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Poster Abstracts

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Redox targeting of solid superionic conductors for high-energy-density batteries

Jose Araujo
PI: Daniel Gamelin

Long-duration energy storage is critical for the success of a sustainable clean-energy grid. Redox flow batteries (RFBs) are attractive for this purpose because of their scalability and ability to decouple energy storage from power generation. RFB deployment has been hampered by high costs and low energy densities, however. One strategy for improving energy density is to add redox-active solids to the electrolyte tanks, whereby these solids increase the electrolyte's volumetric capacity via "redox targeting". In aqueous RFBs, this approach has been almost exclusively limited to the catholyte side of batteries, and no good solutions for aqueous anolyte redox targeting have yet been identified. Here, we demonstrate a versatile redox-active solid that boosts the energy storage capacity of aqueous anolyte mixtures based on either organic or transition-metal redox shuttles. We show that addition of this solid to the anolyte tank can boost the capacity up to 400% of the electrolyte's capacity alone.

A Robust Neural Network for Extracting Dynamics from Time-Resolved Electrostatic Force Microscopy Data

Madeleine Breshears
PI: David Ginger

Advances in scanning probe microscopy (SPM) methods such as time-resolved electrostatic force microscopy (trEFM) now permit the mapping of fast local dynamic processes with high resolution in both space and time, but such methods can be time consuming to analyze and calibrate. Here, we design and train a regression neural network (NN) that accelerates and simplifies the extraction of local dynamics from SPM data directly in a cantilever-independent manner, allowing the network to process data taken with different cantilevers. We validate the NN's ability to recover local dynamics with a fidelity equal to or surpassing conventional, more time-consuming calibrations using both simulated and real microscopy data. We apply this method to extract accurate photoinduced carrier dynamics on n=1 butylammonium lead iodide, a halide perovskite semiconductor film that is of interest for applications in both solar photovoltaics and quantum light sources. NN extracted dynamics from trEFM measurements confirm previous observations of charging rate heterogeneity across microstructures in the perovskite. Finally, we use SHapley Additive exPlanations (SHAP) to evaluate the robustness of the trained model, confirm its cantilever-independence, and explore which parts of the trEFM signal are important to the network.

TBD

Tyson Anthony Carr
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TBD

Emma Cave
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Performance Evaluation of Distance Metrics in Material Acceleration Platforms

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PI: Lilo Pozzo

Material Acceleration Platforms (MAPs) have proven successful in accelerating the material discovery process. It is widely known that the key components of MAPs are the artificial intelligence (AI) agent, the characterization method, and the automated robotic synthesis. However, a commonly overlooked component is the reward function such as a distance metric, which conveys to the AI agent how similar a synthesized material is to the desired target. In our work, we demonstrate that the choice of the distance metric plays a significant role in the performance of MAPs when the characterization method used consists of functional data (e.g., UV-Vis Spectra, Small Angle X-ray Scattering curves) that map a stimulus to a response. To improve the performance of MAPs in such scenario, we adapt the Amplitude-Phase (AP) metric for the application of functional datasets. This metric prioritizes the shape of the function and considers variations in both the x and y axes to compute an appropriate distance between functions. When assigning a "distance", the AP metric computes the length of a geodesic using their Hilbert sphere manifold representations. To evaluate the performance of the AP metric in comparison to the Euclidean metric, we performed parallel optimization campaigns on a model gold nanoparticle synthesis, where the only difference between the two campaigns was the distance metric used as a reward function for the AI agent. Our results show that the AP metric gave the AI agent the ability to distinguish between the regions in the design space that formed cylindrical nanostructures from the ones that formed spherical nanostructures. As a result, it was able to focus its search on the region of interest which resulted in a better match to our predetermined target.

TBD

Ted Cohen
PI: Devin MacKenzie

Decentralized safe reinforcement learning for inverter-based voltage control

Wenqui Cui
PI: Baosen Zhang

Inverter-based distributed energy resources provide the possibility for fast time-scale voltage control by quickly adjusting their reactive power. The power-electronic interfaces allow these resources to realize almost arbitrary control law, but designing these decentralized controllers is nontrivial. Reinforcement learning (RL) approaches are becoming increasingly popular to search for policy parameterized by neural networks. It is difficult, however, to enforce that the learned controllers are safe, in the sense that they may introduce instabilities into the system.

This paper proposes a safe learning approach for voltage control. We prove that the system is guaranteed to be exponentially stable if each controller satisfies certain Lipschitz constraints. The set of Lipschitz bound is optimized to enlarge the search space for neural network controllers. We explicitly engineer the structure of neural network controllers such that they satisfy the Lipschitz constraints by design. A decentralized RL framework is constructed to train local neural network controller at each bus in a model-free setting.

Structure–Property Relationships in Multifunctional 1D Metal–Organic Materials

Ashlyn Kamin
PI: Dianne Xiao

The recent introduction of electrical conductivity and magnetic ordering in metal–organic frameworks (MOFs) represents an important step towards their application in energy storage, electrocatalysis, molecular electronics, chemical sensing, magnetic devices, and more. However, enabling multifunctionally in MOFs requires an understanding of the complex interplay between local structure, supramolecular assembly, and emergent properties. Here, we describe a set of highly tunable metal–organic materials constructed using redox-active dichatecholate ligands. Metalation of these ligands gives rise to 1D metal–organic chains whose geometric structures, electronic structures, and electrical conductivities can be dramatically modulated through solvent, temperature, and redox doping. Electronic and magnetic behavior of these chains are thoroughly characterized and can serve to inform similar structure-property relationships in higher-dimensional MOFs. Additionally, we demonstrate the incorporation of similar dicatecholate moieties into more complex ligand scaffolds, giving rise to extended aromatic synthons that can be used to target metal–organic analogs of multifunctional polycyclic aromatic hydrocarbons.

Probing Catalytic Metal-Support Interfaces within Atomically Precise Nanoclusters

Jonathan Kephart
PI: Alexandra Velian

Solid-state catalysts are central to many critical clean-energy technologies and industrial processes, but their reactive interfaces are notoriously ill-defined, rendering them difficult to study and optimize. In order to study these systems in greater detail, we developed facile synthetic methods to access a family of propeller-shaped trimetallated nanoclusters, M3(L)3Co6Se8L′6 (M3L3; M = Fe, Co, Cr, Zn; L = py, CNtBu, etc.; L′ = Ph2PNTol(−)), in which three low-coordinate "edge" metals decorate the surface of a Co6Se8 "support". We have applied these clusters as molecular platforms to study solid-state catalytic interfaces with atomic precision. This capability was first showcased through our work with the triiron nanocluster, Fe3, in which the redox non-innocence of the Co6Se8 core gives rise to reversible hemilabile Fe–Se coordination to the edge metals (JACS 2019, 141, 19605). Fe3 was found to be an excellent catalyst for the conversion of tosyl-azide and tert-butyl isocyanide to the asymmetric carbodiimide TsN=C=NtBu, but the mechanism of this transformation has remained elusive due to the high reactivity of the catalytic intermediates. More recently, we have shown that the trichromium derivative, Cr3(py)3, also catalyzes this reaction, with well-behaved Cr(II/IV) redox chemistry giving rise to metal-imido intermediates with enhanced stability (JACS 2022, 144, 9206). Catalytic and stoichiometric investigations of tosyl azide activation and nitrene transfer enable the isolation and crystallographic characterization of key intermediates, including the tris(imido) Cr3(NTs)3, the catalytic resting state Cr3(NTs)3(CNtBu)3, and the site-differentiated mono(imido) Cr3(NTs)(CNtBu)2. Using in situ reaction monitoring we find that nitrene transfer proceeds via a stepwise mechanism as the three active sites engage sequentially to produce carbodiimide, their reactivity intertwined through the Co6Se8 support. Further, we demonstrate that the chemical state of one active site regulates the affinity for substrates at neighboring edge sites. Cumulatively, we show that the low-coordinate edge metals of the M3 nanoclusters serve as viable catalytic active sites, and that this composite multi-edge/support architecture provides a powerful platform to model heterogeneous catalytic systems.

TBD

Helen Larson
PI: Brandi Cossairt

TBD

Phuong Le
PI: Dianne Xiao

Metal-support interactions in molecular single-site cluster catalysts

Ben Mitchell
PI: Alexandra Velian

Many industrial catalytic processes rely on solid state catalysts however understanding the dynamic interactions between the substrate, active site, and support is challenging. This study presents atomistic insights into the interface between a single-site catalyst and a transition metal chalcogenide support and illustrates how their cooperativity can be harnessed to modulate catalytic activity. A molecular platform MCo6Se8(PEt3)4(L)2 (1-M, M = Cr, Mn, Fe, Co, Cu, Zn) was designed in which the active site (M)/support (Co6Se8) interactions are interrogated by systematically probing the electronic and structural changes that occur as the identity of the metal varies. All 3d transition metal 1-M clusters display remarkable catalytic activity for coupling tosyl azide and tert-butyl isocyanide, with Mn and Co derivatives showing the fastest turnover in the series. Detailed structural, electronic, and magnetic characterization, including single crystal X-ray diffraction, 1H and 31P nuclear magnetic resonance spectroscopy, electronic absorption spectroscopy, cyclic voltammetry, and computational methods will be presented. Distinct metal/support redox regimes can be accessed in 1-M based on the energy of the edge metal's frontier orbitals with respect to those of the cluster support. As the degree of electronic interaction between the edge and the support increases, a cooperative regime is reached wherein the support can deliver electrons to the catalytic site, increasing the reactivity of key metal-nitrenoid intermediates.

Shelling Quantum Dots With Silica Integrated For Scalable Quantum Photonic Systems

Hao Nguyen
PI: Brandi Cossairt

Colloidal quantum dots (QDs) are excellent candidates for applications as single-photon sources and building blocks for scalable integrated quantum nanophotonic systems when coupled with optical cavities. However, there are many challenges including inhomogeneous broadening, random positioning, and high dephasing rates that hinder the deployment of these solution-processed materials in quantum information science and engineering. With a combination of synthetic and fabrication strategies, we introduce an approach for improving integrated nanophotonics using colloidal QDs. First, we examine the optical properties of giant QDs shelled with silica with different core compositions including CdSe/CdS, CdSe/ZnS, and CdSe/CdS/ZnS and silica shell thicknesses. Without any post-synthetic treatment, the giant QDs show a high thermal- and photo-stability, blinking suppression behavior, and single-photon emission with zero time delay g(2)(0) below 0.4 at room temperature. The giant QDs are then deposited on different nanostructures and show a high degree of dispersion of single particles and deterministic placements. These observations indicate that shelling QDs in silica holds promise to play an important role in the development of integrated quantum nanophotonics.

Exploring alcohol oxidation reactivity of transition metal phosphide nanocrystals

Emily Nishiwaki
PI: Brandi Cossairt

Developing earth-abundant alternatives to noble metal catalysts that convert renewables into commodity chemicals and fuels is a critical step towards global sustainability. Transition metal phosphide (TMP) nanocrystals have been shown to catalyze numerous energy conversion and storage reactions, such as the hydrogen evolution reaction (HER). The high activity of TMPs for HER is attributed to their binary nature, which modulates surface energetics and active site geometry. We hypothesize that the benefits of a binary material can be applied to complex electrochemical reactions due to the tunable polarity of the surface (i.e., various transition metals and stoichiometric variations). This may assist in heterolytic bond cleavage and adsorption of a variety of intermediates required in complex electrochemical reactions. In an initial exploration of TMP reactivity, we studied TMPs as a) thermal transfer hydrogenation catalysts between alcohols and quinones and b) electrocatalysts for alcohol oxidation. So far, Ni2P and CoP have exhibited minimal thermal and electrocatalytic alcohol oxidation activity in non-aqueous conditions. We attribute this to the inadequate oxidation state (1+/2+) of surface Ni and Co and/or inappropriate thermodynamic compatibility between the alcohol and TMPs. Future directions include exploring alcohol electro-oxidation with Ni2P nanocrystals with higher oxidation states, which are accessible in aqueous conditions. We hope to eventually expand our work to other Ni-based nanocrystals to build a rigorous understanding of the effect of different binary material properties on electrocatalytic activity.

Open-Hardware Materials Acceleration Platforms for Accessible and Democratized Materials Discovery

Maria Politi
PI: Lilo Pozzo, Stu Adler, David Beck

We present two high-throughput workflows implementing low-cost and open-hardware based materials acceleration platforms (< $15k), using commercially available materials, and adopting open-science principles for the exploration of soft matter systems involving large chemical design spaces. The first platform addresses the synthesis of deep eutectic solvents (DESs), a novel class of designer solvents with appealing properties for various applications. A wide range of candidate organic precursors (>105) could be used to form DESs with variable properties, leading to a vast design space, which remains largely unexplored. To tackle such a challenge, we have demonstrated the development and use of high-throughput DES formulation workflows and data-driven design strategies for automated synthesis, rapid evaluation, and screening of physical and electrochemical properties. We further synthesized and characterized 600 DES candidate combinations to evaluate their potential use as redox flow battery electrolytes . The second workflow investigated the sonochemical synthesis of CdSe quantum dots and magic-sized clusters at 625 unique sample conditions, including variations in precursor ratios and ligand concentrations. We implemented a configurable and open-source automation platform for sonochemical applications, based on a repurposed 3D-printing platform (Jubilee) with tool-changing capabilities, in combination with an Opentrons OT-2 liquid handling robot and microplate readers for a fully automated workflow, from sample synthesis to characterization. The experimental campaign took less than 2 weeks, making it significantly faster than the traditional, low-throughput hot-injection method. We subsequently use a data-driven approach to corroborate the qualitative relationships observed from the samples' optical characterization. These accessible and affordable systems would enable most laboratories to adopt them with limited funding. Moreover, reduced volumes that are as low as 0.5 mL per sample, allow for cost-efficient and environmentally friendly experimental procedures. Finally, the flexibility, modular nature, and reconfigurability of these high-throughput platforms, makes them adaptable to a variety of soft matter formulation studies.

Directly Probing the Effects of Defect Passivation on Ion Migration in Wide Bandgap Perovskites

Justin Pothoof
PI: David Ginger

Wide bandgap halide perovskite (~1.7 eV) materials are the most promising active layers being studied for use in tandem solar cells utilizing silicon (~1.1 eV) as its bottom light harvesting layer. Being solution processible and having an easily tunable bandgap, perovskites can be tailored to fit the already well optimized and established silicon photovoltaic cell to maximize power conversion efficiency. While perovskites are known to be defect tolerant when discussing device performance, those same defects allow for ionic transport through the crystal lattice leading to device instability in the form of phase segregation, hysteresis, and active layer degradation at interphases or electrodes. In wide bandgap perovskites in particular, this ionic motion is exacerbated by the mixed halide composition necessary to achieve a larger energy gap needed in the tandem architecture. Understanding the phenomenon of ion migration and our ability to control it is paramount to the reproducible fabrication of high efficiency and operationally stable photovoltaics. Here, we use a combination of multimodal scanning probe microscopy and photoluminescence characterization to observe the migration of ions in wide bandgap perovskite films. Importantly, we also use this combination of methods to show the benefits of defect passivation schemes in reducing this deleterious ion migration. Defect passivation, often through chemical post-treatment of the perovskite active layer, has been reported to reduce nonradiative recombination. Here we show that passivation also can reduce ion migration and therefore enhance long-term stability. To measure this effect, we utilize electrical and optoelectronic scanning probe microscopy, such as scanning Kelvin probe microscopy and surface photovoltage, to probe ion motion locally and correlate these measurements with photoluminescence lifetimes and intensity. These results enable future investigations of multiple facets of post-processing treatments on optoelectronic properties, such as carrier lifetimes, photoluminescence enhancement, mitigation of ionic migration, and changes in device metrics among other measurements.

Heavy-atom-free Photon Upconversion Using Thionated Organic Sensitizers

Sarah Pristash
PI: Cody Schlenker

Photon upconversion through triplet–triplet annihilation is of interest for diverse applications, notably as a potential means of exceeding the Shockley–Queisser limits in solar cells. We demonstrate a heavy-atom-free triplet sensitizer based on a thionated squaraine. Using this all-organic sensitizer, we demonstrate upconversion through triplet sensitization of several organic annihilator molecules. Thionated squaraines provide an exciting new platform for developing heavy-atom-free upconversion systems.

TBD

Hunter Ripberger
PI: Brandi Cossairt

(3-Aminopropyl)trimethoxysilane Surface Passivation Improves Perovskite Solar Cell Performance by Reducing Surface Recombination Velocity

Yangwei Shi
PI: David Ginger

We demonstrate reduced surface recombination velocity (SRV) and enhanced power-conversion efficiency (PCE) in mixed-cation mixed-halide perovskite solar cells by using (3-aminopropyl)trimethoxysilane (APTMS) as a surface passivator. We show the APTMS serves to passivate defects at the perovskite surface, while also decoupling the perovskite from detrimental interactions at the C60 interface. We measure a SRV of ~125 + 14 cm/s, and a concomitant increase of ~100 meV in quasi-Fermi level splitting in passivated devices compared to the controls. We use time-resolved photoluminescence and excitation-correlation photoluminescence spectroscopy to show that APTMS passivation effectively suppresses non-radiative recombination. We show that APTMS improves both the fill factor and open-circuit voltage (VOC), increasing VOC from 1.03 V for control devices to 1.09 V for APTMS-passivated devices, which leads to PCE increasing from 15.90% to 18.03%. We attribute enhanced performance to reduced defect density or suppressed nonradiative recombination and low SRV at the perovskite/transporting layers interface.

Oxidative Control of $Cu_3(HHTP)_2$ Nanocrystal Morphology

Kathleen Snook
PI: Dianne Xiao

TBD

Margherita Taddei
PI: Dianne Xiao

In this work show that use of ethylenediamine (EDA) as an additive to perovskite precursor solution, improves the photovoltaic device performance and material stability of high-bromide-content, methylammonium-free, formamidinium cesium lead halide perovskites FA1-xCsxPb(I1-yBry)3 which are currently of interest for perovskite-on-Si tandem solar cells. Using spectroscopy and hyperspectral microscopy, we show that the additive improves film homogeneity and suppresses the phase instability that is ubiquitous in high-Br perovskite formulations. With the addition of 1 mol% EDA we demonstrate 1.69 eV-gap perovskite single-junction p-i-n devices with a VOC of 1.22 V, and a champion maximum power point tracked power conversion efficiency of 18.8%. Moreover, using nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction techniques, we show that EDA reacts with FA in solution, forming imidazolinium cations.

Synthesis of Colloidally-Stable Cs2ZrF6 Nanocrystals for Red-Emissive Mn4+ Phosphors

Eden Tzanetopoulos
PI: Daniel Gamelin

With lighting accounting for ~15% of global energy consumption, developing more efficient lighting technologies than commonplace fluorescent and incandescent lamps is essential to combating anthropogenic climate change. White Light-Emitting Diodes (wLED) show great promise due to their high efficiencies, prolonged lifetimes, and high brightness. The major hindrance of commercial wLEDs is their undesirable blue-tone due to a lack of strong red emission between 600 and 650 nm. Mn4+-doped A2BF6 (A = K+, Na+, Cs+; B = Si4+, Ti4+, Ge4+, Zr4+) lattices offer sharp emission in the desired red regime necessary for wLED implementation but have been prepared solely as microcrystals via wet etching and hydrothermal syntheses. Here, colloidally stable 20 nm Cs2ZrF6 nanocrystals were successfully prepared via a solution-phase Schlenk line synthesis, confirmed by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). This is the first report of colloidally stable sub-micron sized crystals of the A2BF6 composition. The synthesis developed in this report utilizes an NH4F salt dissolved in methanol as the active fluoride source, a safer alternative to the commonly used but hypertoxic HF. A minority impurity species of CsF is observed at the low reaction temperature of 180 ℃ necessary to prepare the monodispersed nanocrystals but is optically inactive and therefore of minimal consequence to the target application. The ongoing work of this research is to introduce Mn4+ dopants into the Cs2ZrF6 nanocrystal lattice using precursor routes such as permanganates, [MnF6]2- salts, and bulky ligand-Mn4+ complexes. The introduction of Mn4+ into the lattice will be studied via photoluminescence spectroscopy and electron paramagnetic resonance measurements.

Sensitized Mn2+ Luminescence In Lead-Free Mn2+:CsEuCl3 Perovskite Nanocrystals

Kelly Walsh
PI: Daniel Gamelin

The emergence of next-generation spintronic and spin photonic technologies will be aided by the development of materials showing strongly coupled magnetic, electronic, and optical properties. Development of these technologies will enable computing advancements that will lessen the energy demands of the technology sector, currently accounting for ~10% of the world’s electricity demands. Previous work in our group has identified CsEuCl3 nanocrystals and thin films as promising candidates for these technologies, given the strong magneto-optical response of these materials. Additionally, both the nanocrystals and thin films undergo a ferromagnetic phase transition at low temperatures (~3 K) and the nanocrystals exhibit circularly-polarized luminescence with a polarization ratio of ~30% at low temperatures and modest magnetic field. Here, we report preliminary results on introducing Mn2+ dopants into the CsEuCl3 nanocrystal lattice, which results in sensitized Mn2+ luminescence and an approximately 10-fold enhancement in the room-temperature photoluminescence quantum yield as compared to the undoped CsEuCl3 nanocrystals.

Coupled process/device modeling of Cu(In,Ga)Se2 solar cells

Xiaofeng Xiang
PI: Scott Dunham

Point defects directly impact solar cell device performance by limiting the carrier lifetime. In this work, density functional theory calculations are firstly used to determine the formation energy and diffusion energy barriers of dominant defects in Cu(In,Ga)Se2. Next, continuum reaction-diffusion models are developed to analyze the redistribution of defects
during manufacturing processes. We estimate defect capture cross sections using a first-principles based approach. These cross sections are combined with our calculated defect profiles and trap energy levels to parameterize a Shockley-Read-Hall (SRH) recombination model, which we implement into a device simulator to predict carrier lifetimes and device performance. In that way, a predictive Technology Computer Aided Design (TCAD) model is built to predict and optimize the performance of Cu(In,Ga)Se2 solar cells.