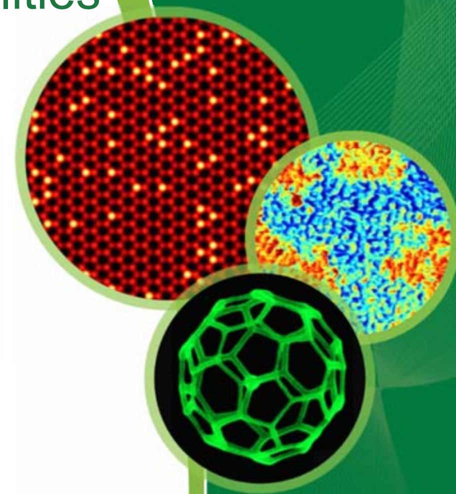
Research and user capabilities at ORNL’s Center for Nanophase Materials Sciences



Hans Christen

CNMS Director

July 18, 2017

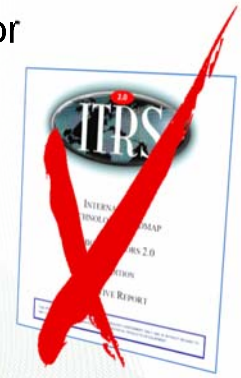
ORNL is managed by UT-Battelle
for the US Department of Energy

Research and user capabilities at ORNL’s Center for Nanophase Materials Sciences

- Why nanoscience?
- Why a user facility?
- What is CNMS, and how can we help?

Materials for neuromorphic computing

- Things known about the brain:
  - It's soft
  - It's three-dimensional
  - It's grown (not built)
  - It changes with time (learning, forgetting)
  - Electrical and chemical signals act at various length and time scales
- This translates to requirements for materials for neuromorphic computing:
  - Non-linear response
  - Time-dependent response
  - Responsive to chemical and electrical stimuli
- Unfortunately, these requirements do not constitute a road-map



Understanding the required materials is fundamentally a nanoscience issue

- The most fundamental requirement for a material for neuromorphic computing is a coupling between electronic and ionic/molecular effects
- These interactions show a pronounced dependence on spatial length scales (ions/molecules and electrons move at different length and time scales)
- Heterogeneities ("defects") are fundamental building blocks
- Structures have to be assembled in 3D at the nanoscale

A user facility is a powerful resource for this type of research

- Nanoscience is an integral part of very broad areas of science (such as the development of materials for neuromorphic computing):
  - A User Facility can add the missing pieces to a research team
  - Users are often "experts elsewhere"
- "User Facility" = "Equipment" + "Staff":
  - Staff maintains instrumentation, controls quality, trains users
  - The staff's scientific vision and expertise enable the adaptation of capabilities to specific applications

DOE Basic Energy Sciences User Facilities: Approximately 15,000 Users (FY2016)

Light Sources, Neutron Sources, and Nanoscale Science Research Centers (NSRCs); located at National Laboratories

- Resources available at no cost to researchers who intend to publish results
- External peer review
- Coordinated access to co-located facilities
- Strong collaborative environment with facility scientists

Five Nanoscale Science Research Centers (NSRCs):
Approx. 3,000 Users (FY2016)
(Three Electron Beam Microcharacterization Centers (EBMCs) were merged into the NSRCs in 2015)

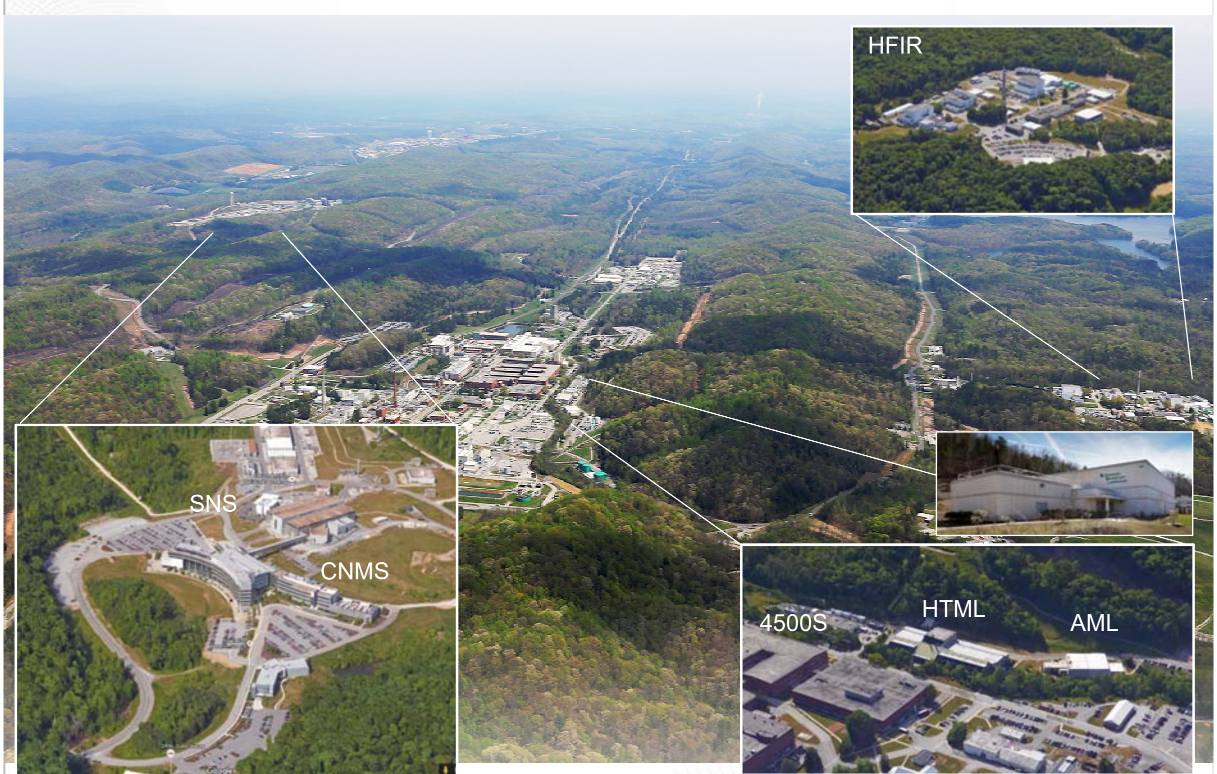
Five NSRCs provide specific focus areas and ties to co-located facilities

Co-Located Facilities

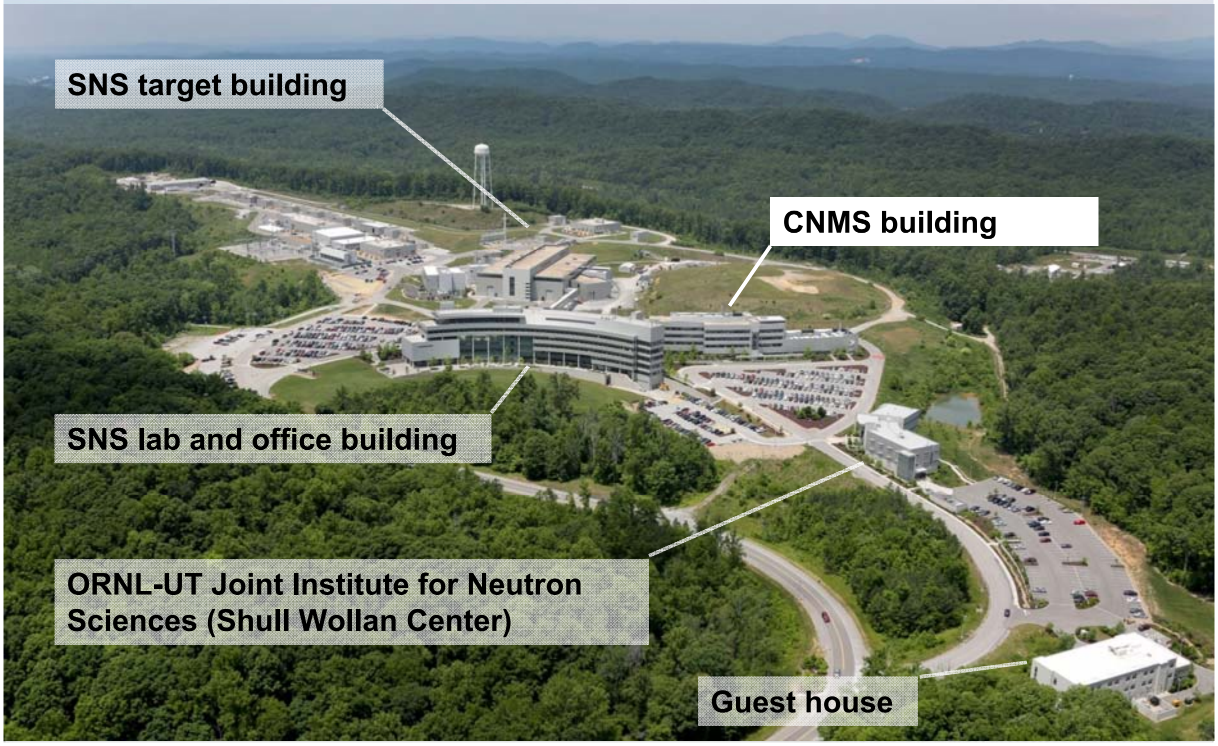
Expertise and Capabilities

- Each NSRC emphasizes specific areas of synthesis, fabrication, imaging/characterization, and theory/modeling/simulation ("*make, characterize, and understand*")
- Users may request multiple capabilities at an NSRC, or perform work at more than one NSRC
- See NSRC Portal: nsrcportal.sandia.gov

The CNMS at ORNL

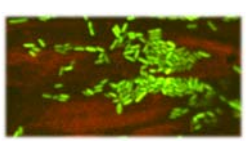


The CNMS at ORNL



CNMS: laboratories, a gateway to neutrons and computing, direct interactions with staff

- CNMS building:
  - Total 80,000 sq. ft., includes 32 laboratory modules and a 10,000 sq. ft. cleanroom (Class 1000; Class 100 in e-beam lithography suite)
- Ultra-quiet space for electron and scanning probe microscopy
- Close ties to ORNL's two neutron facilities (Spallation Neutron Source [SNS] and High Flux Isotope Reactor [HFIR]) and to the Oak Ridge Leadership Computing Facility
- Bio-affiliate laboratories for users with biological sample requirements



OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

CNMS is a hub for cutting-edge research

FY2016 numbers:

– 601 unique users (575 on-site)
  • Average stay at CNMS: ~13 days
  • 50% from US academic institutions
  • 38% faculty; 24% postdocs; 38% students

– 435 refereed regular papers published that acknowledge CNMS
  • 51% in journals with IF>5
  • 36% in journals with IF>7
  • 70% co-authored by users

93 US institutions from 36 states and territories
44 foreign institutions from 19 foreign countries

CNMS journal covers (past 18 months)

User research has a broad impact

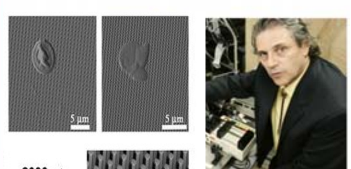
Characterization of nanofermented quantum dot materials

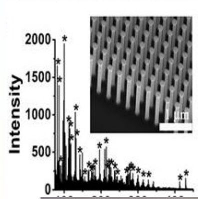
Graduate students start company to commercialize ORNL nanoferrmetation technology

CNMS user projects to characterize and process the nanomaterials.

Single cell mass spec

LDI-MS analysis of single cells (~30 fL volume) on nanofabricated post arrays.





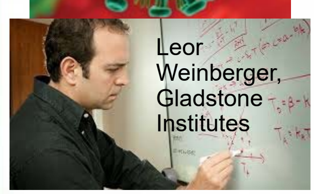
Akos Vertes, George Washington University

The researchers performed nanofabrication and device characterization at CNMS. The work led to the commercial availability of the REDIchip.

B. Walker et al. *Angew. Chem. Int. Ed.* (2013)

Understanding proviral latency in HIV

Understanding how stochastic fluctuations in small molecular populations lead to proviral latency in HIV, the primary clinical problem in AIDS treatment

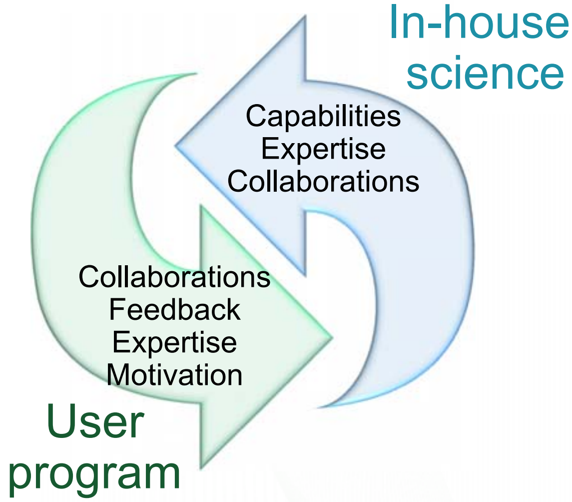


Work at CNMS focused on understanding the fluctuations using time-lapse noise spectroscopy techniques developed at the CNMS.

R. Dar *et al.*, *PNAS* (2012)

In-house science and user program benefit from each other

- Each staff member has the dual responsibility to perform in-house research and to support users
- In-house research has the goal of advancing nanoscience and creating the tools needed by future users



CNMS in-house research focuses on key challenges in nanoscience:

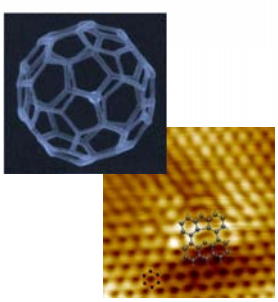
Understanding and Controlling Formation

How do we place individual atoms where we want them to be

How do we create or eliminate individual defects

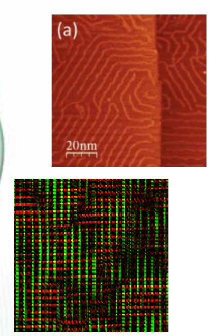
How do we control and direct self-assembly

How do we reproducibly and scalably produce complex and hierarchical matter



How do defects and nanostructure influence energy transport and energy conversion (electrons, photons, excitons, phonons)?

How can we understand and direct mass transport (ionic motion, deformations, droplets)



Understanding and Controlling Function

CNMS in-house research focuses on key challenges in nanoscience:

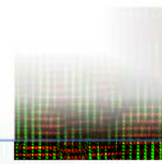
Understanding and Controlling Formation

How do we place individual atoms where we want them to be

How do we control and direct self-assembly

In addressing these challenges, CNMS develops capabilities that then become available to the user community

mass transport (ionic motion, deformations, droplets)



Understanding and Controlling Function

Center for Nanophase Materials Sciences

A DOE User Facility for Creating, Characterizing, and Understanding Nanomaterials

OAK RIDGE National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES

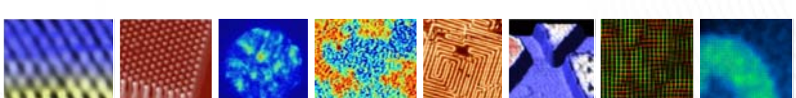
Providing access to staff expertise and equipment at no cost to users who intend to publish the results.

Access to CNMS:

- Two proposal calls per year; proposals for short-term projects are accepted continuously
- Simple 2-page proposal
- Joint proposals with neutron sources (SNS, HFIR)
- Located at Oak Ridge National Laboratory, near Knoxville, TN

Research areas:

- **Synthesis** – Soft matter (precision synthesis, selective deuteration), 2D materials, hybrid structures, epitaxial oxides
- **Nanofabrication** – Direct-write (3D) fabrication, e-beam lithography, multiscale fluidics, 10,000 sq. ft. cleanroom
- **Advanced Microscopy** – AFM, STM, aberration-corrected and *in situ* TEM/STEM, He-ion microscopy, atom-probe tomography
- **Chemical Imaging** – Multiple approaches based on mass spectrometry or optical spectroscopies
- **Functional Characterization** – Laser spectroscopy, transport, magnetism, electromechanical phenomena
- **Theory/Modeling, Data Analytics** – Including gateway to leadership-class, high-performance computing

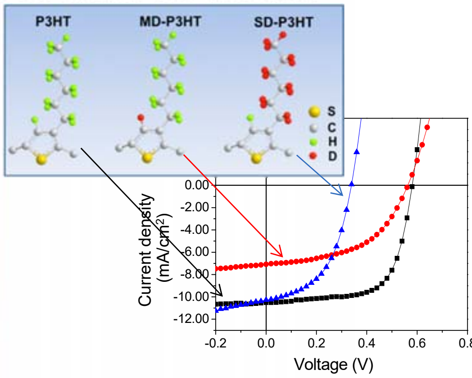


See cnms.ornl.gov

Atom-precise synthesis: soft matter

Selective deuteration introduces a surprising way to modify optoelectronic and structural properties

Selective deuterations on backbone or side-chain of P3HT in P3HT/PCMB photovoltaics



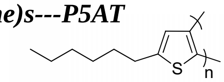
SANS and NR: miscibility, aggregation, phase separation, vertical profiles

Quantum calculations: electron-phonon interactions; led to computational capability for users

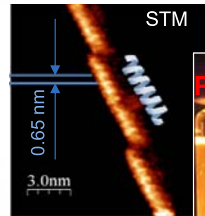
M. Shao *et al.*, *Nat. Commun.* (2014)

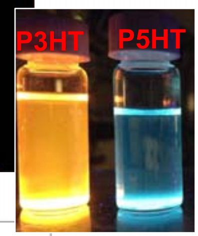
Designing molecules to remove π-π interactions that drive aggregation

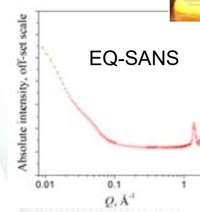
Poly(5-alkyl-2,3-thiophene)s---P5AT



computational simulation



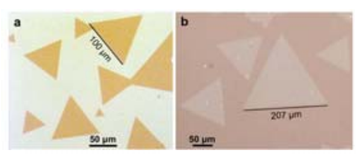




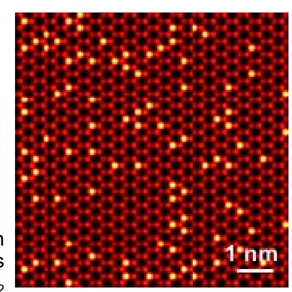
H.H. Zhang *et al.*, *Macromolecules* (2016)

Synthesis of 2-dimensional materials

Isoelectronic doping to modulate carrier type in monolayer $Mo_{1-x}W_xSe_2$ from n- to p-type



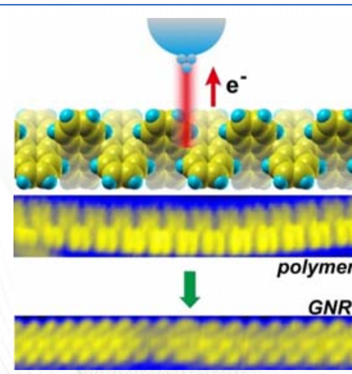
Optical micrographs of $MoSe_2$ on SiO_2/Si and fused quartz



Processed scanning transmission electron micrograph showing locations of W within $MoSe_2$

X. Li *et al.*, *Adv. Mater.* (2016)

Synthesis of graphene nanoribbons from polymer precursors



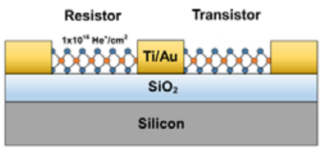
Catalyst-free, bottom-up synthesis of graphene nanoribbons controlled by a STM tip by hole-injection-assisted cyclodehydrogenation of polyanthrylene chains

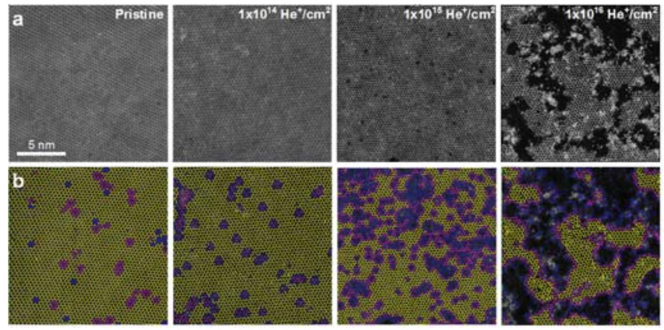
C. Ma *et al.*, *Nature Commun.* (2017)

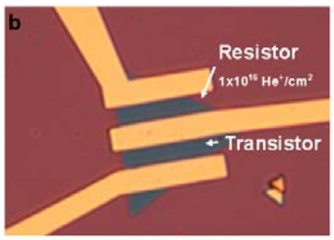
Example: Ultrathin devices based on WSe_2

- Focused He ion beam irradiation of WSe_2 crystals locally modifies the conducting mechanism (percolating network of edge-states, nearest-neighbor hopping conduction)

- Complete inverter circuit can be written entirely into a single flake of WSe_2



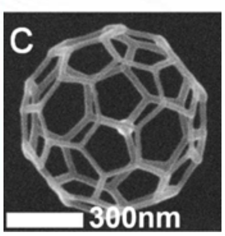




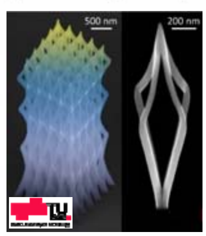
M.G. Stanford *et al.*, *Adv. Funct. Mater. (accepted)*

3D direct-write nanofabrication using focused electrons or ions

E-beam induced deposition (EBID)

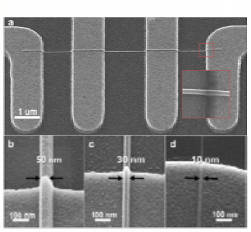


J.D. Fowlkes *et al.*, *ACS Nano* (2016)



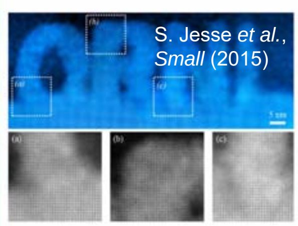
R. Winkler *et al.*, *ACS Appl. Mat. Interf.* (2016)

Ion-beam induced deposition (IBID)



IBID benefits from smaller minimum probe diameter and beam penetration

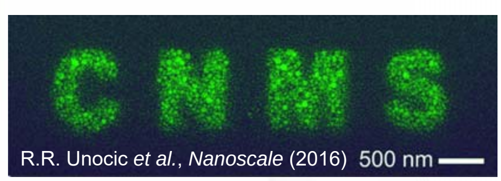
Materials modification and deposition using the Scanning Transmission Electron Microscope



S. Jesse *et al.*, *Small* (2015)

Selective crystallization of $SrTiO_3$

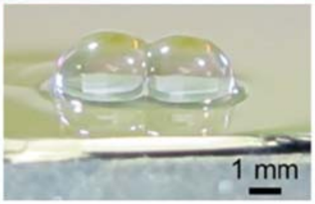
S.V. Kalinin *et al.*, *Nature* (2016)

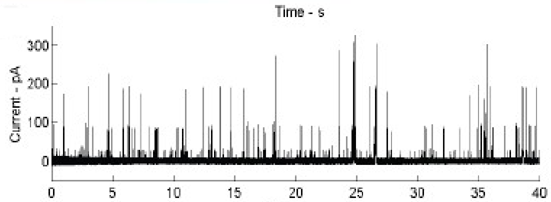


R.R. Unocic *et al.*, *Nanoscale* (2016)

Pd nanocrystals formed from a H_2PdCl_4 aqueous solution in a liquid cell

Nanostructured surfaces and 3D structures



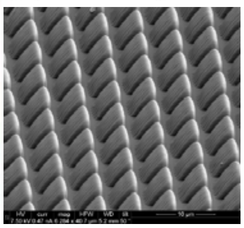


An air-stable droplet interface bilayer can be formed between non-coalescing water droplets on an oil-infused nanostructured surface.
When phospholipids are included in the droplets, single-channel gating events were detected

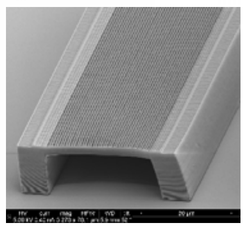
J.B. Boreyko *et al., Proc. Natl. Acad. Sci. USA* (2014).

See Pat Collier, Wednesday, 2:05p

Direct Laser Write based on 2-photon polymerization (liquid, solid precursors)



Asymmetric wettability

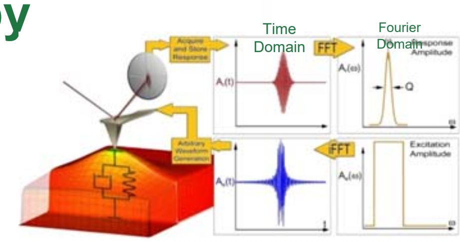


Fluidic structures

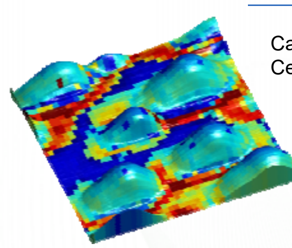
Nanoscribe Photonics Professional GT

Development of band-excitation and G-mode scanning probe microscopy

- Previous techniques used single frequency to excite tip
- Excitation with a band of frequency avoids errors and renders the technique quantitative (spectroscopic)
- Further development lead to Electrochemical Strain Microscopy: minute changes due to chemical modifications are tracked as reversible topography changes
- Breakthroughs in nanoscale electrochemistry studies
- G-mode (general mode): full data capture of tip-surface interactions without operator bias, followed by big data analytics enabled by high speed computing

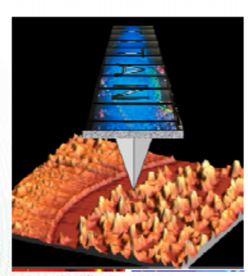


Jesse, Kalinin, *Nanotechnol.* (2007)



Catalyst Particles (Pt) on Fuel Cell Electrolyte Surface (YSZ)

A. Kumar *et al, Nature Chem*. (2011).

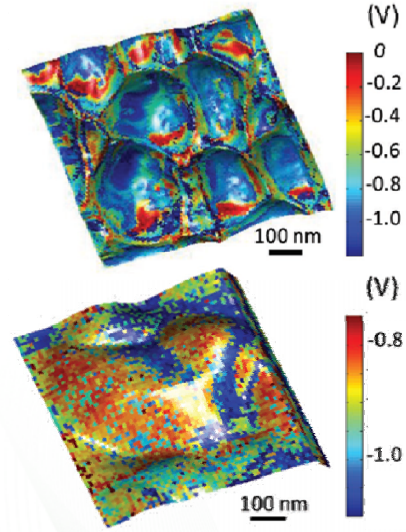


Stiffness and electrostatic response of a mix of polystyrene and polycaprolactone extracted in a single experiment

A. Belianinov *et al, Nature Commun*. (2015).

Example: Extracting local information for ionic mobility

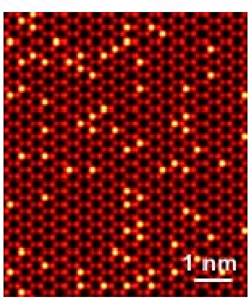
- Ionic mobility determines the functionality of hybrid organic-inorganic perovskites ($CH_3NH_3PbI_3$):
  - Suppression of ion migration leads to stable solar cell performance
  - Unsuppressed ion migration can be used to develop electrically and optically tunable memristors and synaptic devices
- A novel band-excitation Kelvin probe force microscopy method allows to decouple topography and surface potentials
- Doping with mobile Cl^- ions enhances mobility, doping with heavy PCBM reduces mobility



Surface charge overlaid on topographic image of undoped (top) and PCBM-infiltrated (bottom) perovskite film

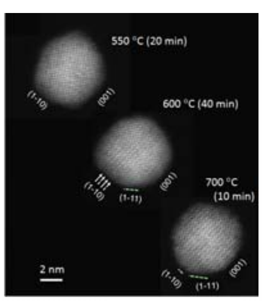
B. Yang *et al, Adv. Funct. Mater.* (2017)

CNMS emphasizes aberration-corrected Scanning Transmission Electron Microscopy (AC-STEM) and Electron Energy Loss Spectroscopy (EELS)



Identifying individual dopant atoms $Mo_{1-x}W_xSe_2$

X. Li *et al.*, *Adv. Mater.* (2016)

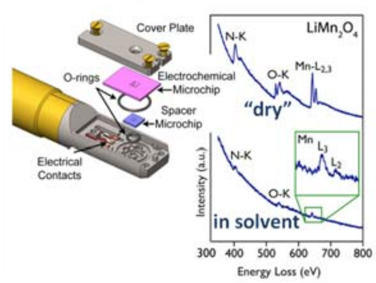


Tracking a single Pt_3Co at high temperature

M. Chi *et al.*, *Nature Commun.* (2015)

Local determination of magnetic properties using controlled aberrations

Rusz *et al.*, PRL (2014)



Quantitative EELS measurements in liquids

R.R. Unocic *et. al.*, *ChemComm* (2015)

- Nion UltraSTEM Cs-corrected STEM (60-100kV)
- FEI Titan S Cs-corrected STEM/TEM (60-300kV)
- Access to Nion HERMES Monochromated AC-STEM
- Access to Hitachi HF3300 TEM/STEM

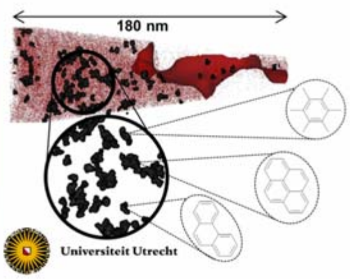
With ~1Å probe and <10meV energy resolution, the MAC-STEM becomes the nanoscale/real-space counterpart to neutron scattering (e.g., phonons)

Atom Probe Tomography and Chemical Imaging

Atom Probe Tomography

Laser-LEAP (local electrode atom probe):
complete 3D reconstruction of atomic positions (within $1 nm^3$);

Applied to non-metallic samples.
Sensitive to any element.

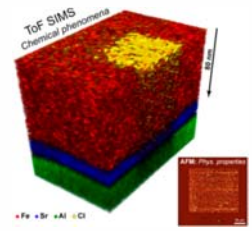


Example: Coke formation in zeolite catalyst

J.E. Schmidt, *et. al.*, *Angew. Chem. Int. Ed.* (2016)

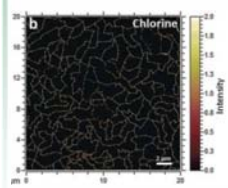
Access to AFM/ToF-SIMS

Developing methodologies to combine chemical imaging and functional mapping



Chemical effects of ferroelectric switching

A.V. Ievlev *et. al.*, *ACS Appl. Mater. Interf.* (2017)



Cl segregation in $CH_3NH_3PbI_3$

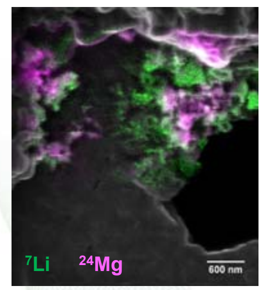
B. Yang *et al*, *JACS* (2016)

Secondary Ion Mass Spectrometry (SIMS) – Helium Ion Microscopy (HIM)

Zeiss Orion NanoFab:

- Outperforms SEM for imaging (especially for insulating samples)
- Highest-resolution ion milling tool

Adding SIMS to nm-scale ion beam imaging:



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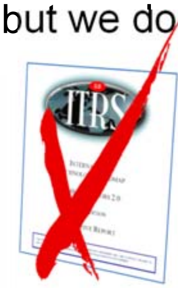
Materials for neuromorphic computing

- We know the general goal, but we don't have a road map



- Materials and structures/devices cannot be independently developed, because of the fundamental importance of
  - interplay between ionic and electronic effects
  - Mechanisms acting at dissimilar length scales that
- A user facility (in the sense of an NSRC) can provide an ideal setting for this type of multidisciplinary research

OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

Center for Nanophase Materials Sciences

A DOE User Facility for Creating, Characterizing, and Understanding Nanomaterials

OAK RIDGE National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES

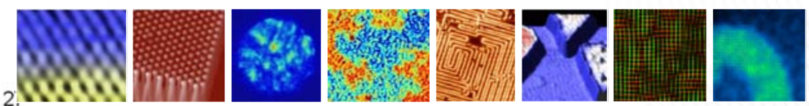
Providing access to staff expertise and equipment at no cost to users who intend to publish the results.

Access to CNMS:

- Two proposal calls per year; proposals for short-term projects are accepted continuously
- Simple 2-page proposal
- Joint proposals with neutron sources (SNS, HFIR)
- Located at Oak Ridge National Laboratory, near Knoxville, TN

Research areas:

- **Synthesis** – Soft matter (precision synthesis, selective deuteration), 2D materials, hybrid structures, epitaxial oxides
- **Nanofabrication** – Direct-write (3D) fabrication, e-beam lithography, multiscale fluidics, 10,000 sq. ft. cleanroom
- **Advanced Microscopy** – AFM, STM, aberration-corrected and *in situ* TEM/STEM, He-ion microscopy, atom-probe tomography
- **Chemical Imaging** – Multiple approaches based on mass spectrometry or optical spectroscopies
- **Functional Characterization** – Laser spectroscopy, transport, magnetism, electromechanical phenomena
- **Theory/Modeling, Data Analytics** – Including gateway to leadership-class, high-performance computing



See cnms.ornl.gov

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