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: July 13, 2023
Period covered: FY23 Quarter 3: April 1 – June 30, 2023

1. User Program:

- 2023 CNMS User Meeting: The 2023 CNMS User Meeting is set for August 7-11, 2023. Over 250 people have registered for the 2-day meeting that will be held at the Crown Plaza Hotel in downtown Knoxville, TN. Plenary talks will be given by David Masiello (University of Washington), Oana Jurchescu (Wake Forrest University), Linda Horton (BES), and Natalie Holder (SLAC). Workshops on Cryo-EM, Charged Polymers, Autonomous Characterization and Synthesis, and Novel Materials for Neuromorphic Computing will be held in conjunction with the user meeting. A CNMS lab tour is also planned.
- Spring 2023B Proposal Call: The Spring proposal call closed on May 3, 2023. 113 proposals out of 149 (75%) were fully approved and will become active on August 1, 2023.
- Proposal Extensions: The user office initiated the proposal extension process for 136 2022B proposals that are set to expire on July 31, 2023, and are eligible for a 1-year extension.
- Active User Proposals as of June 31, 2023: 484 (includes 46 rapid access proposals)
    - Industry-involved: 27
    - University-led: 341
    - ORNL Staff-led: 114
    - Other Government Laboratory-led: 14
    - HBCU-led: 2
    - Unique Institutions: 181
    - Average Requested Proposal Time: 33 days
    - Science Categories: Proposal distribution - 48% Materials Science; 17% Engineering; 9% Chemistry; 4% Instrumentation; 6% Polymers; 6% Biological/Life Sciences; 3% Physics; 3% Optics; 2% 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): 74
        - Director: 1 (1.0 FTE - OB)
        - Division Administrative: 1 (1.0 FTE - OB)
        - R&D Staff: 63 (34.64 FTEs)
        - Matrixed R&D Staff: 9 (2.8 FTEs)
        - Technical Professionals: 4 (3.0 FTEs)
        - Technicians: 5 (2.6 FTEs)
        - User Office: 2 (1.8 FTEs)
        - Administrative: 5 (supported at the directorate level – not included in headcount)
        - Operations (ES&H): 2 (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): 44.84 FTEs

- Other funding sources/programs: 10 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, FECM)

- **New Staff Hires:**
  - Steffi Woo – R&D Associate, Scanning Transmission Electron Microscopy (STEM) Group; previously a post-doc at the Laboratoire de Physique des Solides (LPS), Orsay, France
  - Yongtao Liu – R&D Associate, Data NanoAnalytics (DNA) Group; previous CNMS post-doc in the Functional Atomic Force Microscopy (FAFM) Group
  - Sumner Harris – R&D Associate, Data NanoAnalytics (DNA) Group; previous CNMS post-doc in the Functional Hybrid Nanomaterials (FHN) Group
  - Eric Hoglund – Postdoctoral Research Associate, Scanning Transmission Electron Microscopy (STEM) Group (supported 100% by STEM FWP); from University of Virginia
  - Yajie Zhao – Postdoctoral Research Associate in Materials MicroÅnalysis (MMÅ) Group (supported 100% by Fossil Energy and Carbon Management Office) from the University of Tennessee
- **Staff Departures:**
  - Kunlun Hong – Senior R&D Staff, Macromolecular Nanomaterials (Macro) Group; retired.
  - Mark Oxley – R&D Staff, Scanning Transmission Electron Microscopy (STEM) Group; resigned.
- **Honors and Awards:**
  - Rigoberto Advincula – awarded 2023 Netzsch North American Thermal Analysis Society (NATAS) Fellow Award
  - Arpan Biswas – awarded People's Choice Award for Oral Presentation at the 11th Oak Ridge Post-doctoral Association (ORPA) Research Symposium, Oak Ridge, TN, May 18-19, 2023
  - Yongtao Liu - awarded 2023 Microscopy Society of America (MSA) Postdoctoral Scholar Award for paper titled "Machine Learning-Driven Autonomous Microscopy for Materials and Physics Discovery."
  - Eric Hoglund - awarded 2023 Microscopy Society of America (MSA) Postdoctoral Scholar Award for paper titled "The Influence of Local Stoichiometry, Bonding, and Structure on Interface Vibrations."
  - Jonathan Poplawsky – member of research team receiving DOE EERE VTO for "DuAlumin-3D: An Additively Manufactured Dual-Strengthened Aluminum Alloy Designed for Extreme Creep and Fatigue Resistance, developed by ORNL, General Motors and Beehive3D." June 2023.
  - Physical Sciences Directorate Technician Awards (award luncheon held on June 19, 2023):
    - James Burns – Core Values Award for Impact through Outstanding Contributions
    - Dale Hensley – Core Values Award for Service to the Community
    - Leslie Wilson – One ORNL Award
- **Significant Invited Talks:**
  - Rigoberto Advincula, "Colloidal Nanoparticle Assemblies: Templating Electropolymerizations, Brushes, and Viruses," 2023 MRS Spring Meeting, San Francisco, CA, April 9-14, 2023.
  - Rigoberto Advincula, "3D and 4D Printing: High Performance and Stimuli-Responsive Polymer Materials," 2023 MRS Spring Meeting, San Francisco, CA, April 9-14, 2023.

- Rigoberto Advincula, "3D and 4D Printing of High-Performance Composites, Filters, and Membranes," American Filtration Society Annual Meeting (AFS-FILTCON 2023), Louisville, KY, May 1-3, 2023.
- Matthew Boebinger, "Advanced *In situ* Characterization Techniques Using Electron Microscopes to Investigate Nanoscale Transformations in Materials," UTK Deep Learning for Microscopy Image Analysis in Nuclear Materials, Knoxville, TN, June 5, 2023.
- Jan Michael Carrillo, "Beyond Implicit Solvents: Advancing Soft Matter Simulations with Explicit Solvent Molecular Dynamics," Joint VT-ORNL Soft Matter and Biological Physics Symposium, Blacksburg, VA, May 17-18, 2023.
- Marti Checa, "High Speed Mapping of Surface Charge Dynamics via Spiral Scanning Kelvin Probe Force Microscopy," 9th Multifrequency AFM Conference, Madrid, Spain, June 2023.
- Miaofang Chi, "Layer-Number Dependency of Phase Transitions in 2D Layered Materials Revealed by Cryogenic STEM," 2023 MRS Spring Meeting, San Francisco, CA, April 10-14, 2023.
- Miaofang Chi, "Emerging STEM for Solid State Battery Research – Probing Ion Conduction of Single Interfaces," 243rd Electrochemical Society (ECS) Meeting, Boston, MA, May 28-June 2, 2023.
- Neus Domingo, "Physical Chemistry of Ferroelectric Surfaces – Ice, Water, and H_2 Economy," Hurtigruten Ferroelectrics Workshop 2023, Norway, April 24, 2023.
- David Geohegan, "Controlling Laser Interactions for the Precision Synthesis of 2D Crystals Using Real-Time *In Situ* Diagnostics: Janus Monolayers by PLD," CLEO'23, San Jose, CA, May 5-10, 2023.
- Jordan Hachtel, "Taking Low Energy Excitations at Hight Spatial-Resolution to Low Temperatures with Monochromated EELS," 2023 MRS Spring Meeting & Exhibit, San Francisco, CA, April 10-14, 2023.
- Jordan Hachtel, "The Oxide Vibe: Using High Spatial/Spectral Resolution Microscopy to Unveil Nanoscale Vibrations in Oxide Heterostructures and Grain Boundaries," 6th Workshop on Complex Oxides, Spetses, Greece, June 16, 2023.
- Jingsong Huang, "Theoretical Studies of Functional Materials for Photochromic, Thermochromic, and Electrochemical Applications," 2023 International Nature Inspires Creativity Engineers (N.I.C.E.) Rendezvous, Nice, France, June 20-22, 2023. Virtual.
- Jacek Jakowski, "Quantum Chemical Simulations of CO_2 and N_2 Capture in Reline, a Prototypical Deep Eutectic Solvent," Southeastern Theoretical Chemistry Association 2023 (SETCA 2023), Columbia, SC, May 11-13, 2023.
- Ivan Kravchenko, "Solvent-free Development of Patterns Exposed by Focused Ion Beam in ZEP and PMMA Resists," 66th International Conference on Electron, Ion and Photon Beam Technology and Nanofabrication (EIPBN), San Francisco May 31 - June 3, 2023.
- An-Ping Li, "Revealing Magnetic Skyrmions and Spin-Momentum Locked Conductance with Spin-Polarized STM," 8th Conference on Spin Polarized STM and Nanoscale Magnetic Imaging, Ohio State University, Columbus OH, June 8-10, 2023.
- Peter Maksymovych, "The Multiwells: Switching Portraits of the Thiophosphate Family," 2023 MRS Spring Meeting & Exhibit, Virtual, April 25-27, 2023.
- Kinga A. Unocic, "Insight into Materials Degradation in Extreme Environments with *In situ/Operando* Electron Microscopy," UTK Deep Learning for Microscopy Image Analysis in Nuclear Materials, Knoxville, TN, June 5, 2023.

- Rama Vasudevan, "Automated and Autonomous Scanning Probe Microscopy for Understanding and Controlling Dynamics," 2023 TechConnect World Innovation Conference & Expo, June 19-21, 2023.
- Yangyang Wang, "Spatial Correlations of Polymer Dynamics," Joint VT-ORNL Soft Matter and Biological Physics Symposium, Blacksburg, VA, May 17-18, 2023.
- Kai Xiao, "Tuning the Optical Properties of 2D Materials by Nonequilibrium Synthesis and Processing," CLEO '23, San Jose, CA, May 5-10, 2023.
- Yue Yuan, "Biodeuteration of polysaccharides from microorganisms," 2023 Neutron Scattering User Meeting, Oak Ridge National Laboratory, June 6-7, 2023.
- Maxim Ziatdinov, "From Human-Centric to AI-Driven Experimentation Workflows for Materials Characterization," New Mathematics for the Exascale: Applications to Materials Science, Workshop III: Complex Scientific Workflows at Extreme Computational Scales, UCLA, Los Angeles, CA, May 1, 2023.
- Maxim Ziatdinov, "AI-Powered Imaging Experiments with and without Human in the Loop" Artificial Intelligence (AI) Machine Learning (ML) Methods for Neutron Scattering Workshop, College Park, MD, June 21-23, 2023.
- Michael Zachman, Invited Keynote Presentation, "Advanced Electron Microscopy for Energy Storage and Conversion Materials Research," Oak Ridge Postdoctoral Association's 11th Annual Research Symposium, Oak Ridge, TN, May 18, 2023.

3. Postdocs Supported by FWP

- Total number of post-docs in CNMS Division: 24 FTEs (in addition, 3 positions have been filled and post-docs are on-boarding; 7 positions are open)
- Number of post-docs supported by CNMS FWP: 5 FTEs (in addition, 3 positions have been filled and post-docs are on-boarding, 2 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:**

The goal of precision atomic assembly for quantum information is being addressed along the three directions proposed: infrastructure and experiment, artificial intelligence/machine learning, and computation and theory. Our dedicated Infinity low-temperature STM has been installed however requiring a new pulse tube cooling system which has been delivered and warranty repair scheduled. Additional equipment including tip preparation and surface analysis by Low Energy Electron Diffraction have been purchased and will be installed during the repair. A staff member hired for atomic assembly is waiting on visa approval; meanwhile a new search for staff has been opened for this project. Progress on related microscopes continues including the selection of vendors to develop and supply a cryogenic sample system for STEM and to provide helium recycling for our four-probe and millikelvin STMs. Reinforcement learning for synthesis are ongoing along with interviews for a postdoc dedicated to ML for STM. Computationally, scaling tests of the real-space multi-grid (RMG) DFT code have been performed on the Frontier supercomputer at ORNL, including spin-orbit coupling for topological magnetism. In addition, new functionality in the DCA++ code has been implemented to support multi-impurity single-site dynamical mean-field theory (DMFT) calculations in addition to cellular DMFT calculations for problems with multiple atoms in the unit cell. This will enable lower temperature calculations

of complex quantum materials where many orbitals are contributing to the low-energy effective electronic structure.

- **Publications:** None this quarter
- **Invited Presentations:** None this quarter
- **Budget summary:**
  - FTE funded staff/post-docs = 1.33 FTE (no post-docs originally on this project but new position posted in Q1 FY23)
  - (a) Second year of Award - Received $2,000,000 in OPE and $0 in EQU
  - (b) Funds received to date (OPE and EQU) – $5,350,000
  - (c) Funds spent to date (OPE and EQU) - $1,796,779
  - (d) Committed equipment funds - $143,706

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

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

- **Progress:** Ongoing research focuses on the utilization of cryo-STEM techniques to study transition-metal trihalides. In recent years, a significant emphasis has been placed on unraveling the phase transformation behavior of trihalides with respect to temperature and atomic layer numbers. Notable examples of trihalides are $CrCl_3$, $RuCl_3$, and CrI_3. Our investigations have revealed the strong correlation between the phase transitions in these materials and the bonding strength of interlayers. These findings hold great importance for their application in devices such as spintronics and electronics, where they are used as ultrathin flakes consisting of only a few atomic layers. The discovery of layer number-dependent phase transformation behavior opens possibilities for exploiting a wide range of electronic and spintronic properties for practical applications. We are currently preparing a manuscript to report on these findings. Concurrently, in our quest to comprehend the charge-lattice-phonon correlations in charge density wave (CDW) materials, we have recently developed an innovative cryogenic 4D-STEM method. This method allows us to precisely quantify lattice variations in CDW features. For example, we have successfully unraveled the intricate atomic structure of the long-wavelength incommensurate CDW material, $EuAl_4$. $EuAl_4$ has garnered significant attention due to its diverse magnetic phases at low temperatures, including four magnetic phases and two skyrmion phases. However, the origin of these phases remains elusive, particularly because skyrmion phases are typically associated with noncentrosymmetric structures, whereas X-ray analysis revealed $EuAl_4$ to be centrosymmetric. Our method enables the precise quantification of both symmetry and atomic position variations at the picometer scale. We discovered that $EuAl_4$ exhibits localized symmetry breaking within the CDW period while maintaining global centrosymmetry. This finding provides an explanation for the potential presence of the Dzyaloshinskii-Moriya interaction (DMI), which often triggers skyrmion phases. We are currently engaged in further data interpretation and manuscript writing to elaborate on these findings.
- **Publications:**
  - Smith, J., Huang Z., Gao, W., Zhang, G., and Chi M., "Atomic Resolution Cryogenic 4D-STEM Imaging via Robust Distortion Correction," *ACS Nano* **17** (12), 11327-11334 (2023). DOI: 10.1021/acsnano.2c12777.
  - Chao, H., Venkatraman K., Moniri S., Jiang, Y., Tang, X., Dai, S., Gao, W., Miao, J. and Chi, M., "*In Situ* and Emerging Transmission Electron Microscopy for Catalyst Research," *Chemical Reviews* **123** (13), 8347-8394 (2023). DOI: 10.1021/acs.chemrev.2c00880.
  - Kim, N. Y., Cao, S., More, K. L., Lupini, A. R., Miao, J. and Chi, M., "Hollow

Ptychography: Toward Simultaneous 4D Scanning Transmission Electron Microscopy and Electron Energy Loss Spectroscopy," *Small*, Online version, 2208162 (2023). https://doi.org/10.1002/smll.202208162
    - Robinson, A. W., Wells, J., Nicholls, D., Moshtaghpour, A., Chi, M., Kirkland, A. I. & Browning, N. D., "Towards Real-time STEM Simulations through Targeted Subsampling Strategies," *Journal of Microscopy* **290**, 53-66 (2023). https://doi.org/10.1111/jmi.13177.
- **Invited Presentations:**
    - "Emerging Electron Microscopy Techniques for Studying Interfaces in Energy Materials," 243rd ECS Meeting with the 18th International Symposium on Solid Oxide Fuel Cells (SOFC-XVIII), May 26-June 2, 2023, Boston , MA.
    - "Layer-number Dependency of Phase Transitions in 2D Layered Materials Revealed by Cryogenic STEM," 2023 MRS Spring Meeting, April 10-17 (virtual), San Francisco, CA.
- **Budget Summary:**
    - FTE funded staff/post-docs = 1.16/3.08 (since awarded in FY19)
    - First year of Award - FY19 – $500,000 received in FY23 Q3
    - Funds received to date (OPE and EQU) – $ 2,499,910
    - Funds spent to date (OPE and EQU) - $1,114,874

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 post-doc hired for this project, Elizaveta Tiukalova, has been assembling electron energy loss (EELS) data from elements in different valence states and coordinating with collaborators at LBNL. She has acquired off-axis EELS, using a direct electron detector, and 4D-STEM data on the samples that LBNL supplied.
    - Budget Summary:
        - FTE funded staff/post-docs - 0.32/0.67 FTE
        - First year of Award – FY20 – no new funds received in FY23 Q3
        - Funds received to date (OPE and EQU) – $391,000 OPE; $0 EQU
        - Funds spent to date (OPE and EQU) - $246,429
- FWP ERKCZ60 "A Collaborative Machine Learning Platform for Scientific Discovery" led by LBNL. Having successfully designed and implemented a Bayesian-optimized spectral recommender system for microscopes, our team's attention has now pivoted towards creating multifidelity active learning routines. These routines provide an alternative solution for circumstances where a physical model's complexity makes it impractical or infeasible to directly incorporate it into the active learning surrogate model (e.g., its evaluation at each step is too costly or its programmatic implementation lacks full differentiability). Our approach involves running theoretical simulations across the required parameter space beforehand, then utilizing these simulations to guide our automated experiments through an appropriate multitask kernel function. Currently, we are rigorously testing these newly developed multi-fidelity models against a synthetic dataset with a well-defined ground truth. This is an essential precursor to their application in actual experimental scenarios. In addition, we have submitted two papers based on the work in Q2 which are currently under review. We have also extensively contributed to

preparing a renewal proposal that has been submitted by the LBNL PI and we are currently waiting for the decision.
  - Budget Summary:
    - FTE funded staff/post-docs - 0.35/0.86 FTE
    - First year of Award – FY20 – no new funds received in FY23 Q3
    - Funds received to date (OPE and EQU) – $495,000 OPE; $0 EQU
    - Funds spent to date (OPE and EQU) - $386,253
- FWP ERKCZ61 "A Digital Twin for Spatiotemporally Resolved Experiments" led by ANL. We are finalizing the development of a ML algorithm-approach for generating structure factor for scattering based on real potential parameters vs. using latent space representations. A renewal proposal was submitted by ANL.
  - Budget Summary:
    - FTE funded staff/post-docs - 0.26/0.40 FTE
    - First year of Award – FY20 – no new funds received in FY23 Q3
    - Funds received to date (OPE and EQU) – $270,000 OPE; $0 EQU
    - Funds spent to date (OPE and EQU) - $185,170

7. Operations Equipment (OPE or EQU) Investments:

Instrument or Capability	Description	Cost ($K)	Expected Delivery
SQUID Magnetometer	Replacement	$650 K	Installed; users are accessing
Gatan ELSA double-tilt cryo-holder for Nion MAC-STEM	Side entry cryo-holder for new cryo-stage on MAC-STEM	$75 K	Delivered and being used on MAC-STEM
Unisoku vector-field mK STM	Ordered as part of original QIS infrastructure project (PI Chris Rouleau)	$1,800 K	Installed; performance assessment underway; user access expected summer FY23
Nion IRIS electron energy loss spectrometer (EELS)	Ultra-high energy resolution EELS for Nion UltraSTEM 100	$620 K	Delivery expected fall FY23 - will be retrofit with Dectris direct electron detector and delivered at the same time
Dectris Direct Electron Detector for Nion UltraSTEM 100	Ultrafast detector/camera for Nion UltraSTEM 100	$325 K	Delivery expected fall FY23 - will be retrofit with Nion IRIS EELS and delivered at the same time
Heating/cleaning unit for side-entry holders for JEOL NeoARM STEM	Low-T heating unit to bake/clean holders and samples before insertion in STEM	$60 K	Delivered and installed
JEOL Octa Segmented Annular All-field detector	9-sector segmented detector for JEOL NeoARM STEM	$230 K	Delivery expected by end of CY23
Thermo Fisher Helios Ga+ focused ion beam (FIB) instrument	Support specimen preparation for atom probe and TEM/STEM	$1,200 K	Delivery expected September 2023
Four additional nodes for CNMS cloud infrastructure	Additional nodes to complete CNMS cloud infrastructure	$125 K	Delivery expected September 2023
AFM to Nanoscope 6	Replacement AFM for rapidly evaluating 2D samples and thin films	$100 K	Delivery expected September 2023

WiTec (Oxford) Alpha 300 Apyron Confocal Raman Microscope	Will be integrated with a 2D materials stamping system	$354 K	Delivery expected before end of CY23
Scanning Nv Microscope	New method/instrument to study quantum materials and microelectronics	$950 K	Delivery expected Spring FY24
Nanomanipulator/Biasing holder for JEOL NeoARM	Specialized specimen holder for the NeoARM to enable in situ AFM and biasing	$135 K	Delivery expected in Spring FY24

8. Covid Impact:

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

9. Safety Updates:

- None to report

10. Concerns and Challenges

- No new challenges to report

11. Other News:

- Jihua Chen – elected to the Executive Committee of the American Physical Society (APS0 Data Science Topical Group, 2023-2026.
- Liam Collins – named CNMS Postdoctoral Coordinator, June 1, 2023.
- Liam Collins – Symposium Co-Chair, SPMConnect at TechConnect World Innovation Conference & Exposition, Washington DC, June 19-21, 2023.
- Liam Collins – Panelist "SPM User Facilities Leadership Panel," SPMConnect at TechConnect World Innovation Conference & Exposition, Washington DC, June 19-21, 2023.
- Rajeev Kumar – Reviewer, Laureate Award 2023 on behalf of the Irish Research Council
- Nick Lavrik – "Rational Design and Nanofabrication of Deterministically Patterned SERS Active Structures," Augusta University, Augusta, GA, April 28, 2023.
- Karren More – External Advisory Board, NSF Southeastern Nanotechnology Infrastructure Corridor (SENIC), North Carolina A&T State University, Greensboro, NC, May 8, 2023.
- Jonathan Poplawsky - Invited Webinar for CAMECA Inc.: "Revealing Nanoscale Atom Distributions in Zeolite Catalysts with Atom Probe Tomography," June 2023. https://www.atomprobe.com/pressreleases/news/2023/june/jon-poplawsky-webinar-june-2023
- Rama Vasudevan – Review Panel, DOE Advanced Scientific Computing Research (ASCR) DRS, May 5, 2023.
- Hanyu Wang – Guest Editor for journal *Polymers* Special Issue "Recent Developments in Polymer Composites for Photoelectrocatalytic Applications."
- Zili Wu – Symposium Co-Organizer "Advanced Mechanistic Understanding of Catalysis through In Situ / Operando X-ray Absorption Spectroscopy, Neutron Spectroscopy, and NMR Spectroscopy," 28th North American Catalysis Society Meeting, Providence, RI, June 17-23, 2023.
- Yue Yuan – "Biobased Macromolecules and Bioinspired Nanomaterials," Seminar Series, School of Chemical and Biomolecular Engineering, Georgia Tech, Atlanta, GA, April 21, 2023.

- Eva Zarkadoula – "ORNL's Culture and Core Values," presentation for New Employee Orientation.
- Eva Zarkadoula – will serve another 2-year term as Advisor for the journal of the Minerals, Metals, and Materials Society (TMS), the *Journal of Metals (JOM)*.

12. Science Supported by FWP

Three highlights will be submitted in FY23 Q3:

1. Zening Liu, Jong Keum, Tianyu Li, Jihua Chen, Kunlun Hong, Yangyang Wang, Bobby Sumpter, Rigoberto Advincula, and Rajeev Kumar,* "Anti-polyelectrolyte and Polyelectrolyte Effects on Conformations of Polyzwitterionic Chains in Dilute Aqueous Solutions," *PNAS Nexus*, (2023, in press). https://doi.org/10.1093/pnasnexus/pgad204

   Sole CNMS Publication: Understanding and controlling conformations of polyzwitterions (PZs) in aqueous solutions by adding salt are of paramount interest in areas such as antimicrobial materials, antifouling coatings, drug-delivery, membranes, and polymer electrolytes. We show that the polysulfobetaines, a special class of PZs, remain hydrated in salt-free conditions, contrary to an expectation of globular conformation due to attractive dipole–dipole interactions. Despite having a net positive charge in the solutions, the polysulfobetaine do not exhibit typical polyelectrolyte behavior like two diffusive modes in dynamic light scattering and a peak in small-angle X-ray scattering. Added salt affect the net charge and electrostatic interactions to change chain conformations in a nonmonotonic manner so that both anti-polyelectrolyte and polyelectrolyte effects are observed with an increase in the salt concentration in the solutions of the same PZs. Overall, we show that controlling the salt concentration is an effective strategy to tune net charge and conformations of the PZs.

2. Kyle Kelley,* Anna Moroskova, Eugene Eliseev, Yongtao Liu, Shelby Fields, Samantha Jaszewski, Takanori Mimura, Jon Ihlefeld, and Sergei Kalinin, "Ferroelectricity in Hafnia Controlled via Surface Electrochemical State," *Nature Materials* (2023, in press). https://doi.org/10.1038/s41563-023-01619-9 (not activated yet).

   CNMS-user co-led collaborative publication: Ferroelectricity in binary oxides including hafnia and zirconia have riveted the attention of the scientific community due to highly unconventional physical mechanisms and the potential for integration of these materials into semiconductor workflows. Here we explore the evolution of ferroelectric behaviors in hafnia using the environmental Scanning Probe Microscopy. We demonstrate that the environment can trigger transitions between ferroelectric and antiferroelectric phases in this material. This in turn establishes that the primary state of hafnia-based devices is the antiferroionic state, an unusual state of materials defined as the interplay between bulk antiferroelectric behavior coupled to surface/interface electrochemistry. While here, we explore the surface behaviors using phenomenological Landau-type modeling, which considers competing polar and structural anti-polar distortive long-range orders in $HfZrO_2$ at the mesoscopic level while considering the possible role of doping and oxygen vacancies, finding excellent agreement with experimental observations. We propose a new explanation for the observed ferroelectric like responses in hafnia that opens new pathways for predictive modeling and device engineering of these devices. Given the importance of these materials for the semiconductor industry and the long-standing controversy regarding the origins of observed functionalities, we believe this manuscript will be of interest to an extremely broad scientific community.

3. Matthew Boebinger,* Courtney Brea, Li-Ping Ding, Sudhajit Mishra, Olugbenga Olunloyo, Yiling Yu, Kai Xiao, Andrew Lupini, Feng Ding, Guoxiang Hu, Panchepakesan Ganesh, Stephen Jesse, and Raymond Unocic,* "The Atomic Drill Bit: Precision Controlled Atomic Fabrication of 2D Materials," *Advanced Materials* **35** (14), 2210116 (2023). DOI: 10.1002/adma.202210116.

   CNMS-led publication: The ability to deterministically fabricate nanoscale architectures with atomic precision is the central goal of nanotechnology, whereby highly localized changes in the atomic structure can be exploited to control device properties at their fundamental physical limit. Here, we report on an automated, feedback-controlled atomic fabrication method and demonstrate formation of 1D-2D heterostructures in MoS_2 through selective transformations along specific crystallographic orientations. We use the atomic-scale probe of an aberration corrected scanning transmission electron microscope (STEM) and control the shape and symmetry of

the scan pathway relative to the sample orientation. The focused and shaped electron beam is used to reliably create Mo_6S_6 nanowire (MoS-NW) terminated metallic-semiconductor 1D-2D edge structures within a pristine MoS_2 monolayer with atomic precision. From these results, it is found that a triangular beam path aligned along the (zig-zag sulfur terminated) ZZS direction forms stable MoS-NW edge structures with the highest degree of fidelity without resulting in disordering of the surrounding MoS_2 monolayer. Density functional theory (DFT) calculations and ab initio molecular dynamic simulations (AIMD) are used to calculate the energetic barriers for the most stable atomic edge structures and atomic transformation pathways. These discoveries provide an automated method to improve understanding of atomic-scale transformations while opening a pathway towards more precise atomic-scale engineering of materials.

- **Publications:** All FY23 Q1, Q2, and Q3 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 Publications FY23_Q1_Q2_Q3"). In Q1 (updated), CNMS had 64 publications with 36 publications in journals with an IF > 7 (56%); in Q2 (updated), CNMS had 89 publications with 42 publications in journals with IF > 7 (47%); in Q3, CNMS had 71 publications with 44 publications in journals with IF > 7 (62%).
- **Invention disclosures, patents, other products:**
  - None to report

13. FWP Budget details

- Budget information included in Excel spreadsheet (separate document " FY23 ORNL CNMS Budget_Q3").