CNMS Operations: Quarterly Report

NSRC Name, DOE Laboratory(s): Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL)
NSRC Director: Karren More
Date: January 17, 2023
Period covered: FY23 Quarter 1: October 1 – December 31, 2022

1. User Program:

- 2023 CNMS User Executive Committee Election: The election for the 2023 CNMS User Executive Committee (UEC) was completed during November and results were provided to the CNMS User Group in December. Piran Kidambi of Vanderbilt University was elected as the 2023 Vice Chair and will become the 2024 UEC Chair. In addition, three new UEC members were elected to two-year terms starting in January 2023: Jon Camden of the University of Notre Dame, Ethan Self of ORNL), and Wan-Yu Tsai of ORNL. Returning to the UEC in 2023: officers Shengxi Huang of Rice University (Past Chair), Massoud Mahjouri-Samani of Auburn University (Secretary) and At-Large members Tatiana Allen of the University of Tennessee - Chattanooga), Liam Collins of ORNL, and Jacob Swett of Recognition Analytix who serves as the UEC's Industrial Liaison.
- Fall 2023A Proposal Call: The Fall proposal call closed on October 19, 2022 - 165 new user proposals were submitted, and 148 proposals were approved. All PIs were notified of results by December 20, 2022. The new CNMS projects will start February 1, 2023.
- Proposal Extensions: The user office initiated the process to review extension requests for 154 projects that are due to expire on January 31, 2023.
- User Statistics for FY2022: Our annual BES facility report for FY22 was submitted in October. CNMS reported 811 unique users during FY22. CNMS reported 52% first-time users and academic users accounted for 66% (53% US academic). Users came from 40 US states and territories (Puerto Rico and the District of Columbia) plus 24 foreign countries (111 users).
- Active User Proposals as of December 31, 2022: 680 (includes 41 rapid access proposals)
    - Industry-led: 19
    - University-led: 482
    - ORNL Staff-led: 147
    - Other Government Laboratory-led: 26
    - MSI and HBCU-led: 17 MSI, 3 of which are HBCUs
    - Unique Institutions: 223
    - Average Requested Proposal Time: 31 days
    - Science Categories: Proposal distribution - 45% Materials Science; 16% Engineering; 9% Chemistry; 5% Instrumentation; 4% Polymers; 10% Biological/Life Sciences; 3% Physics; 3% Optics; 1% Earth/Environmental Sciences; 1% Medical

2. PIs and Technical Staff Supported by FWP:

- **Numbers:**
    - Number (Headcount) of Staff in CNMS Division (not including post-docs): 70
        - Director: 1 (1.0 FTE)
        - Division Administrative: 1 (1.0 FTE)
        - R&D Staff: 56 (37.1 FTEs)
        - Tech Professionals: 4 (3.0 FTEs)
        - Technicians: 6 (2.6 FTEs)

  - User Office: 2 (1.8 FTEs)
  - Administrative: 5 (supported at the directorate level – not included in headcount)
  - Operations (ES&H): 1 (supported at lab level – not included in headcount)
  - Finance: 1 (supported at lab level – not included in headcount)
- Total # FTEs supported on CNMS FWP (not including post-docs): 46.5
- Other funding sources/programs: 2 LDRD projects, 2 BES-MSED-FWPs, 1 BES-SUFD-ECA, 1 BES-SUFD-QIS Infrastructure FWP, 3 BES-SUFD-AI/ML FWPs, QSC, 3 EFRCs, multiple EERE offices (BETO, HFTO, VTO)

- **New Staff Hires:**
  - Yue Yuan – ORNL Distinguished Staff Fellow (Wigner Fellow), Macromolecular Nanomaterials Group
  - Sujoy Ghosh – R&D Associate, Nanofabrication Research Laboratory (NRL)
  - Eva Zarkadoula – R&D Staff, Nanomaterials Theory Institute (transfer from Materials Science & Technology Division)
  - Lisa Goins – named CNMS User Program Coordinator (replaced Sandy Lowe)
- **Staff Departures:**
  - Mark Arnould – Technical Professional in Macromolecular Nanomaterials Group; departed for a position in industry
  - Zening (Zach) Liu – post-doc in Nanofabrication Research Laboratory (NRL) Group took a new position at Moleaer in Los Angeles, CA
- **Honors:**
  - Michael Zachman - received the Scientist Medal from the International Associate of Advance Materials (IAAM); award is given for professional impact in an interdisciplinary field considering contributions made in the decade preceding the year of the award.
  - Rama Vasudevan - elected APS Fellow for "pioneering and visionary development of open-sourced physics-based machine learning methods in atomic-scale and mesoscopic imaging, and their application in physics."
  - Rigoberto Advincula – received the 2022 University of the Philippines Alumni Association (UPAA) Lifetime Distinguished Achievement Award at the awards ceremony held at the University of the Philippines on November 9, 2022.
  - Rigoberto Advincula – named Fellow of the Royal Society of Chemistry for "significant contributions to the chemical sciences, and in particular to polymer chemistry."
  - Yongtao Liu, Kyle Kelley, Rama Vasudevan, Hiroshi Funakubo (Tokyo Institute of Technology), Maxim Ziatdinov, and Sergei Kalinin (University of Tennessee) received the Outstanding Scholarly Output Award at ORNL's Awards Night on November 7, 2022 for "Experimental Discovery of Structure-Property Relationships in Ferroelectric Materials via Active Learning," *Nature Machine Intelligence* **4** 341-350 (2022).
  - Eva Zarkadoula – received the ONE ORNL Award and the Director's Award at ORNL's Awards Night, November 7, 2022
  - Miaofang Chi, Karren More, and David Cullen – named to Clarivate Analytics 2022 List of Highly Cited Researchers (Miaofang's 3rd and Karren's 2nd time on the Highly Cited list).
  - Kinga Unocic – received the 2023 Brimacombe Medalist Award from TMS, The Minerals, Metals, and Materials Society; award is given to mid-career professionals by TMS in recognition of sustained service and achievement in science related to materials science and engineering.

- Yue Yuan – Research named as one of ORNL Neutron Scattering Directorate's Top 10 Science Achievements in 2022 for "Biocatalytic Yarn for Peroxide Decomposition with Controlled Liquid Transport," https://onlinelibrary.wiley.com/doi/full/10.1002/admi.202002104

- **Significant Invited Talks:**
  - Arpan Biswas, "A Latent Bayesian Optimization Approach in High Dimensional Hyperparameter Optimization of Unsupervised Joint (Rotationally-Invariant) Variational Auto-Encoder," International Mechanical Engineering Congress & Exposition (IMECE), Columbus, OH, October 30 – November 3, 2022.
  - Miaofang Chi, "Advanced Scanning Transmission Electron Microscopy for Energy Storage Research," Gordon Research Conference: Liquid Phase Electron Microscopy, Ventura, CA October 9-14, 2022.
  - Miaofang Chi, "Elucidating Interfaces in Solid State Batteries Using Advanced Scanning Transmission Electron Microscopy (STEM)," Materials Research Society (MRS) Fall Meeting & Exhibit, Boston, MA, November 27 – December 2, 2022.
  - Miaofang Chi, "Cryogenic STEM Imaging and Spectroscopy for Energy and Quantum Materials," Materials Research Society (MRS) Fall Meeting & Exhibit, Boston, MA, November 27 – December 2, 2022.
  - David Cullen, "Automating Correlative Electron Microscopy for Heavy Duty Fuel Cell Development," 242nd Electrochemical Society (ECS) Meeting, Atlanta, GA, October 9-13, 2022.
  - David Cullen, "New Insights into Fuel Cell Catalysts through Automated Analytical Electron Microscopy," 5th Israeli Fell Cells Consortium Workshop, Tel Aviv, Israel, November 14-15, 2022.
  - Neus Domingo, "Coupling of Ferroelectric Domain Walls with Liquid and Magnetic Interfaces," Materials Research Society (MRS) Fall Meeting & Exhibit, Boston, MA, November 27 - December 2, 2022.
  - Neus Domingo, Invited Tutorial "Piezoresponse Force Microscopy," IEEE Ferroschool Winter 2022, Calgary, Alberta, Canada, December 5-9, 2022.
  - P. Ganesh, "Harnessing Anharmonicity and Electron Correlations for Energy Efficient Computing," Inaugural VU-ORNL Collaborative Workshop on Nanoscience, Nashville, TN, November 21, 2022.
  - P. Ganesh, "Topological Electronics," Purdue/ORNL Microelectronics Workshop, December 13, 2022. (Virtual)
  - Jordan Hachtel, "Opportunities, Challenges, and Solutions in the Ultrahigh Energy Resolution Regime," NGEM Seminar Series at the University of Tokyo, Tokyo, Japan, October 6, 2022.
  - Kunlun Hong, "Charged Chain End: A Powerful Parameter in Tuning Polymer Structures and Dynamics" ORNL Soft Matter Symposium, Oak Ridge, TN, October 26-27, 2022.
  - Kyle Kelley, "Oxygen Vacancy Injection as a Pathway to Enhancing Electromechanical Response in Ferroelectrics," US-Japan Seminar on Dielectric and Piezoelectric Ceramics, Charleston, SC, November 13, 2022.
  - Rajeev Kumar, "Plasmon Mode in Semi-Dilute Polyelectrolyte Solutions," ORNL Soft Matter Symposium, Oak Ridge, TN, October 26-27, 2022.
  - An-Ping Li, "Synthesis of Atomically Precise Graphene Nanoribbons with Tunable Electronic Properties," MS&T 2022, Pittsburgh, PA, October 9-12, 2022.

- An-Ping Li, "Atomically Precise Graphene Nanoribbons for Quantum Electronics," American Vacuum Society (AVS) 68th International Symposium & Exhibition, Pittsburgh, PA, November 6-11, 2022.
- An-Ping Li, "Quest for Structure-Property Relationships Down to the Atomic Scale via Scanning Tunneling Microscopy," Inaugural VU-ORNL Collaborative Workshop on Nanoscience, Nashville, TN, November 21, 2022.
- Liangbo Liang, "Manipulating Interlayer Magnetic Orders of 2D Magnets by Stacking Rotation," 8th Nano Boston Conference, Boston, MA, October 31 - November 2, 2022.
- Yongtao Liu, "Machine Learning Driven Automated Microscopy: Applications in Ferroelectric and Optoelectronic Materials," Seagate Minnesota Campus AI/ML Distinguished Speaker Series, October 7, 2022. (Virtual)
- Andy Lupini, "Atomic Scale Dopant Control," Materials Research Society (MRS) Fall Meeting & Exhibit, Boston, MA, November 27 - December 2, 2022.
- Peter Maksymovych, "Phase Transitions through the Looking Glass," Inaugural VU-ORNL Collaborative Workshop on Nanoscience, Nashville, TN, November 21, 2022.
- Jonathan Poplawsky, "Designing Stable $\theta'/L1_2$ Co-precipitates in Cast and Additively Manufactured Al-Cu-Mn-Zr Alloys," MS&T 2022, Pittsburgh, PA, October 9-12, 2022.
- Steven Randolph, "Multiple Ion Plasma: Emerging Opportunities in FIB Materials Processing," Plasma FIB Workshop, University of Tennessee, Knoxville, TN, October 6, 2022.
- Bobby Sumpter, "Understanding the Materials and Chemical World, Atom-by-Atom," Advanced Materials World Congress 2022, October 11, 2022. (Virtual)
- Bobby Sumpter, "Accelerating Materials Design using Physically Informed Prediction," Korean Physical Society Fall Meeting, October 21, 2022. (Virtual)
- Kinga Unocic, "Oxidation Behavior of Model FeCrAl Steel and APMT Alloy After Exposure in Steam," MS&T 2022, Pittsburgh, PA, October 9-12, 2022.
- Raymond Unocic, "Quantifying Electrochemical Reactions with *in situ* ec-STEM," Gordon Research Conference: Liquid Phase Electron Microscopy, Ventura, CA, October 9-14, 2022.
- Rama Vasudevan, "Autonomous Experiments in Scanning Probe Microscopy: Opportunities for Rapid Inference and Decision Making," Fast Machine Learning for Science Workshop 2022, Southern Methodist University, Dallas, TX, October 3-6, 2022.
- Rama Vasudevan, "Characterizing and Exploiting Topological and Point Defects in Ferroelectric Thin Films: Optimizing Electromechanical Response and Investigating Energy Landscapes with Automated Experiments," Materials Research Society (MRS) Fall Meeting & Exhibit, Boston, MA, November 27 – December 2, 2022.
- Rama Vasudevan, "Advancing Microscopy with Machine Learning: Lessons and Insights from Scanning Probe Microscopy," Institute for Pure and Applied Mathematics (IPAM) Multi-Modal Imaging with Deep Learning and Modeling Workshop, University of California, Los Angeles, CA, November 28-29, 2022.
- Rama Vasudevan, "Machine Learning for Ferroelectrics," IEEE Ferroschool Winter 2022, Calgary, Alberta, Canada, December 5-9, 2022.
- Yangyang Wang, "Some Open Problems in Dynamics and Rheology of Polymers: A Personal Take Based on Recent Studies," ORNL Soft Matter Symposium, Oak Ridge, TN, October 26-27, 2022.
- Alexis Williams, "Cryo EM – Low Dose Imaging of Beam Sensitive Samples," ORNL Soft Matter Symposium, Oak Ridge, TN, October 26-27, 2022.

- Kai Xiao, "Tailoring the Heterogeneities in 2D Materials by Non-equilibrium Synthesis and Processing," Physics Colloquium, School of Science and Engineering, Tulane University, New Orleans, LA, October 31, 2022.
- Michael Zachman, "Simultaneous Imaging of Light and Heavy Elements at Atomic-Resolution in Energy Materials by CoM-STEM," International Association of Advanced Materials – Advanced Materials Congress Scientist Medal Lecture, October 31, 2022. (Virtual)

3. Postdocs Supported by FWP

- Total number of post-docs in CNMS Division: 22 FTEs (in addition, 5 positions have been filled and post-docs are on-boarding; 10 positions are open)
- Number of post-docs supported by CNMS FWP: 5 FTEs (in addition, 2 positions have been filled and post-docs are on-boarding, 3 positions are currently open)

4. Progress and Budget Summary on BES NSRC-supported QIS FWP:

FWP ERKCZ62 "Precision Atomic Assembly for Quantum Information Science," PI - Art Baddorf

- **Progress:**
  - Equipment:
    - The central microscope, an "Infinity" closed-cycle, low-temperature STM from Scienta Omicron, was delivered in late December. Installation is scheduled for January.
    - An ion sputter gun for sample surface cleaning was delivered in December.
    - Auxilary equipment, including evaporators and low energy electron diffraction, has been discussed with vendors, evaluated, and priced.
    - Laboratory preparations have been completed.
  - Staff:
    - CNMS hired a new R&D Associate, Mykola Telychko, to contribute to STM experimentation on this project. Dr. Telychko is scheduled to arrive in Spring 2023.
    - A postdoctoral position for ML applications to STM is now posted. We have scheduled interviews.
  - Research:
    - Density functional theory (DFT) calculations of the Kagome metals FeSn and CoSn, were performed and a tight-binding model was developed to reproduce low-energy band-structures and Fermi-surfaces.
    - Random-phase approximation (RPA) calculations were employed to analyze the DFT-derived tight-binding model for FeSn. Results were used to determine if an effective two-dimensional model can adequately capture the material's magnetic excitation spectrum.
- **Budget summary:**
  - FTE funded staff/post-docs = 0.81 FTE (no post-docs originally on this project but new position posted in Q1 FY23)
  - (a) Second year of Award - Received $75,000 in OPE and $0 in EQU
  - (b) Funds received to date (OPE and EQU) – $3,425,000
  - (c) Funds spent to date (OPE and EQU) - $1,368,769
  - (d) Committed equipment funds - $145,069

5. Progress and Budget Summary on BES NSRC-supported ECRP FWP:

FWP ERKCZ55 "Probing Electrons in Electrides and Beyond," PI - Miaofang Chi

- **Progress:**
  Work continues regarding the transition-metal trihalide project investigated using cryogenic scanning transmission electron microscopy (Cryo-STEM) techniques. High-angle annular dark-field STEM (HAADF-STEM) imaging revealed the structural transition of low-dimensional $CrCl_3$ showing distinct changes in stacking contrast from bulk to thin samples. In addition to observing unique stacking transitions as a function of temperature and thicknesses for $CrCl_3$, other metal trihalides such as $RuCl_3$ and $RhCl_3$, have also been studied and compared to draw a generalized understanding of phase transition behavior and their correlated quantum phenomena in the family of metal trihalides. We discovered similarly complex stacking at low temperatures for $RuCl_3$, whereas $RhCl_3$, with no bulk phase transition, showed resistance to stacking shifts even at low dimensions. To confirm the reproducibility of the observed phase transitions, temperature cycling experiments were performed on $CrCl_3$ while visualizing the return of phase at each temperature stage, thereby indicating the capacity for reliable device integration. Furthermore, simulations of the acquired HAADF-STEM images were conducted to determine the stacking sequence accountable for the observed contrast. A manuscript is being prepared for this work. Future work will involve developing an algorithm for automated determination of stacking from acquired HAADF image contrast, which will facilitate accelerated understanding of stacking changes of 2D materials.
- **Publications:** None to report this quarter
- **Invited Presentations:** Two invited presentations at MRS Fall Meeting
- **Budget Summary:**
  - FTE funded staff/post-docs = 1.06/2.97 (since awarded in FY19)
  - First year of Award - FY19
  - Funds received to date (OPE and EQU) – $ 2,099,910.33 (no funds received in FY23 to date)
  - Funds spent to date (OPE and EQU) - $1,005,660.13

6. Progress on BES SUF-supported Data FWP(s)

CNMS staff are collaborators on three externally led BES-SUFD Data Projects:

- FWP ERKCZ59 "4D Camera Distillery: From Massive Electron Microscopy Scattering Data" led by LBNL. The overarching project is targeted at artificial intelligence and machine learning (AI/ML) based analysis of the huge datasets that are generated by a new generation of ultra-high speed electron detectors. The new post-doc, Elizaveta Tiukalova, started her position in late September and her work has been concentrated on collecting representative electron energy loss (EEL) spectra from compounds with the same elements in different valence states to validate the AI models, with initial results collected from a variety of titanium and zirconium samples.
  - Budget Summary:
    - FTE funded staff/post-docs - 0.32/0.22 FTE
    - First year of Award – FY20
    - Funds received to date (OPE and EQU) – $391,000 OPE; $0 EQU
    - Funds spent to date (OPE and EQU) - $176,572
- FWP ERKCZ60 "A Collaborative Machine Learning Platform for Scientific Discovery" led by LBNL. Demonstrated the working prototype of the Bayesian-optimization-based and deep kernel learning-based spectral recommender system using atomic force microscopes at CNMS. The alpha release of the developed code was made available via GitHub and will be incorporated into the MLExchange ecosystem in the near future. Worked with the LBNL team to adapt invariant variational autoencoders developed at ORNL for annotation and anomaly discovery in imaging

datasets from ALS. Continuing to work on implementing physics-based custom loss functions for invariant variational autoencoders.
  - Budget Summary:
    - FTE funded staff/post-docs - 0.32/0.32 FTE
    - First year of Award – FY20
    - Funds received to date (OPE and EQU) – $495,000 OPE; $0 EQU
    - Funds spent to date (OPE and EQU) - $258,977
- FWP ERKCZ61 "A Digital Twin for Spatiotemporally Resolved Experiments" led by ANL. Optimal design of star block copolymers (SBC) has been investigated via fusion of molecular dynamics (MD) simulations and machine learning (ML) - various parameters of these macromolecules can be tuned to obtain desired surface properties, including the number of arms, composition of the arms and the degree-of-polymerization of blocks (or the length of the arm). This makes identification of the optimal SBC design highly non-trivial as the total number of plausible SBC architectures is experimentally or computationally intractable. In this work, we used MD simulations coupled with reinforcement learning based Monte Carlo tree search (MCTS) to successfully identify SBC designs that minimizes the interfacial tension between polar and non-polar solvents. Overall, this work provides an efficient approach to solve design problems via fusion of simulations and ML and establishes important groundwork for future experimental investigation of SBC sequences for various applications.
  - Budget Summary:
    - FTE funded staff/post-docs - 0.18/0.38 FTE
    - First year of Award – FY20
    - Funds received to date (OPE and EQU) – $270,000 OPE; $0 EQU
    - Funds spent to date (OPE and EQU) - $148,717

7. Operations Equipment (OPE or EQU) Investments:

- **Ordered:** SQUID Magnetometer - EQU $650k - delivery and installation expected in January 2023
- **Ordered:** High energy resolution Nion IRIS electron energy Loss Spectrometer (EELS) for Nion UltraSTEM U100 - EQU $620k - ordered in FY21 with delivery expected in Spring FY23
- **Ordered**: Holder heating/cleaning unit for JEOL NeoARM - OPE $60k - delivery expected in Spring FY23
- **Ordered:** Low temperature manipulator for STM to add new functionality – OPE $130k – delivery expected in early FY23
- **Ordered:** Gatan double-tilt, side-entry, cryo-holder and controller for Nion MAC-STEM – OPE $75k – delivery expected in early FY23
- **Ordered:** Thermo Fisher Scientific Hydra Ga^+ Focused Ion Beam (FIB) instrument to support specimen preparation for atom probe and microscopy – EQU $1.2M – delivery expected in summer FY23
- **Ordered:** Segmented detector for JEOL NeoARM – OPE $200k – delivery expected in summer FY23
- **Delivered:** Spin-polarized mK-STM (initial QIS Infrastructure project led by Chris Rouleau) was delivered on September 15, 2022; installation stated in October and is undergoing inspections, tuning, and testing.

8. Covid Impact:

- All ORNL staff returned to working full-time, on-site on May 16, 2022; current community status is MEDIUM
- CNMS staff continue to work remotely with CNMS users when appropriate

9. Safety Updates:
None to report

10. Concerns and Challenges
- Staff retention is an ongoing problem, although CNMS attrition rate is somewhat lower than ORNL's overall.
- On-boarding of new staff hires and post-docs is taking much longer than expected – numerous delays have been encountered, primarily due to visa issues.

11. Other News:
- Karren More, Brad Lokitz, Scott Retterer, P. Ganesh, and Stephen Jesse visited the NSF Southeastern Nanotechnology Infrastructure Corridor (SENIC) facility at Georgia Tech on October 5, 2022 to discuss how SENIC and CNMS could coordinate user access to complementary capabilities at the different facilities. The visit was reciprocated when researchers from SENIC (from Georgia Tech, North Carolina A&T State University, and the University of North Carolina Greensboro) came to CNMS on October 27, 2022. Protocols are being established to facilitate some type of arrangement for sharing facilities.
- Kinga Unocic – Organizer of Symposium "Additive Manufacturing: Mechanisms and Mitigation of Aqueous Corrosion and High Temperature Oxidation – Corrosion Behavior of Additively Manufactured Metals and Alloys," MS&T 2022, Pittsburgh, PA, October 9-12, 2022.
- Bobby Sumpter, Yangyang Wang, and Rigoberto Advincula - Co-organizers of the ORNL Soft Matter Symposium 2022 held October 27-28, 2022.
- Miaofang Chi – Advisory Committee for NSF Workshop on Future Scientific Instruments for Alloys, Amorphous, and Composite Materials Research, Chicago, IL, November 7-8, 2022.
- Kai Xiao – Secretary for AVS 68th International Symposium & Exhibition, Pittsburgh, PA, November 6-11, 2022.
- P. Ganesh – Co-organizer of Symposium "Harnessing Functional Defects for Energy and Electronic Frontiers," Materials Research Society (MRS) Fall Meeting & Exhibit, Boston, MA, November 27 - December 2, 2022.
- Jordan Hachtel – Elected to Board of Directors for the Microanalysis Society, 2023-2026
- Jingsong Huang - named Associate Editor for journal *Frontiers in Soft Matter*
- Zheng Gai – named Section Editor-in-Chief of Spin Crossover and Spintronics for journal *Magnetochemistry*
- Kai Xiao, Member of the AVS 2D Materials Technical Group (2DMTG) Executive Council (EC)
- Art Baddorf – Member of the External Advisory Board for Energy Frontier Research Center (EFRC) "Manipulation of Atomic Ordering for Manufacturing Semiconductors" (μ-Atoms) led by the University of Arkansas.
- Kinga Unocic - Chair of TMS Corrosion and Environmental Effects Committee 2022-2024
- P. Ganesh – Mentoring SCGSR Daniel Staros from Brown University; Daniel is applying correlated electronic structure methods to understand the properties of 2D magnets and their heterostructures.

12. Science Supported by FWP

Three highlights will be submitted in FY23 Q1:

1. M.S. Kavrik, J.A. Hachtel, W. Ko, C. Qian, A. Abelson, E.B. Unlu, H. Kashyap, A.-P. Li, J.C. Idrobo, and M. Law, "Emergence of Distinct Electronic States in Epitaxially Fused PbSe Quantum Dot Superlattices," *Nature Communications* **13**, 6802 (2022). DOI: 10.1038/s41467-022-33955-w

   CNMS-user co-led collaborative publication: Quantum coupling in arrayed nanostructures can produce novel mesoscale properties such as electronic minibands to improve the performance of optoelectronic devices, including ultra-efficient solar cells and infrared photodetectors. Colloidal PbSe quantum dots (QDs) that self-assemble into epitaxially-fused superlattices (epi-SLs) are predicted to exhibit such collective phenomena. Here, we show the emergence of distinct local electronic states induced by crystalline necks that connect individual PbSe QDs and modulate the bandgap energy across the epi-SL. Multi-probe scanning tunneling spectroscopy shows bandgap modulation from 0.7 eV in the QDs to 1.1 eV at their necks. Complementary monochromated electron energy-loss spectroscopy demonstrates bandgap modulation in spectral mapping, confirming the presence of these distinct energy states from necking. The results show the modification of the electronic structure of a precision-made nanoscale superlattice, which may be leveraged in new optoelectronic applications.

2. S.H. van Vreeswijk, M. Monai, R. Oord, J.E. Schmidt, A.N. Parvulescu, I. Yarulina, L. Karwacki, J.D. Poplawsky, and B.M. Weckhuysen, "Detecting Cage Crossing and Filling Clusters of Magnesium and Carbon Atoms in Zeolite SSZ-13 with Atom Probe Tomography," *JACS Au* **2**, 2501-2513 (2022). DOI: 10.1021/jacsau.2c00296

   CNMS-user co-led collaborative publication: The conversion of methanol to valuable hydrocarbon molecules is of great commercial interest, as the process serves as a sustainable alternative for the production of, for instance, the base chemicals for plastics. The reaction is catalyzed by zeolite materials. By the introduction of magnesium as a cationic metal, the properties of the zeolite, and thereby the catalytic performance, are changed. With atom probe tomography (APT), nanoscale relations within zeolite materials can be revealed: i.e., crucial information for a fundamental mechanistic understanding. We show that magnesium forms clusters within the cages of zeolite SSZ-13, while the framework elements are homogeneously distributed. These clusters of just a few nanometers were analyzed and visualized in 3-D. Magnesium atoms seem to initially be directed to the aluminum sites, after which they aggregate and fill one or two cages in the zeolite SSZ-13 structure. The presence of magnesium in zeolite SSZ-13 increases the lifetime as well as the propylene selectivity. By using operando UV−vis spectroscopy and X-ray diffraction techniques, we are able to show that these findings are related to the suppression of aromatic intermediate products, while maintaining the formation of polyaromatic compounds. Further nanoscale analysis of the spent catalysts showed indications of magnesium redistribution after catalysis. Unlike zeolite H-SSZ-13, for which only a homogeneous distribution of carbon was found, carbon can be either homogeneously or heterogeneously distributed within zeolite Mg-SSZ-13 crystals as the magnesium decreases the coking rate. Carbon clusters were isolated, visualized, and analyzed and were assumed to be polyaromatic compounds. Small one-cage-filling polyaromatic compounds were identified; furthermore, large-cage-crossing aromatic molecules were found by isolating large coke clusters, demonstrating the unique coking mechanism in zeolite SSZ-13. Short-length-scale evidence for the formation of polyaromatic compounds at acid sites is discovered, as clear nanoscale relations between aluminum and carbon atoms exist.

3. G. Minnik, B.T. Safa, J. Rosenbohm, N.V. Lavrik, J. Brooks, A.M. Esfahami, A. Samaniego, F. Meng, B. Richter, W. Gao, and R. Yang, "Two-Photon Polymerized Shape Memory Microfibers: A New Mechanical Characterization Method in Liquid," *Advanced Functional Materials* (2022). DOI: 10.1002/adfm.202206739

   CNMS-led publication: Based on large-scale molecular dynamics simulations, the assembly process of charged star block copolymers was detailed for the first time. The results and understanding developed captures the findings of our concurrent experiments for these copolymers at oil/water interfaces. Based on these results and the model developed, we envision that we can couple this methodology with high-throughput simulations and machine learning algorithms thereby allowing for the optimization of key parameters such as degree-of-polymerization of arms, chemical composition of arms, number of arms, block sizes, and sequence of blocks. This will not only enhance our understanding, but also predict interfacial properties of the general class of

charged star block copolymers for applications as stealth surfactants or amphiphiles for novel chemical transformations and separations.

- **Publications:** All FY23 Q1 CNMS publications for categories (publication types) (a) *Sole NSRC-led*, (b) *NSRC-led Collaborative*, (c) *NSRC/User Co-led Collaborative*, (d) *User-led Collaborative*, and (e) *User-only* are documented in the Excel spreadsheet (separate document "CNMS FY23 Q1 Publications"). CNMS had 56 publications in Q1 with 28 publications in journals with an IF > 7 (50%). Stat
- **Invention disclosures, patents, other products:**
  - **Patent**: US Patent #11518674 - "Atomic-scale e-beam Sculptor," Sergei Kalinin, Stephen Jesse, Albina Borisevich, Ondrej Dyck, Bobby Sumpter, and Raymond Unocic. Issued December 6, 2022.

13. FWP Budget details

- Budget information included in Excel spreadsheet (separate document " FY23 Q1 ORNL CNMS Budget").