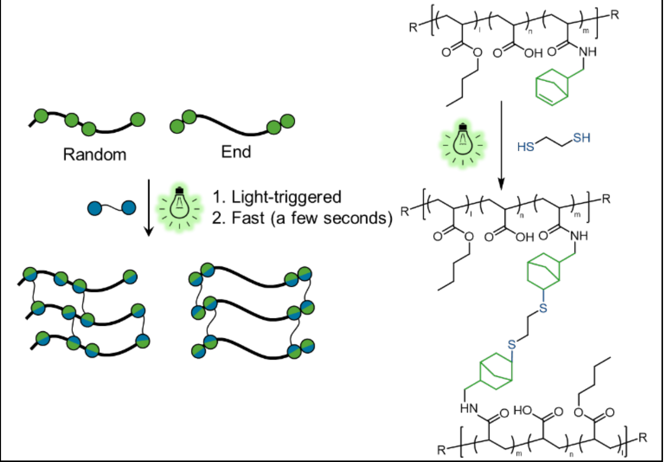
Traditional pressure sensitive adhesives (PSAs) are polydisperse materials containing large amounts of poly n-butyl acrylate doped with poly acrylic acid to increase physical properties and generate crosslinking sites. It has been shown via molecular mechanics simulations that the crosslinking position along the polymer backbone is critical in optimizing PSA performance, however, the simulations have yet to be corroborated experimentally. Herein, we present the synthesis and characterization of architecturally defined polymers for PSA applications utilizing active ester chemistry. By adding pentaflourophenyl acrylate into the traditional PSA formulation we can precisely tune crosslinking position with post-polymerization functionalization. Utilizing living RAFT polymerization we have developed ABA' triblock copolymers and compared them to the traditional, statistically random analogues. ^{1}H NMR and size exclusion chromatography (SEC) were used to compare polymer composition; showing low polydispersity (<1.5), high molecular weight (>100 kDa) and similar crosslinkable mole fraction. Rheological analysis highlighted key physical differences between the polymers including much higher storage and loss moduli for the triblock copolymer in the terminal regime. Finally, 180° peel testing and lapshear were completed to show that both the adhesive and cohesive strength of the ABA' polymer increased compared to its random analogue. Overall, experimental evidence aligned with simulations to inform how next generation PSAs might be optimized via synthetic chemistry.



An architecturally tunable, light responsive system, for pressure sensitive adhesion utilizing thiol-ene click chemistry

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Continuous passive solar desalination via thin-film condensation in microporous membrane

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Passive solar desalination is an emerging low-cost technology for fresh water production. However to date, wicking structures that cause salt accumulation limit continuous desalination and salt rejection in state of the art desalinators.[1] To overcome these challenges, we designed a passive inverted single stage solar membrane desalinator that achieves continuous desalination and salt rejection with a novel architecture. By placing salt water on a radiative absorbing, porous, hydrophobic evaporator membrane, salt water stays on the membrane while allowing heated gaseous water vapor to transport to and condense on a cooler microporous membrane below. Our design utilizes thin-film condensation which offers ample three-phase contact region to enhance the phase change heat transfer.[2] In addition, by condensing within the microporous membrane instead of forming droplets, we reduce the gap distance between the condenser and evaporator membranes, which effectively reduces the vapor transport resistance. With this design, we demonstrated continuous salt rejection using advection and diffusion over the evaporator membrane. We experimentally demonstrated a record-high continuous desalination and salt rejection test duration of 7 days under one-sun illumination, where 31% of the incoming solar energy was converted to heat to vaporize water. Prior state of the art work demonstrated 12 hours of continuous desalination due to salt accumulation on the wicking evaporator.[3] In addition, our desalinator achieved a water-collection rate of 0.487 kg m^{-2} h^{-1}. This work signifies an improvement in the robustness of current state of the art desalinators and presents a new architecture to further optimize passive solar desalinators.

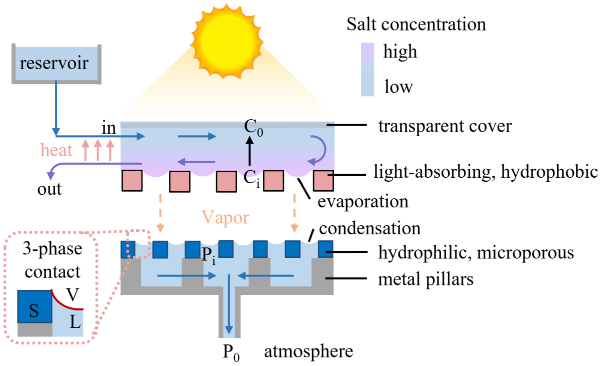

Fig. 1 Inverted single stage architecture.

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Hydrogen Bonding Bottlebrush Networks: Self-healing Materials from Super-soft to Stiff

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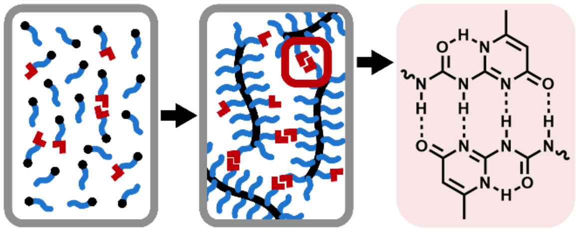
The impact of polymer architecture on network dynamics and self-healing is presented using bottlebrushes containing side chains that are end-functionalized with 2-ureido-4[1H]-pyrimidinone (UPy). The synthesis of these materials is straightforward through a three-step process: (1) synthesizing rubbery poly(4-methylcaprolactone) macromonomers (P4MCL-OH) with a norbornene-based initiator, (2) functionalizing the terminal hydroxyl group with UPy-isocyanate (P4MCL-UPy), and (3) statistically copolymerizing P4MCL-OH and P4MCL-UPy via ring-opening metathesis polymerization (ROMP) to form hydrogen-bonding bottlebrushes having a fraction (p) of side chains functionalized with UPy. Attaching UPy to the free end of bottlebrush side chains dilutes the impact of friction from complementary UPy interactions on segmental dynamics, leading to a much weaker dependence of the glass-transition temperature (T_g) on p than observed in linear analogues, while the activation energy to dissociate UPy–UPy bonds (41–47 kJ/mol) remains mostly unchanged. Longer side chains result in a competition between reducing T_g and inducing entanglements that influence hydrogen-bonded network dynamics. Increasing the backbone length extends the sticky-Rouse region without affecting the network modulus (G_x) or UPy–UPy dissociation time (τ_s). G_x scales linearly with p and ranges from 27 kPa to 1.6 MPa, while τ_s remains nearly constant in contrast to linear telechelic ionomers, implying a similar self-healability across bottlebrush networks containing different amounts of UPy. These stretchable networks with $p \leq 0.25$ undergo self-healing upon repeated rupture and melt pressing at ≤ 100 °C while retaining similar tensile properties. In summary, decorating bottlebrush polymers with hydrogen bonds creates opportunities to independently manipulate associative network dynamics and mechanical moduli.



This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Award Number DE-SC0019001. The research reported here used shared facilities of the UC Santa Barbara Materials Research Science and Engineering Center (MRSEC, NSF DMR-1720256), a member of the Materials Research Facilities Network (http://www.mrfn.org). The authors gratefully acknowledge partial financial support from the Mitsubishi Chemical Center for Advanced Materials.

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Diffusion of Brønsted Acidic Dopants in Conjugated Polymers

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Depth-dependent doping levels in electrically doped organic semiconductor films are controlled by the relative rates of reaction and diffusion of the dopant. Many semiconductor devices (e.g., light emitters and photovoltaics) utilize heterojunctions that depend on dopant gradients to control charge transport. To understand the formation and stability of gradients requires understanding of dopant diffusion and the complex changes in polymer properties that arise during doping. Here, the doping of thin films of poly(3-hexylthiophene) (P3HT) using bistriflimide acid (HTFSI) from solution in methanol is evaluated. The contributions of the reaction rate and diffusion to doping were deconvoluted by examining the evolution in films of P3HT with varying thickness using a combination of spectroscopic techniques. The rate dependency of doping by hydrogenated and deuterated acids shows a significant kinetic isotope effect, indicating that doping is limited by proton transfer to the polymer. Dynamic secondary ion mass spectrometry (DSIMS) of doped films show that H/D is retained in doped films after the doping process in contrast to propositions in literature of hydrogen evolution. To assess diffusion limitations to the doping process, dopant concentration profiles were measured and quantified using complementary XPS and DSIMS depth profiling. The dopant concentration profiles show evidence of enrichment at the P3HT top surface. These limited concentration profiles suggest that dopant diffusivity varies inversely with dopant concentration due to doping-induced changes to the semiconducting polymer.

Structure and Lithium Insertion in Oxides of Molybdenum

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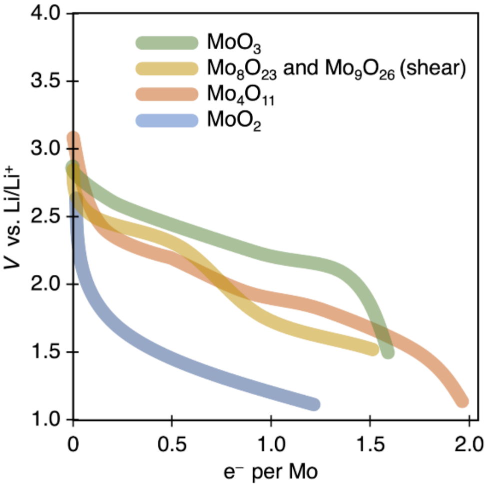
Oxides of molybdenum (MoO_x) have a rich structural chemistry arising from the accommodation of oxygen deficiency as MoO_3 is reduced, and varied redox behavior arising from the ability of Mo to take on several different oxidation states. We present a review of MoO_3, MoO_2, and all the reduced Mo oxides with intermediate compositions for their performance as Li-ion battery electrode materials. These reduced oxides are perhaps the most structurally diverse in the field of energy storage materials, taking on structures ranging from ones with crystallographic shear to bronze-like structures and distorted rutile. Crystal structure can have a significant impact on the performance of battery materials, which makes the reduced Mo oxides a promising domain of study. Electrochemical studies of these oxides from as early as 1971 to as recently as 2022 are compiled, and characteristics of capacity, capacity retention, and rate performance are compared. We find that certain oxides indeed display promising and highly reversible capacities for Li+ storage. Typical redox voltages for Mo oxides lie in a regime that hinders maximizing energy density when they are paired with higher-voltage cathodes or lower-voltage anodes. The possibility of decreasing the redox voltage in the future will expand the promise of these materials, while offering an alternative to more critical elements such as Nb.



Schematic of characteristic galvanostatic discharge curves for four categories of Mo oxides.

The research reported in the paper was supported by RCV's NSF GRFP and as part of the SCALAR, an Energy Frontier Research Center funded by the U.S. Department of Energy.

Dual-mode organic electrochemical transistors based on self-doped conjugated polyelectrolytes for reconfigurable electronics

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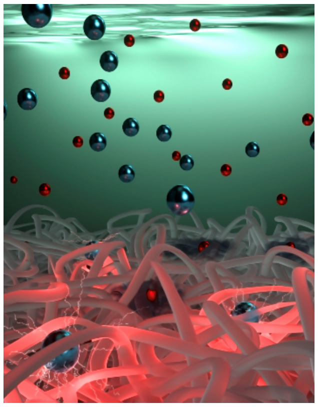
Dual mode transistors, the type of transistors that work in both depletion mode and enhancement mode, were reported more than 50 years ago using inorganic semiconductors (with silicon in 1963 and with III-V semiconductors in 1966). Thus far however, this type of devices has not been shown in organic electronics. Here, we report the dual mode organic transistors based on organic electrochemical transistors (OECTs) using self-doped conjugated polyelectrolytes as the active material. With spectroelectrochemical measurement, we revealed a unique dual ionic transport property of these materials: they can be both doped and dedoped upon the interaction with anions and cations in an electrolyte. This property enables dual-mode functionality in OECTs, whose mode switching is accomplished by simply altering the polarity of the applied gate and drain voltages. Furthermore, we developed a device physics model which accurately describes the behavior of these transistors. We also demonstrated the utilization of dual-mode organic transistors in reconfigurable electronics by fabricating logic gates that could be switched between AND and NOR, and OR and NAND on the fly. Being simple, power efficient, and compatible with high throughput microfabrication techniques, dual mode OECTs are a promising candidate for the next generation of efficient computing systems and adaptive electronics.



Schematics of the dual ionic transport property in self-doped conjugated polyelectrolytes

This work was supported by the National Science Foundation (DMR-1922042). T.N.-D. acknowledge the UCSB's "Otis Williams Fellowship" for financial support. J.C. thanks Vidyasirimedhi Institute of Science and Technology (VISTEC) for the funding of the internship at UCSB. The authors thank Prof. Guillermo C. Bazan for fruitful discussion.

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Persistent hot carrier diffusion in boron arsenide single crystals imaged by ultrafast electron microscopy

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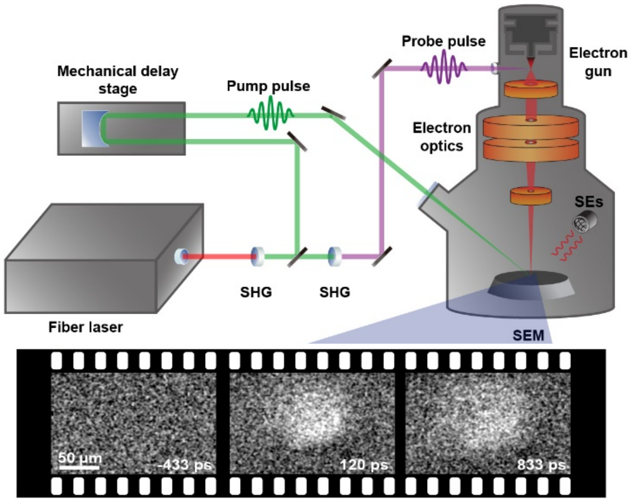

Schematic of SUEM and representative contrast images

Cubic boron arsenide (BAs) is a promising material for microelectronics thermal management applications because of its high thermal conductivity. Recently, its potential as an optoelectronic material has also been explored. However, it remains challenging to measure its photocarrier transport properties because of the small sizes of available high-quality crystals. Here, we use scanning ultrafast electron microscopy (SUEM) to directly visualize the diffusion of photocarriers in BAs single crystals. SUEM integrates the temporal resolution of femtosecond lasers with the spatial resolution of scanning electron microscopes (SEMs). The change in local secondary electron (SE) yield as a result of the optical excitation is measured and used to form contrast images. Given the shallow escape length of SEs (a few nanometers), SUEM is highly sensitive to surface charge dynamics and has been used to study photocarrier diffusion. We observed ambipolar diffusion at low optical fluence with persistent hot carrier dynamics for above 200 ps, which can likely be attributed to the large frequency gap between acoustic and optical phonons, the same feature that is responsible for its high thermal conductivity. At higher optical fluence, we observed spontaneous electron-hole separation. Our results show BAs is an attractive optoelectronic material combining high thermal conductivity and excellent photocarrier transport properties. Our study also demonstrates the capability of SUEM to probe photocarrier transport in emerging materials.

The work conducted at UCSB, is based on research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under award DE SC0019244 and by the U.S. Army Research Office under award W911NF-19-1-0060. The growth of high-quality BAs crystals at the University of Houston was supported by the U.S. Office of Naval Research under Multidisciplinary University Research Initiative grant N00014-16-1-2436. D.-S.Y. acknowledges the support by the R. A. Welch Foundation (E-1860).

Thermoelectric Effect in a Confined Topological Dirac Semimetal

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The topological Dirac semimetal Cd3As2 is a potential thermoelectric material due to its high electron mobility and low lattice thermal conductivity. However, in its bulk form, Cd3As2 has no band gap, which is detrimental for the thermopower. One way to open a band gap in the bulk is through quantum confinement and strain in thin films. In this project, we investigate and contrast the thermoelectric properties of epitaxial Cd3As2 films with three different thicknesses (950 nm, 95 nm and 25 nm). Resistivity and quantum oscillation measurements established the semimetal nature of the thick sample, while the thin sample showed semiconducting features, suggesting the presence of a bulk gap due to confinement. The thermoelectric properties of these three samples were qualitatively different. The thick sample exhibited a semi-metallic behavior, where its Seebeck coefficient can be fitted by a semiclassical model, while a sign change of the Seebeck coefficient was observed in the thin sample at low temperatures. In addition, the Nernst coefficient of the thick sample showed a dispersive (Drude-like) peak versus the magnetic field and an anomalous Nernst effect appeared below 50 K, in agreement with previous bulk measurements. In contrast, the thin sample showed a monotonically increasing Nernst coefficient versus magnetic field and an absence of anomalous Nernst effect down to 2 K. Our results open possibilities for engineering the thermoelectric properties of topological semimetals through quantum confinement. This work is based on research supported by a NSF DMREF project under the award number DMR-2118523.