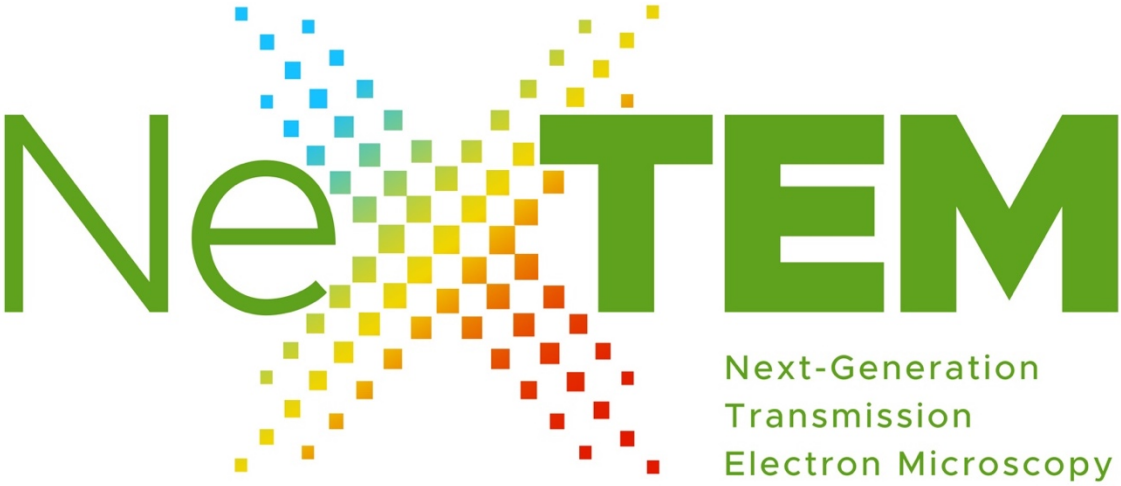


Beyond Current Limits of Resolution, Environment, and Data Analysis

Pre-Meeting Congress
Microscopy and Microanalysis 2019

Supported by Aberration-Corrected Microscopy FIG

August 4, 2019
7:30 am – 6:00 pm

Oregon Convention Center
Rooms F149-150

Welcome

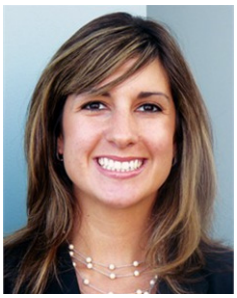
It is our pleasure to welcome you to the second annual Next-Generation Transmission Electron Microscopy (NexTEM) meeting, held as a Pre-Meeting Congress for Microscopy and Microanalysis 2019. The microscopy field continues to evolve at a rapid pace, enabling transformative discoveries across the scientific world. This year we focus on the advanced detectors, *in situ* capabilities, and unique data science tools being developed to address longstanding questions in materials science, chemistry, and physics.

NexTEM 2019 welcomes experts from across all domains of electron microscopy. We showcase work spanning high-speed detectors, magnetic field-free imaging, machine learning, and ultra-high-resolution spectroscopy. Our goal is to connect microscopists, instrument manufacturers, and scientists of all backgrounds to facilitate cross-disciplinary collaborations and identify the developments needed to for breakthroughs in important research areas. The workshop is again organized to allow for both the exchange of research and the building of bridges between researchers. We are particularly excited to host many students and early career scientists, whose contributions in the coming years will shape the trajectory of the field.

As before, we hope that NexTEM will help frame a vision for the more meaningful, efficient, and dynamic microscopy of tomorrow. We're glad that you can join us!

Warm regards,

Steven R. Spurgeon
Staff Scientist
Energy and Environment Directorate
Pacific Northwest National Laboratory



Mitra L. Taheri
Professor
Department of Materials Science and Engineering
Johns Hopkins University

Demie Kepaptsoglou
Senior Lecturer
SuperSTEM Laboratory and University of York

Agenda

7:30 – 8:30 a.m.	**REGISTRATION, COFFEE, AND BREAKFAST**
8:30 – 8:45 a.m.	**Opening Remarks** Steven Spurgeon | Pacific Northwest National Laboratory Mitra Taheri | Johns Hopkins University Demie Kepaptsoglou | SuperSTEM Laboratory
8:45 – 10:30 a.m.	**Session 1: Advanced Detector Technologies for New Imaging Modalities**
8:45 – 9:15 a.m.	**Introduction to Direct Electron Detector Technologies and Applications** David Muller | Cornell University
9:15 – 9:45 a.m.	**The Need for Speed: Opportunities in Materials Characterization Created by Fast Detectors and High Speed Electron Beam Control** Paul Voyles | University of Wisconsin – Madison
9:45 – 10:15 a.m.	**Magnetic-field-free Atomic Resolution STEM** Naoya Shibata | University of Tokyo
10:15 – 10:30 a.m.	**Open Discussion** All Attendees
10:30 – 11:00 a.m.	**Morning Break: Coffee and Refreshments** All Attendees
11:00 – 12:15 p.m.	**Session 2: Frontiers of *In Situ* Imaging and Analysis**
11:00 – 11:30 a.m.	**Tentative: Electron Microscopy Advances in Catalysis** Stig Helveg | Haldor Topsoe
11:30 – 12:00 p.m.	**In-Situ S/TEM and their Applications for Energy Materials: The Challenge and Opportunities** Chongmin Wang | Pacific Northwest National Laboratory
12:00 – 12:15 p.m.	**Open Discussion** All Attendees
12:15 – 1:15 p.m.	**Lunch Break** All Attendees
1:15 – 2:30 p.m.	**Session 3: High-Resolution Electron Spectroscopies**
1:15 – 1:45 p.m.	**Vibrational Spectroscopy in STEM-EELS at High Spatial Resolution** Quentin Ramasse | SuperSTEM Laboratory

1:45 – 2:15 p.m.	**Optical Spectroscopy with an Electron Microscope and a Light Collector / Injector** Luiz Tizei | Université Paris Sud
2:15 – 2:30 p.m.	**Open Discussion** All Attendees
2:30 – 3:00 p.m.	**Afternoon Break: Coffee and Refreshments** All Attendees
3:00 – 5:00 p.m.	**Session 4: Emerging Machine Learning, Image Processing, and Simulation Methods**
3:00 – 3:30 p.m.	**Solving Electron Microscopy: Towards Reconstruction Methods for Thick, Strongly Scattering Materials** Hamish Brown | Lawrence Berkeley National Laboratory
3:30 – 4:00 p.m.	**Theory-experiment Matching via Machine Learning Physics-Coupled Frameworks** Rama Vasudevan | Oak Ridge National Laboratory
4:00 – 5:00 p.m.	**Discussion: Harnessing Emerging Techniques** All Attendees
5:00 – 6:00 p.m.	**Reception: Appetizers and Drinks** All Attendees

NeXTEM
Next-Generation Transmission Electron Microscopy

We appreciate the support of our sponsors – thank you!

Gold

ThermoFisher SCIENTIFIC

JEOL Solutions for Innovation

Silver

Protochips Quantifiably Better™

GATAN

Direct Electron INNOVATION PROPELLING DISCOVERY

Bronze

HUMMINGBIRD SCIENTIFIC

nion

Introduction to Direct Electron Detector Technologies and Applications

David A. Muller[1,4,*], Zhen Chen[1], Yi Jiang[2], Kayla X. Nguyen[3], Yu-Tsun Shao[1], Yimo Han[1], Prafull Purohit[2], Mark W. Tate[2], Sol M. Gruner[2,4], Veit Elser[2]

[1.] School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853, USA
[2.] Department of Physics, Cornell University, Ithaca, NY 14853, USA
[3.] Department of Materials Science, University of Illinois, Urbana, IL 61801, USA
[4.] Kavli Institute at Cornell for Nanoscale Science, Ithaca, NY 14853, USA
* Corresponding author: David.a.Muller@cornell.edu

The new generation of direct electron detectors are reshaping what can be measured with electron microscopes. Monolithic active pixel sensors (MAPS) detectors, which are optimized for a large number of low-dose-rate, small pixels, have revolutionized cryo-electron and in-situ TEM. These detectors are poorly-suited to the large currents and concentrated intensities that characterize STEM signals. Here, pixel array detectors (PADs) such as the EMPAD, where large pixels allow for more sophisticated charge measurements, have demonstrated the necessary sensitivity, dynamic range and dose-rates to record the full scattering distribution of every transmitted electron at every probe position [1], enabling quantitative and dose-efficient imaging of strains with sub-pm precision, magnetic fields from layers only a few atoms thick, ferroelectric textures and vortices, and ptychographic imaging well beyond the diffraction limit of the microscope.

For all of these applications, the key performance metrics for STEM is the ability to record a low-noise signal with a large dynamic range in as short a time as possible. Figure 1a shows the accuracy of recording the angular deflections of the center of mass of a diffraction disk is dominated by the counting statistics, requiring a large number of electrons for a precise measurement, and relatively few pixels are needed, with diminishing returns beyond 10x10 pixels per diffraction disk. Fig 1b shows measurements of magnetic Skyrmions in a sub-nm thick cobalt film, with a precision of 0.1μrad.

By combining our new design of electron microscope pixel array detector (EMPAD) [1] which has the dynamic range to record the complete distribution of transmitted electrons at every beam position, and a ptychographic phase retrieval algorithm to process the data, we have been able to increase the spatial resolution well beyond the traditional lens limitations reaching a 0.39 Å resolution for MoS_2, at 80 keV, the same dose and imaging conditions where conventional imaging modes reach only 0.98 Å [2]. The improved resolution, dose efficiency and robustness to environmental noise enabled by ptychography make it easy to identify defects such as sulfur monovacancies, as well as subtle structural arrangements and tilts on the sulfur sublattice that are undetectable by conventional imaging modes. For twisted bilayers we are able to resolve the shear distortions and interactions between the layers (Figure 1). [3]

References:

[1] MW Tate, *et al*, Microscopy and Microanalysis **22** (2016), p. 237.
[2] Y. Jiang *et al*, Nature **559**, (2018), p343.
[3] We thank Jiwoong Park, Saien Xie, Hui Gao, Ming-Hui Chiu, and Lain-Jong Li for samples. Research supported by US National Science Foundation (grants DMR-1539918, DMR-1429155, DMR-1719875), DARPA (D18AC00009) & US Department of Energy Basic Energy Sciences (DE-SC0005827).

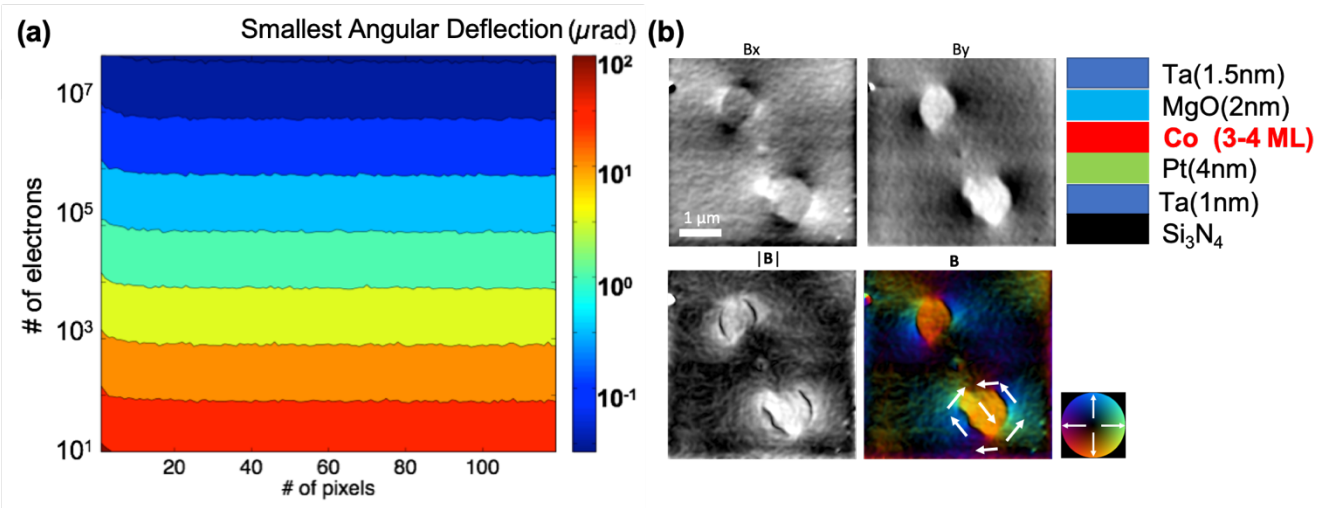


Figure 1. Measuring the angular deflections needed for strain mapping and magnetic field imaging. (a) The smallest measurable angular deflection depends strongly on the dose, and only weakly on the number of pixels. Usually only 10 pixels/disk diameter are needed. However, for rapid mapping, a high dose rate (>10^7 e/ms/disk) is essential. This translates to a few pA/pixel which is beyond the linear count rate of all pulse counting detectors, but still achievable with charge integrating designs. (b) EMPAD measurements at 0.1μrad precision of magnetic fields from Néel-type Skyrmions in a single 0.9 nm thick cobalt film, sandwiched between heavy metal layers.

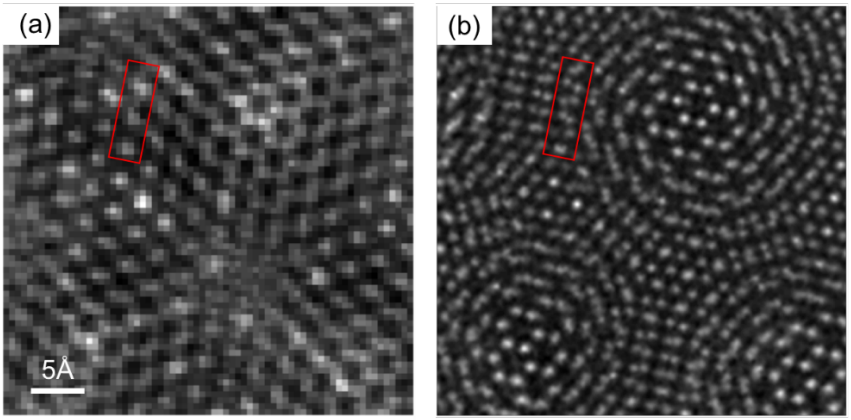


Figure 2. Real space resolution demonstration of full-field, in-focus ptychography using a twisted bilayer MoS_2. (a) Synthesized ADF image; (b) Phase image from ptychographic reconstruction. Data adapted from [3]

The Need for Speed: Opportunities in Materials Characterization Created by Fast Detectors and High Speed Electron Beam Control

Paul M. Voyles[1*]

[1.]Department of Materials Science & Engineering, University of Wisconsin-Madison, Madison, WI USA
* Corresponding author: paul.voyles@wisc.edu

High speed electron scattering with pulsed sources has revealed a variety of phenomena at timescales from μs to fs. However, pulsed sources add instrument complexity and expense and space charge effects in pulses impose special requirements, such as single electron pulses limited to stroboscopic experiments and megavolt voltages. High speed electron microscopy with continuous sources has the potential to create new opportunities in materials characterization. The key enabling technologies are fast pixelated direct electron detectors and high speed beam manipulation using electrostatic deflectors or RF cavities.

The current state of the art in electron cameras operate at frame rates up to ~5000 frames per second (fps), but this is far from the limit of CMOS-based cameras, as light cameras can achieve operate at up to 1,000,000 fps [1]. Faster cameras are coming to electron microscopy. The Molecular Foundry at Lawrence Berkeley lab recently tested a camera with 576×576 pixels operating at 87,000 frames per second [2]. The UW-Madison Materials Research Science and Engineering Center and Direct Electron Inc. are developing a camera that will operate at 2,000 to 120,000 fps as the pixel count is reduced from 1024×1024 to 128×128. The UW camera also will feature low, high, and high dynamic range gain modes, operation in rolling or global shutter mode, and correlated double sampling readout for reduced noise.

These new cameras will enabling 4D STEM experiments with μs pixel dwell times similar to what is commonly used with integrating STEM detectors currently. The high speed will reduce the influence of instabilities, enable drift correction, and enable experiments including time-resolved 4D STEM, densely-sampled strain maps over large areas, and diffraction tomography. High speed will also enable improved detector dynamic range by rapid frame averaging.

However, μs time resolution experiments using TEM imaging with current continuous sources will be strongly limited by low intensities. An alternative is take a statistical approach, in the electron equivalent of x-ray photon correlation spectroscopy, electron correlation microscopy (ECM) [3-5]. ECM uses intensity fluctuations in diffraction, measured either in dark-field TEM or STEM nanodiffraction, to characterize fluctuations in a system from the time autocorrelation function of the intensity, $I(t)$.

$$g_2(t) = \frac{\langle I(t')\rangle\langle I(t'+t)\rangle}{\langle I(t')\rangle^2},$$

The noise in $g_2(t)$ is largely governed by the total number of detected electrons, not the signal in particular measurement $I(t)$, so ECM can tolerate very low dose per image.

ECM has been used to study structural fluctuations in metallic glass forming liquids as a function of temperature above the glass transition temperature, T_g using *in situ* heating [3-5]. Figure 1 shows spatial maps of the structural relaxation time, τ, derived from ECM data on $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ nanowires [5]. These data show that the motion of atoms in a liquid are spatially heterogeneous. At the nanometer scale, τ varies by as much as an order of magnitude. This spatial variation is central to theories of the glass transition. Figure 1 also shows a ~1 nm thick surface layer with order of magnitude faster dynamics than the bulk, which promotes homogenous nucleation of crystals without catalytic nucleation from the surface.

The structural relaxation time in a liquid in equilibrium is related to the viscosity, which describes the liquid response to pressure, by the Debye-Stokes-Einstein (DSE) relation. The DSE is one example of a fluctuation dissipation relation, which connect the behavior of a system under external stimuli to its fluctuations in equilibrium. Any fluctuations that produce diffraction are amenable to characterization with ECM. Examples of include fluctuating domains in ferroelectrics or ferromagnets at constant field, which are connected to domain switching behavior, and atomic hopping without a concentration gradient, which is related to diffusivity. Current cameras limit the time resolution of ECM to 10s of ms, but next-generation cameras will enable probing of time scales <100 μs.

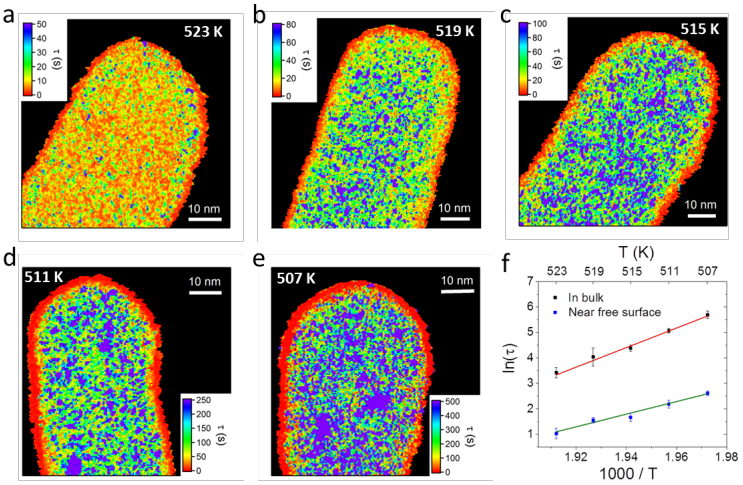


Figure 1: (a)-(e) ECM-derived maps of τ for a Pt-based metallic glass nanowire showing spatially heterogeneous dynamics within the wire and a surface layer with fast dynamics. (f) Arrhenius temperature dependence of surface and bulk τ.

The second key technology is fast beam control, with electrostatic systems offering beam positioning at nanosecond timescales and RF cavities offering switching at picosecond timescales. Kisielowski *et al.* recently demonstrated that RF modulation of a continuous electron beam can dramatically reduce beam damage in $MgCl_2$ compared to the same dose in a continuous beam [6]. The RF modulation was so fast that many of the "on" pulses did not contain even a single electron, but ensuring that the beam is off for certain periods allowed the material to recover, rather than accumulating damage. Nanosecond beam positioning will enable ultrafast STEM scanning and acquisition schemes based on compressed sensing. Compressed sensing will enable multiplexing of signals on a pixelated detector for even faster readout, and, while it does not reduce the total dose required to acquire an image at fixed signal to noise ratio [7], it does allow that dose to be distributed amongst fewer spatial positions [8]. For samples with limited ability to dissipate dose at short length scales, this may also limit accumulation of beam damage [9].

References

[1] S Okura et al., 2014 Symp VLSI Circuits Dig Tech Pap, 10.1109/VLSIC.2014.6858429(2014), p. 1.
[2] Successful Demonstration of Fastest Electron Detector Ever Made, (2019), https://foundry.lbl.gov/2019/03/17/successful-demonstration-of-fastest-electron-detector-ever-made/
[3] L He et al., Microscopy and Microanalysis **21** (2015), p. 1026.
[4] P Zhang et al., Ultramicroscopy **178** (2017), p. 125.
[5] P Zhang et al., Nature Communications **9** (2018), p. 1129.
[6] C Kisielowski et al., Advanced Functional Materials **29** (2019), p. 1807818.
[7] W Van den Broek et al., IEEE Transactions on Computational Imaging, DOI: 10.1109/tci.2019.2894950(2019).
[8] A Béché et al., Applied Physics Letters **108** (2016), p. 093103.

[9] Development of ECM is supported by the NSF (DMR-1807241). Development of advanced detectors and microscopy facilities are supported by the Wisconsin MRSEC (DMR-1728933).

Magnetic-field-free Atomic Resolution STEM

Naoya Shibata[1,2]

[1.] Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656 Japan
[2.] Nanostructures Research Laboratory, Japan Fine Ceramic Center, Nagoya 456-8587, Japan
shibata@sigma.t.u-tokyo.ac.jp

Atomic-scale structures of defects in materials and devices are essential to control their functional properties. Aberration-corrected scanning transmission electron microscopy (STEM) is a powerful technique to directly observe atomic-scale structures of individual defects, such as interfaces, inside materials and devices. In state-of-the-art aberration-corrected STEM, a probe size of less than 0.5Å in diameter has been realized [1], which is smaller than the Bohr radius of a hydrogen atom. The following interesting question arises: beyond just atoms, what might become observable by using such fine probes?

One answer to this question may come from exploring new possibilities in phase-contrast imaging in STEM. By using more elaborate detectors, we can not only image atomic structures of materials, but can also image local electromagnetic fields inside materials through differential phase contrast (DPC) imaging techniques [2-4]. Applying DPC imaging in atomic resolution STEM [5], we can now directly visualize the electric field distribution within single atoms [6,7], i.e. the electric field between the positively charged atomic nucleus and the negatively charged electron cloud. Moreover, that the electric field distribution inside an atom can be quantitatively observed should further mean that this image can be converted into the total charge density distribution according to the relevant Maxwell equation. That is to say, we may be able to directly image the charge density distribution inside an atom or in between atoms in real space. Thus, atomic-resolution DPC STEM opens a new stage of microscopy that enables directly visualization of the structure within individual atoms via electric field imaging.

It then becomes tempting to directly observe magnetic fields at atomic resolution, which should strongly correlate with the properties of magnetic materials and devices. However, by using conventional electron microscopes, atomic-resolution observation of magnetic materials is essentially very difficult, because high magnetic fields (2-3T) are always exerted on samples inside the magnetic objective lens. Very recently, we have developed a new magnetic objective lens system that realizes a magnetic field free environment at the sample position [8]. Using this new objective lens system combined with the state-of-the-art higher order aberration corrector [9], direct atom-resolved imaging in a magnetic field free environment has finally been achieved by STEM [10]. Figure 1 shows an annular dark field STEM image of Fe-3%Si alloy, one of the most important engineering soft magnetic materials. This novel electron microscope (Magnetic-field-free Atomic Resolution STEM: MARS), shown in Figure 2, is expected to be used for research and development of advanced magnetic materials and devices. The details of this new STEM will be presented in the talk.

[1] S. Morishita *et al., Microscopy,* **67**, 46 (2018).
[2] N.H. Dekkers and H. de Lang, *Optik*, **41**, 452 (1974).
[3] H. Rose, *Ultramicroscopy*, **2**, 251-267(1977).
[4] J.N. Chapman, I.R. McFadyen and S. McVitie, *IEEE Trans. Mag.*, **26**, 1506-1511(1990).
[5] N. Shibata *et al.*, *Nature Phys.*, **8**, 611-615 (2012).
[6] N. Shibata *et al.*, *Nature Comm.* **8**, 15631 (2017).

[7] R. Ishikawa *et al.*, *Nature Comm.,* **9**, 3878 (2018).
[8] Y. Kohno, S. Morishita and N. Shibata, *Microsc. Microanal.* **23** (Suppl. 1), 456-457 (2017).
[9] H. Sawada *et al*., *J. Electron Microsc.*, **58**, 341-347 (2009).
[10] N. Shibata *et al.*, *Nature Comm.* **10**, 2380 (2019).
[11] The author thank all the collaborators of this research, especially Y. Kohno, T. Seki, S. Morishita, A. Nakamura, A. Kumamoto, H. Sawada, T. Matsumoto, S.D. Findlay and Y. Ikuhara for their contribution to the works shown in this presentation. The author acknowledges support from the JST SENTAN Grant Number JPMJSN14A and the JSPS KAKENHI Grant number JP17H01316.

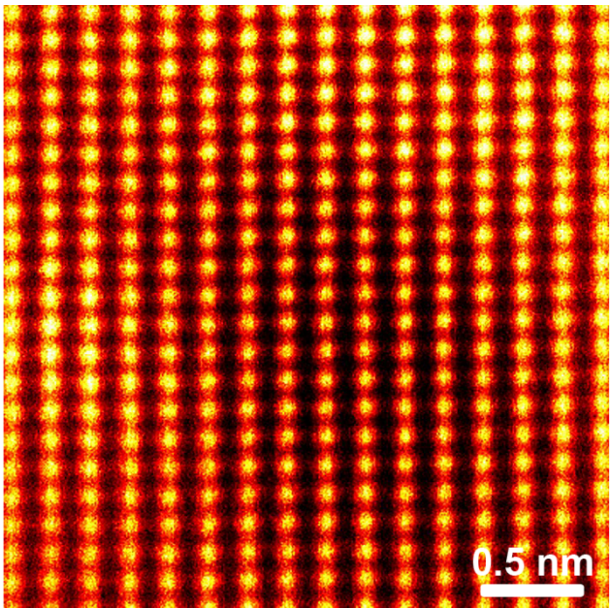


Figure 1. Atomic-resolution annular dark field STEM image of Fe-3%Si alloy observed from the [110] direction. The magnetic field at the sample position is kept well below 0.2mT.

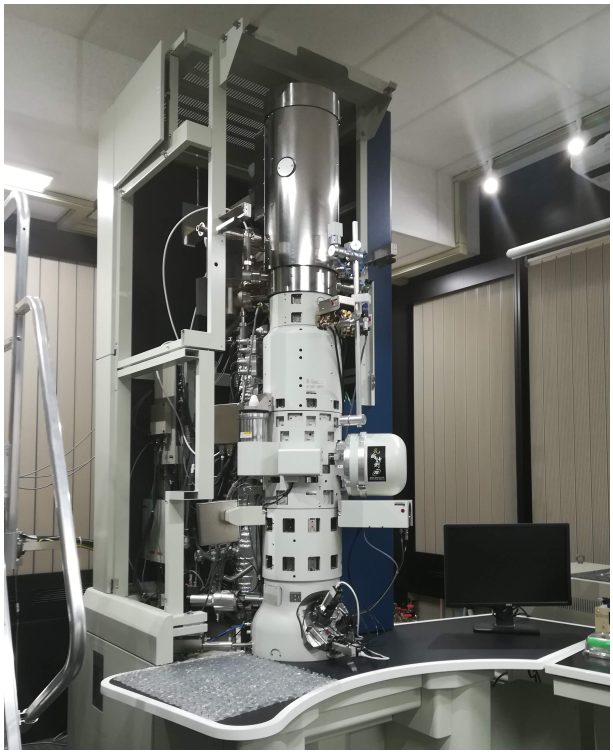


Figure 2. The MARS microscope installed in the University of Tokyo.

In-Situ S/TEM and their Applications for Energy Materials: The Challenge and Opportunities

Chongmin Wang

Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, USA

Direct observation of process under a device operating condition, as generically termed as *in-situ* and *operando*, appears to be one of the most promising and efficient approaches for revealing mystery that leads a system to deviate from the otherwise ideal operating condition, typically such as answering the questions why and how a rechargeable battery fade. Often, *in-situ and operando* observations are not straightforward, demanding appropriate unique deliberation, if not an invention, of new capabilities to allow the system to be observed while operating at normal conditions. Scanning/transmission electron microscopy (S/TEM), as a powerful analytical tool for addressing many unique scientific problems in various disciplines, shows no exception to this general expectation of coupling in *in-situ* and *operando* imaging for solving the challenging science questions. This is especially true as considering tremendous progress has been made on the development of aberration corrected S/TEM and scanning transmission electron microscopy. The questions now come to how we extend the microscopy and spectroscopy methodologies to analyze materials under operating condition, typically such as real time observation of structural and chemical evolution of electrode materials in batteries, catalytic process, oxidation and reduction, bio-tissue in a liquid cell, defects generation and interaction under deformation conditions, and mass and charge transport process.

Approaches that are employed to provide in-situ observation of chemical reactions and microstructural evolution include, but are not limited to, the use of differential pumping technologies, the modification of sample holders to enable the application of an external stimulus such as an electromagnetic field or stress, employing thin membrane closed cells for experiments involving liquids or gases, and use of liquid with low vapor pressure. In view of these developments, this work will focus on in-situ techniques that developed for probing into the energy materials, highlighting direct observation of structural and chemical evolution, solid-gas interface, nanoparticle interaction, phase transformation and their correlation with mass and charge transport, providing insights as how active materials failure during the cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the in-situ S/TEM imaging and spectroscopic methods for both functional and structural materials and other field will also be discussed.

As a specific example, nanoparticles of either as an active functioning component or as a reaction product is of great importance for a range of science and engineering, such as catalysis, nucleation and growth, metal air-battery, and oxidation and corrosion. A typical quesion is the deactivation of catalyst particles. It has been commonly realized that deactivation of catalysts stems from surface area loss due to particle coarsening, however, for which the mechanism remains largely unclear. Direct in-situ TEM observation reveals unprecedented details at atomic scale with respect to the behavior of Pt nanoparticles for fuel cell application, especially the coarsening dynamics of Pt nanoparticles on bare CNTs surface and in Nafion covered Pt/CNTs under O_2 and H_2O gas environment. We found that the coarsening of Pt nanoparticles proceeded through migration and

coalescence process. The migration rates of Pt nanoparticles on bare CNT surface is much faster in O_2 than that in H_2O. The strong oxygen chemisorption on Pt nanoparticles weakens the interaction between Pt and CNT surface, leading to a fast migration in O_2. Incorporation of Nafion electrolyte layer put on a mechanically confinement to Pt/CNTs which reduces the Pt migration rate in O_2. However, this mechanical confinement is largely relieved by introducing H_2O, and a lubricated interface is created, both leading to a faster migration rate of Pt in H_2O than that in O_2. These results bridge the gap between the previous *in situ* TEM studies in idealized conditions and the technological relevant conditions of Pt catalyst for PEMFC, thus provide insights to rational design of Pt/carbon catalysts incorporating Nafion electrolyte to achieve a long-lasting PEM fuel cells.

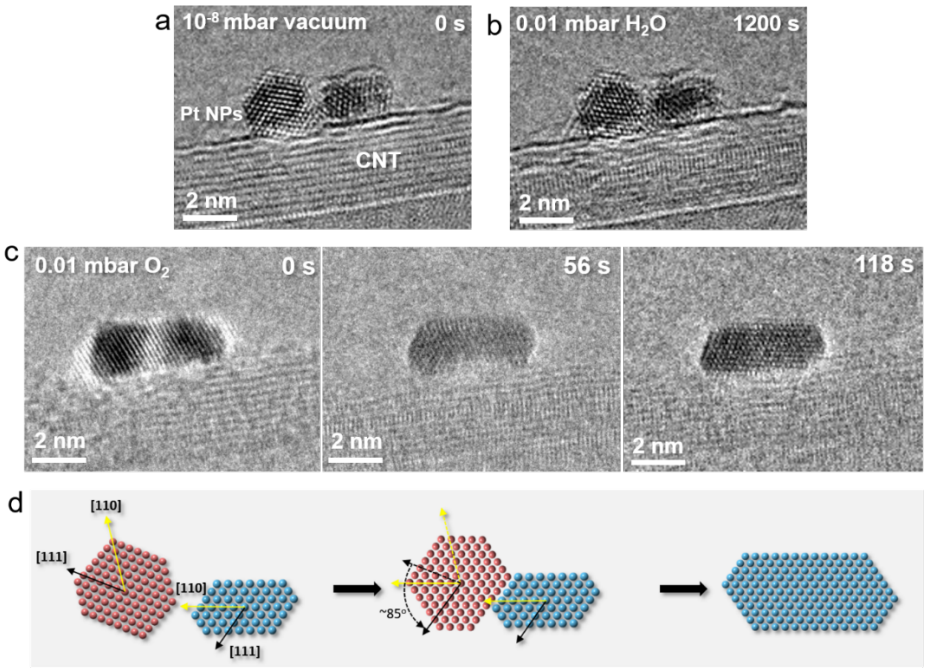


Figure 1. Migration and coalescence process of Pt/CNTs at 100 °C. (a) HRTEM image shows two separated Pt nanoparticles in vacuum. (b) HRTEM image shows the distance between two Pt nanoparticles decreased but still maintained their individual shape and orientation after 30 minutes in H_2O. (c) A series of time-lapsed HRTEM images show the coalescence process of two Pt nanoparticles after switching gas from H_2O to O_2. (d) Schematic illustrates the coalescence of these two Pt nanoparticles involves rotation of one NP and growth through orientation match.

References

[1] Yuyan Shao, Jiehe Sui, Geping Yin, and Yunzhi Gao, "Nitrogen-doped carbon nanostructures and their composites as catalytic materials for proton exchange membrane fuel cell", Applied Catalysis B: Environmental. 2008, 79, 89-99.

[2] The work was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at PNNL.

Vibrational Spectroscopy in STEM-EELS at High Spatial Resolution

Quentin M. Ramasse[1,2], Fredrik S. Hage[1], Demie Kepaptsoglou[1,3], Rebecca J. Nicholls[4], Jonathan R. Yates[4], Leslie J. Allen[5,6]

[1.] SuperSTEM Laboratory, STFC Daresbury Campus, Keckwick Lane, Daresbury WA4 4AD, U.K.
[2.] School of Physics and School of Chemical and Process Engineering, University of Leeds, Leeds, U.K.
[3.] School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia
[4.] Department of Materials, University of Oxford, Oxford United Kingdom
[5.] Ernst-Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungzentrum Jülich, Jülich, Germany
[6.] School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia

A new generation of electron beam monochromators has recently pushed the energy resolution of (scanning) transmission electron microscopes deep into the sub 10meV range [1]. In addition to the obvious increase in resolution which has made exploring the phonon region of the EELS spectrum possible [1], the increased flexibility of these instruments is proving hugely advantageous for materials science investigations. The energy resolution, beam current and electron optics can be adjusted seamlessly and traded off each other as necessary within a greatly increased range.

In an early application to the field of two-dimensional materials, the cubic (*c*-BN) and hexagonal (*h*-BN) phases of boron nitride were shown to give rise to markedly different phonon excitations in EELS [2]. A better understanding of this phonon response can be achieved by observing the dependence of the phonon peak under different optical conditions, mapping the energy and intensity of the peaks in momentum space. Such momentum-resolved vibrational measurements had so far been limited to "bulk" techniques (e.g. inelastic x-ray and triple-axis neutron scattering spectroscopies), the average surface response (e.g. reflection EELS) or small momentum transfers (e.g. optical techniques). Carefully balancing the intrinsic trade-off between simultaneously achievable resolutions in real and momentum space, it is possible to map the vibrational response of boron nitride along different directions of the Brillouin zone, using a ~1nm electron probe thus probing a sample volume ~10^{10}-10^{20} times smaller than with optical techniques [3,4].

A related technical approach can also be used to achieve atomic resolution in phonon spectroscopy at atomic resolution. By displacing the EELS collection aperture away from the optic axis of the instrument to angles similar to those used for Z-contrast image detectors, the contribution of electrons that have undergone dipole scattering as well as elastic scattering is minimised and this optical geometry favours instead the highly localised impact transitions in the recorded vibrational spectrum [5].

Simulations based on the quantum excitation of phonons (QEP) formalism show good agreement with the experimental data and reproduce the atomic-resolution contrast obtained in the experimental images. These demonstrate conclusively and directly that inelastic scattering associated with phonon excitations plays a central role in generating the contrast widely used for atomic resolution high angle annular dark field imaging [6].

References

[1] OL Krivanek *et al.*, Phil. Trans. Roy. Soc. **367** (2009), pp. 3683-3697; T.Miyata *et al.*, Microscopy **5** (2014), pp. 377-382 ; O.L. Krivanek *et al.*, Nature **514** (2014), pp. 209-212.
[2] RJ Nicholls *et al.*, Microsc. Microanal. **21** Suppl.3 (2015), pp. 1469-1470.
[3] FS Hage, RJ Nicholls, JR Yates *et al.*, Science Advances **4** (2018), eaar7495.
[4] RJ Nicholls, FS Hage, DG McCulloch *et al.*, PRB **99** (2019), 094105.
[5] FS Hage, DM Kepaptsoglou, QM Ramasse *et al.*, PRL **122** (2019), 016103. (2019).
[6] SuperSTEM is the UK National Research Facility for Advanced Electron Microscopy, funded by the Engineering and Physical Sciences Research Council (EPSRC).

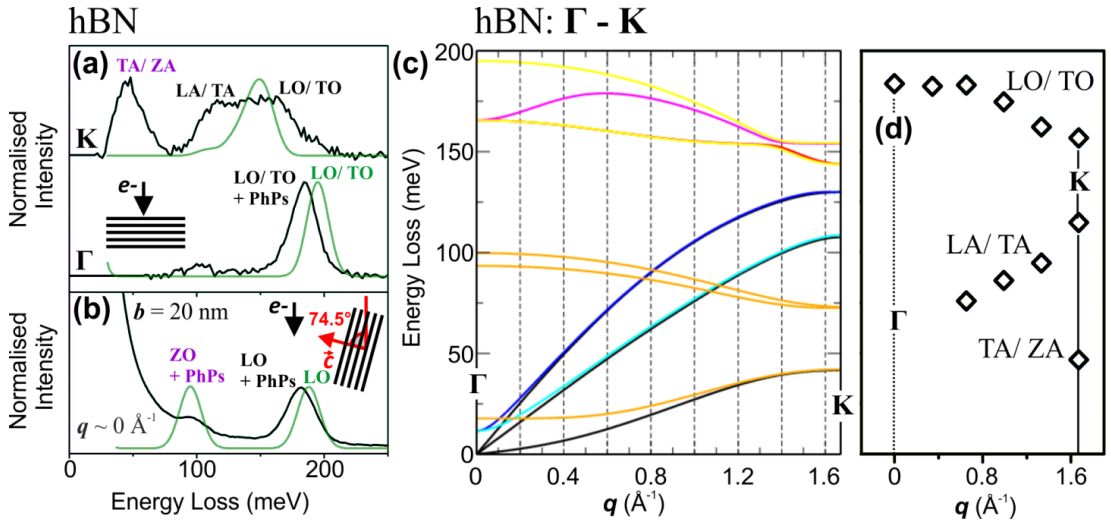


Figure 1. (a) Selected **experimental** and **modelled** momentum resolved hBN EEL spectra. **(b)** "Aloof" hBN EEL spectrum, acquired at a beam incidence of 74.5° to the crystallographic c-axis and at an impact parameter of ***b*** = 20nm. **In-plane** and **out-of-plane** phonon mode contributions are indicated. **(c)** Modelled and **(d)** experimental phonon dispersions, where ***q*** is the wave vector.

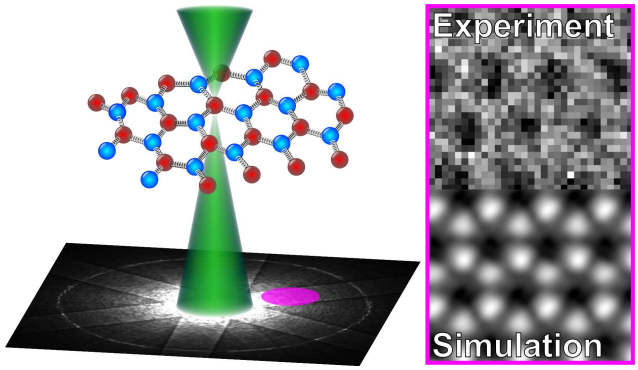


Figure 2. Left: Experimental geometry for atomic-resolution vibrational spectroscopy; Right: Comparison between experimental phonon image for hexagonal boron nitride (integrating the phonon sector of the spectrum) and simulation of the inelastic scattering using the QEP formalism [5].

Optical Spectroscopy with an Electron Microscope and a Light Collector / Injector

Luiz H. G. Tizei[1*], Noémie Bonnet[1], Pabitras Das[1], Yves Auad[1], Steffi Woo[1], Alberto Zobelli[1], Jean-Denis Blazit, Marcel Tencé[1], Odile Stéphan[1], and Mathieu Kociak[1]

[1.] Laboratoire de Physique des Solides, Université Paris-Sud, CNRS-UMR 8502, Orsay 91405, France
* Corresponding author: luiz.galvao-tizei@u-psud.fr

Traditionally, optical spectroscopy is performed with light as the excitation source, with a spatial resolution (with few exceptions for specific techniques) limited by light diffraction. For this reason, optical spectroscopy using electrons has been developed either in absoprtion (electron energy loss spectroscopy, EELS) or in emission (cathodoluminescence, CL) leading to nanometer spacial resolution [1-3]. The increased spectral resolution due to modern monochromators (sub 10 meV) [4,5] has attracted more attention to EELS for nanooptics and stretched its applicable range into the infrared.

In this contribution, we will start by describing a home-made light collection/injection system [6] designed for scanning transmission electron microscopes. Recent cathodoluminescence experiments at cryogenic temperatures performed with this system will be described, specially the detection of single point defects throught their light emission statistics [7, 8]. Specifically, non-sequential electron beam scan patterns (i. e. random scan patterns) have allowed us to follow the slow scale (seconds) evolution of defects' emission (blinking and spectral diffusion) under electron irradiation [9].

Despite a clear interest due to the increased spacial resolution, there are many aspects accessible in standard optical spectroscopy that are missed in traditional spectroscopies with electrons: excitation energy, polarization, and temporal selection, to cite a few. Moreover, electron-matter and photon-matter interaction are different, leading to different in CL and photoluminesnence (PL) signals (as recently observed for nitrogen-vacancy centers in diamond [10]). Finally, electron-photon interactions mediated by matter [11,12] give access to properties that cannot be probed by electrons or photons independently at the nanometer scale [13].

So we will take a step back and show how we can use the same light collection/injection system to perform ~µm scale PL mapping of NV centers in diamonds. For this, we have used the parabolic mirror of the light collection/injection system to focus a 543 nm laser onto a few micron wide spot and to collect the emitted light signal from diamonds. Using this setup, the emitted light under electron, laser or combined excitation can be observed (Figure 1a). Spatial maps of the signal variation were measure by scanning the electron microscope sample state (Figure 1b-d).

Laser excitation concomitant with electron spectroscopy has been used to perfom gain spectroscopy [11, 12, 14]. We have developped an electron gain setup which, contrary to existing ones, does not require a pulsed gun and can be, therefore, a more easily democratized. We will discuss how the ability to form a few micrometer wide laser spot has significantly advanced gain experiments in our setup, allowing the detection of polarization- and energy-resolved signals [15].

References:

[1] N. Yamamoto, K Araya, and F. J. G. de Abajo, Phys. Rev. B **64** (2001), p. 205419.
[2] J. Nelayah, et al, Nat. Phys. **3** (2007), p. 348.
[3] L. F. Zagonel, et al, Nano Lett. **11** (2011), p. 568.
[4] O. Krivanek, et al, Nature, **514** (2014), p. 209.
[5] L. H. G. Tizei et al, Phys. Rev. Lett. **114** (2015), p. 107601.
[6] M. Kociak, L. F. Zagonel, Ultramicroscopy **176** (2017) p. 112.
[7] L. H. G. Tizei and M. Kociak, Phys. Rev. Lett. **110** (2013) p. 153604.
[8] R. Bourrellier, et al, Nano Lett. **16** (2016) p. 4317.
[9] A. Zobelli, et al in preparation (2019).
[10] Meuret, private communication.
[11] S. T. Park, M. Lin, and H. Zewail, New Journal of Physics **12** (2010) p. 123028.
[12] A. Feist, et al, Nature **521** (2015) p. 200.
[13] V. Di Giulio, M. Kociak, and F. J. G. de Abajo, arXiv:1905.06887 (2019).
[14] P. Das, et al, Ultramicroscopy **203** (2019) p. 44.
[15] Y. Auad and M. Kociak, unpublished results (2019).
[16] The authors acknowledge funding from the program of future investment TEMPOS-CHROMATEM (No. ANR-10-EQPX-50).

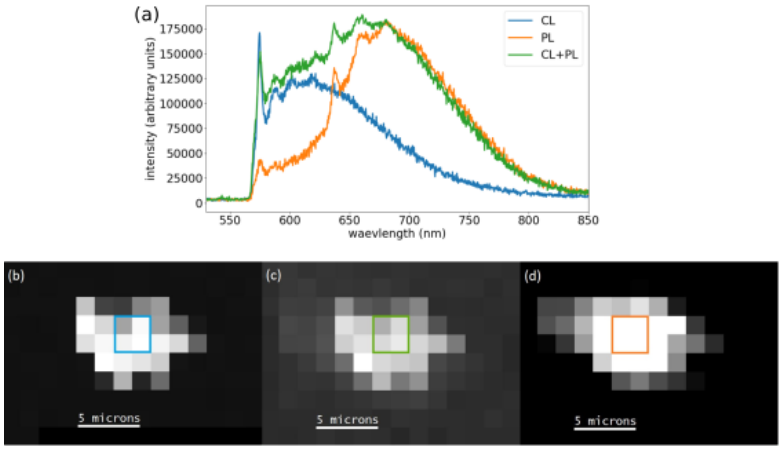


Figure 1: a) Spectra measured with electron (CL, blue), 543 nm laser (PL, orange) and both excitations (CL+PL, green). **b-c)** Spectrum images acquired by scanning the sample with electron, electron+laser and laser excitations, respectively.

Solving Electron Microscopy: Towards Reconstruction Methods for Thick, Strongly Scattering Materials

Hamish G. Brown[1]

[1.] National Centre for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, USA

A relativistic electron is an excellent tool for imaging condensed matter, it has a short wavelength (~ 2 pm) so can be focused to a small spot with modern electron optics. Since electrons are charged particles they interact strongly with atoms via the coulomb force, making possible studies of very small amounts of matter such as individual grain boundaries in graphene or single atomic dopants within a material. A side-effect of this strong interaction with matter is that electrons will often undergo complicated multiple scattering in all but the thinnest samples. In this talk I will discuss how modern technologies in scanning transmission electron microscopy (STEM), in particular fast readout electron cameras, give us data of sufficient quantity and quality to solve the equations governing multiple scattering of the electron beam. This suggests a future where we can "solve" the physics of electron scattering and render STEM results more directly interpretable.

A fully quantum mechanical approach to the electron sample interaction is given by the Schrodinger equation with a few approximations appropriate for a relativistic electron. The canonical solution to these equations is the scattering (**S**) matrix solution [1], Fig. 1(a). However most reconstruction approaches, such as ptychography and differential phase contrast (DPC) reconstruction, assume a very thin specimen, the projection approximation, Fig. 1(b), which models specimen beam interaction by multiplication of the illumination wave function with a transmission function [2]. Applications of ptychography and DPC are wide-spread, for microscopy specimens that are indeed very thin, ptychography and DPC provide directly interpretable maps of the electrostatic potential of the specimen [3,4]. Relative to conventional STEM techniques, these techniques often provide additional benefits such as higher-resolution, better signal to noise and computational correction of residual aberrations. For thicker specimens these techniques still provide useful qualitative results, such as making weakly scattering atoms more visible [4].

In this talk I will discuss how with fast readout electron cameras in STEM we record four dimensional datasets – a full 2D diffraction pattern for a 2D raster scan of the electron probe – sufficient information to reconstruct the full scattering matrix, Fig 2 [5]. This provides an approach to tackling the reconstruction of the specimen in the presence of full multiple scattering of the electron beam. For a crystalline specimen the electrostatic potential can be solved directly from the scattering matrix [6,7], for the general case a depth-section approach or inverse multislice approach is promising in some situations [8].

A final approach to overcoming the limits of the projection approximation is via the next generation of electron lens aberration correctors. Recent developments make possible a probe with phase curvature that is flat out to 50 mrad, or greater, in reciprocal space [9]. Such a probe would have a small depth of field such that it would interact with a small volume of the specimen – thus enabling reconstruction via methods that assume a weak interaction with the specimen [10].

References:

[1] Sturkey, L. "The calculation of electron diffraction intensities." Proceedings of the Physical Society **80** (1962), p. 321.
[2] Cowley, J. M., and Moodie, A. F., "The scattering of electrons by atoms and crystals. I. A new theoretical approach." Acta Crystallographica **10** (1957) p. 609.
[3] Jiang, Y, et al. "Electron ptychography of 2D materials to deep sub-ångström resolution." Nature **559** (2018), p. 343.
[4] Shibata, N., et al. "Electric field imaging of single atoms." Nature communications **8** (2017) 15631.
[5] Findlay, S. D., "Quantitative structure retrieval using scanning transmission electron microscopy." Acta Crystallographica Section A **61** (2005), p. 397.
[6] Allen, L. J. et al., "Inversion of dynamical electron diffraction data including absorption." Acta Crystallographica Section A **56** (2000), p. 119.
[7] Brown, H. G. et al., Physical Review Letters **121**, (2018) 266102.
[8] Gao S. et al., "Electron ptychographic microscopy for three-dimensional imaging", Nature Communications **8** (2017) p. 163.
[8] Hosokawa, F., et al. , Microscopy **62**, (2013) p. 23.
[9] Brown, H. G., et al. "Large angle illumination enabling accurate structure reconstruction from thick samples in scanning transmission electron microscopy." Ultramicroscopy **197** (2019) p. 112.

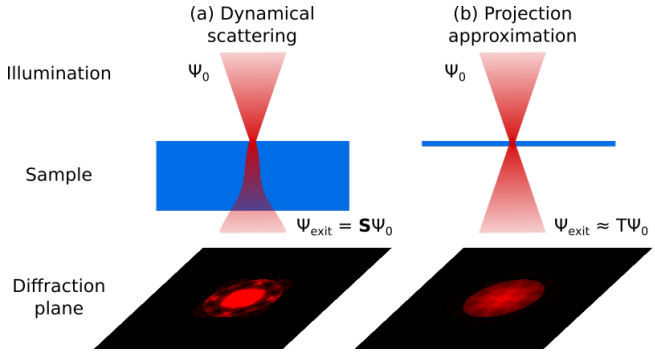


Figure 1. (a) In general the scattering of a fast electron (incident wave ψ_0) must be modeled using a scattering matrix (**S**). (b) The projection approximation assumes a very thin specimen, resulting in a simpler model where the illumination is multiplied by a specimen transmission function T in real space .

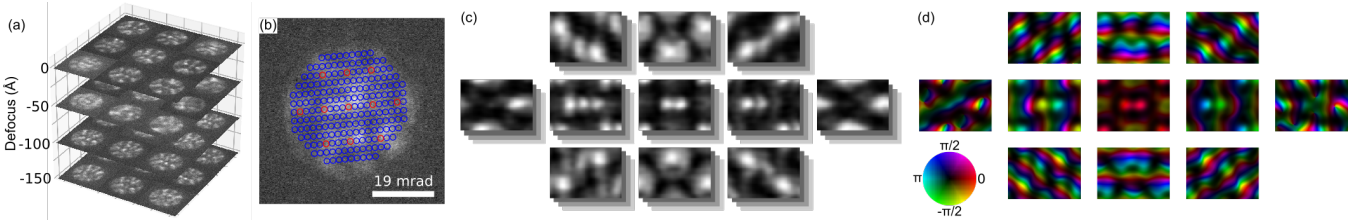


Figure 2. Reconstruction of the scattering matrix for a 4D-STEM data set. (a) A through focal scan of 4D-STEM datasets is recorded for a Si110 crystal and images are synthesized by integrated circular regions of the diffraction pattern in (b) to make focal series images of STEM bright-field images in (c). An iterative through-focal series phase reconstruction method is used to reconstruct the phase in (d) and the result is a representation of the scattering matrix.

Theory-experiment Matching via Machine Learning Physics-Coupled Frameworks

R. K. Vasudevan[1], N. Borodinov[1] L. Vlcek[2], M. Oxley[1], A. Lupini[1], S. V. Kalinin[1]

[1.] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge TN 37830
[2.] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge TN 37830

Recent advances in imaging, and specifically in electron microscopy, have resulted in a wealth of data on complex and disordered systems. Of special note is the ability to acquire convergent beam electron diffraction (CBED) patterns across a sample with extremely high (sub unit-cell) precision, within so-called 4D STEM, theoretically enabling much more structural information to be gathered on the sample than using more conventional 2D imaging modes [1]. However, the tremendous increases in data volume and complexity brings forth several basic questions, including (a) how can the 4D STEM data be adequately utilized in a real structure determination setting, and (b) given the structural information down to the picometer level, how can one utilize this data to gain information on the system. These data can generally be simulated to a high degree of accuracy; yet, the methods of theory-experiment matching for such data are still nascent.

To answer the first question, we created a workflow that can be followed for any structure determination problem that marries deep learning, generative adversarial modelling, and simulations. The idea is shown in Figure 1 (a). First, the CBED patterns are modelled based on a suite of N possible structures. One caveat here is that the real structure (which is unknown) should nevertheless be in this dataset of N modelled structures. For limited problems, this is not a major limitation – for example, if observing intermixing across an epitaxial atomic interface, it is possible to model all possible levels of intermixing. Second, based on the modelled structures, the resulting CBED patterns should be simulated. These can then be used to train a classifier, which can be based on some machine learning model (e.g., a deep convolutional neural network) that takes as input the simulated images, and outputs the structural descriptors (for example, the degree of intermixing across the interface). Finally, this can then be applied to experimental data to yield the structure, thus solving the inversion problem.

Naturally, there exist many somewhat mundane but still important issues when comparing the experimental and simulated datasets for 4D STEM. Apart from obvious ones such as microscope drift and associated registration difficulties, the fact remains that most simulations are still imperfect realizations of the actual experimentally observed structure. Microscope corrections (e.g., spatial decoherence) can be artificially added, but other imperfections, including those of unknown origin, may exist. We can tackle this problem again using modern tool from computer science and generative modelling, shown in Figure 1 (b). Here, we have data from two distributions – one from simulated images, another from experimental images, and the goal is to learn a mapping from one distribution to the other, essentially learning the transfer function $\boldsymbol{F}$ shown in the figure. This can be achieved using an adversarial approach, where a discriminator is trained to distinguish between images from the transformed simulated image data and the experimental data, whilst a generator is trained on minimizing the ability of the discriminator to perform the task by learning the appropriate transfer function that, when applied to the simulated images, makes them indistinguishable from the experimental images. To avoid mode collapse, and since paired examples are not available, this should be done with cycle-consistency loss within the cycleGAN framework [2] that ensures that a mapping between the two domains forward and backward results in minimal deviation. We applied this framework to structural

determination for 4D STEM data across the oxide interface between $LaAlO_3$ and $SrTiO_3$ and show that the lack of this learned transfer function severely limits the ability to distinguish between different structures in the 4D STEM data.

The second question asks what can be done once the structural details are obtained. Here, we will discuss our recent work on developing a framework that utilizes principles of statistical physics to derive lattice Hamiltonians to describe systems based on atomically resolved images in combination with other macroscopic data (if available). The key insight is that imaging of the system provides a window to the microstates, and therefore, understanding this distribution enables predictive modelling. By combining information on local ordering derived from machine learning of local atomic neighbourhoods, it provides a method to study phase transitions and underlying driving forces of disordered materials. [3,4].

References:

[1] C. Ophus et al., Microscopy and Microanalysis **20**(S3), 62 (2014).
[2] J.Y. Zhu et al., Proc. IEEE Int. Conf. Comp. Vis. 2223 (2017).
[3] L. Vlcek et al., ACS Nano **11**, 10313 (2017).
[4] L. Vlcek et al., ACS Nano **13**, 718 (2019).
[5] This work was supported by the US Department of Energy (DOE), Office of Science, Materials Sciences and Engineering Division (RKV, SVK, LV, AL, MO). This work was conducted at the Center for Nanophase Materials Sciences, a US DOE Office of Science User Facility.

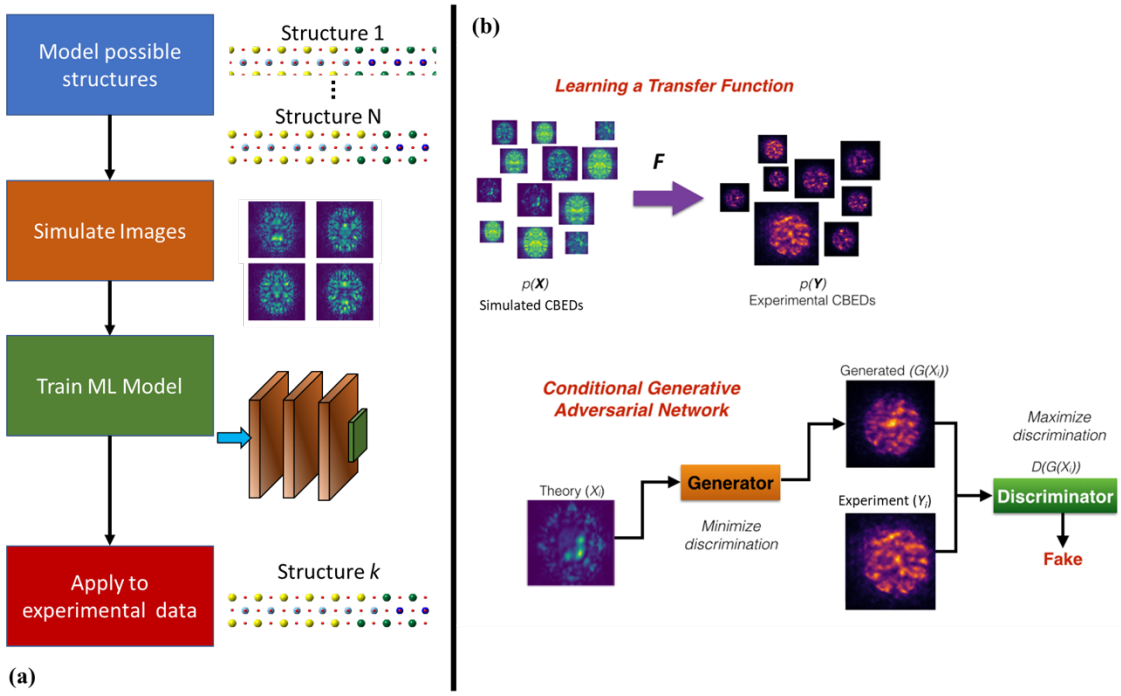


Figure 1. (a) Workflow for structural determination problems utilizing simulations, experiment and machine learning. (b) Generative adversarial modeling to learn a transfer function that converts simulated CBED patterns to be closer to those from the experimentally derived distribution.

Solutions for Innovation

70 YEARS STRONG

The name JEOL has been synonymous with microscopy and microanalysis for 70 years. Today, we continue to evolve our SEM, TEM, and EPMA technologies through dedication to advancing science and the flow of ideas.

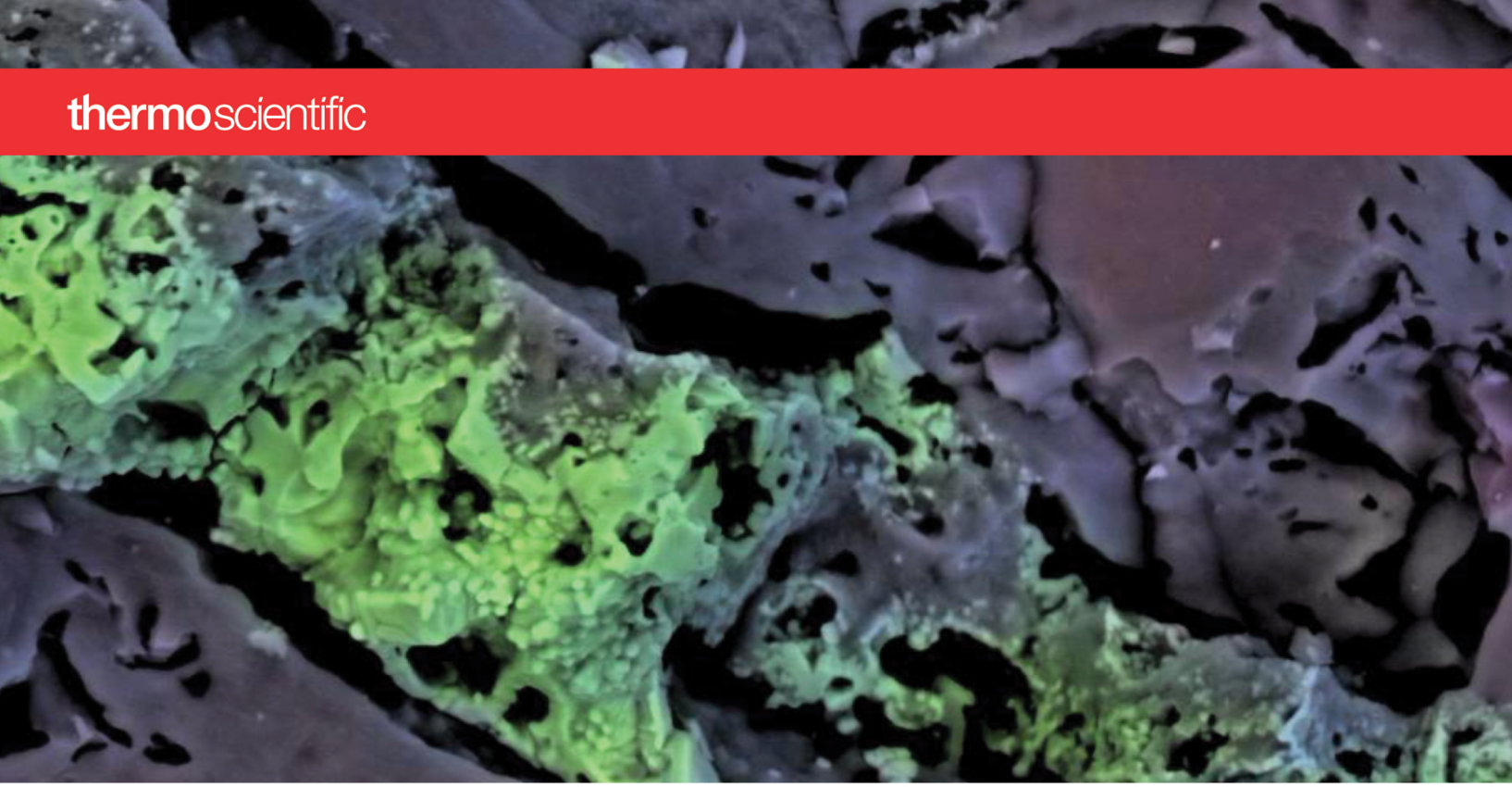
JEOL's innovative solutions lead the way in TEM. The next-generation NEOARM provides users the ultimate in flexibility for both high-spatial and high-energy resolution, yielding superior imaging and spectroscopy capabilities down to the atomic scale, from 30 – 200 kV. Our Monochromated TEM features the unique Spot-in-Spot-out double Wein filter. And the JEOL 300kV CRYOARM for single particle analysis and 3D reconstruction is making breakthroughs in Cryo EM.

Thank you to our customers for being part of our history of leadership in this field and our vision for the future. We are proud to be a part of your important viewpoint and success!

JEOL

www.jeolusa.com
salesinfo@jeol.com
978-535-5900

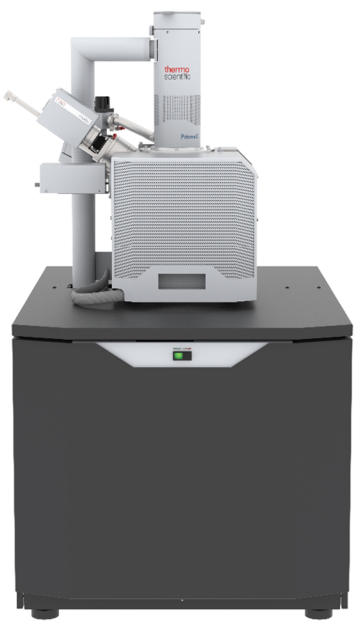
thermoscientific



ColorSEM Technology: See The Difference

The world isn't greyscale, so why are your electron microscopy images? New Thermo Scientific™ ColorSEM™ Technology makes elemental analysis a matter of routine thanks to always-on integrated energy-dispersive x-ray spectroscopy. Obtain elemental information 2–4x faster than conventional techniques, immediately revealing defects or imperfections that you might have otherwise missed.

See the difference color can make with ColorSEM Technology.



Thermo Scientific™ Prisma™ E with ColorSEM technology

Find out more at **thermofisher.com/colorSEM**

ThermoFisher SCIENTIFIC

ATMOSPHERE FOR CATALYSIS

BRINGING YOU CLOSER TO NANOSCALE OPERANDO EXPERIMENTS

VISIT US AT **BOOTH #644**

REALISTIC OPERATING ENVIRONMENTS

Accurately blend and flow custom gas mixtures to re-create even the most complex catalyst operating environments. Utilize anything from a single component gas to a custom industrial exhaust and add up to 1000ºC of heat.

CONTROLLABLE VAPOR INTRODUCTION

Software-controlled introduction of water and solvent vapors enables a level of precision and reproducibility otherwise unattainable. Introduce humidity, alcohols, light alkanes, and other sources as pure vapors or mix them with a carrier gas while preventing condensation.

INTEGRATED GAS ANALYSIS

Integration of the residual gas analyzer (RGA) enables superior image stability and rapid gas detection during your experiments. Software-controlled cleanliness checks ensure safe exposure of the gas manifold to the RGA for residual gas inspection prior to and in between experiments.

VENDOR TUTORIALS @ 5:45 P.M.

Sign up at the MSA MegaBooth
FREE to attend

Tuesday, 6 August
Location: Protochips Booth #644

In Situ TEM: Creating more Realistic Experimental Environments for Materials Research by Precisely Controlling the Introduction of Humidity
Kinga Unocic of ORNL

Wednesday, 7 August
Location: Protochips Booth #644

Operando Liquid-electrochemical TEM for Monitoring the Charge/Discharge Processes inside Li/Na-ion Batteries
Arnaud Demortiere of CNRS

Protochips
Quantifiably Better™

Revolutionizing Science

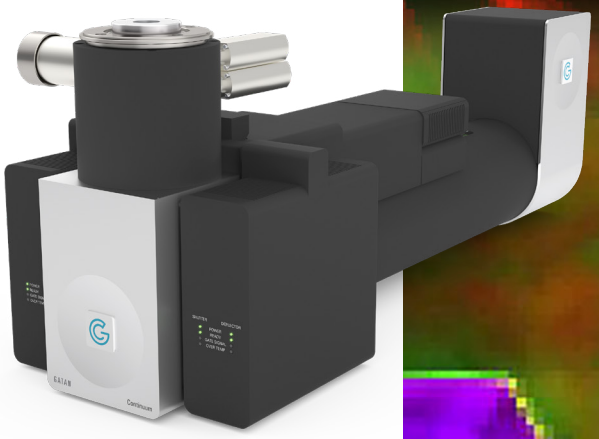
Continually breaking boundaries in electron microscopy

Gatan proudly showcases the K3™ IS direct detection camera, the GIF Continuum™ systems, and the Monarc™ cathodoluminescence (CL) detector. With these best-in-class systems Gatan continues to set new benchmarks in electron microscopy.

K3 IS

- Count 1,500 full fps – 3.75x the frame rate of K2
  - K3 IS model (1027) – 24 megapixels (5,760 x 4,092)
  - K3 Base IS model (1026) – 14 megapixels (3,456 x 4,092)
- Store 75 fps at full sensor resolution to 1,200 fps with sub area, no binning required

Continuum



- The next generation of advanced systems for EELS & EFTEM
- >8,000 spectra per second at >95% duty cycle
- >10x faster system tuning
- Streamlined, workflow-based user interface

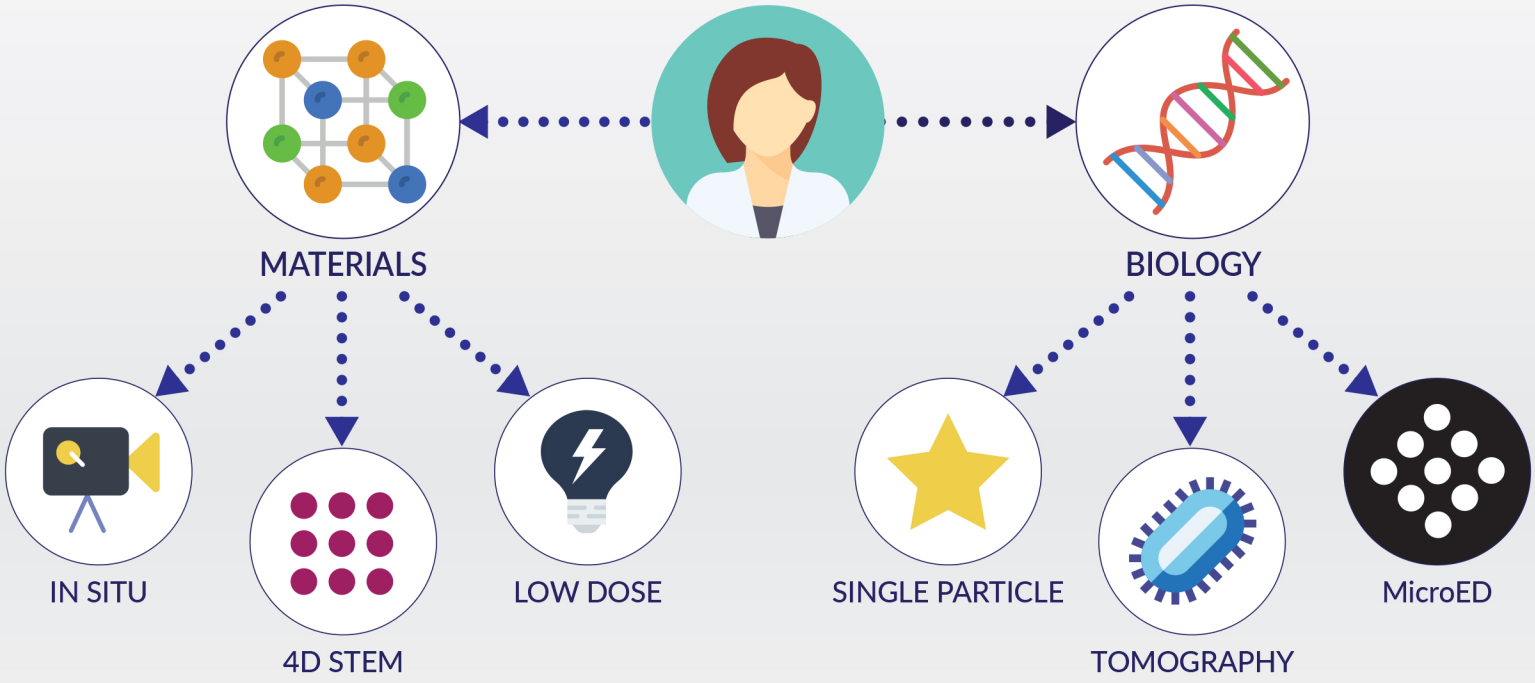
Monarc

- Acquire CL data with unmatched spatial (<10 nm), angular (1°), and wavelength (0.1 nm) resolutions
- Simultaneously capture angle- and wavelength-resolved CL data
- Collect hyperspectral data up to 30 times faster than other CL detectors

GATAN

www.gatan.com

CHOOSING THE BEST TEM CAMERA



VENDOR TUTORIALS AT BOOTH #518

MONDAY - Materials Science
TUESDAY - 4D STEM
WEDNESDAY - Cryo-EM

SIGN UP AT MSA MEGABOOTH
VENDOR TUTORIALS AT 5:45 PM

Direct Electron®

INNOVATION PROPELLING DISCOVERY

HUMMINGBIRD SCIENTIFIC

M&M 2019 MICROSCOPY & MICROANALYSIS August 4–8 · Portland, OR

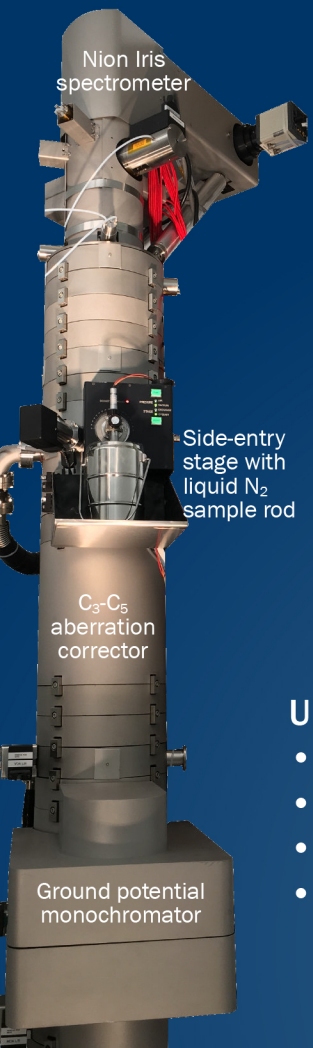
Launching five new in-situ TEM products

- Optical Liquid-Electrochemistry
- Cryo-Biasing
- New Double-Tilt MEMS Biasing + Heating
- Vacuum/Inert Gas Transfer Biasing
- Generation V Bulk Liquid-Electrochemistry

Visit us in booth #1045

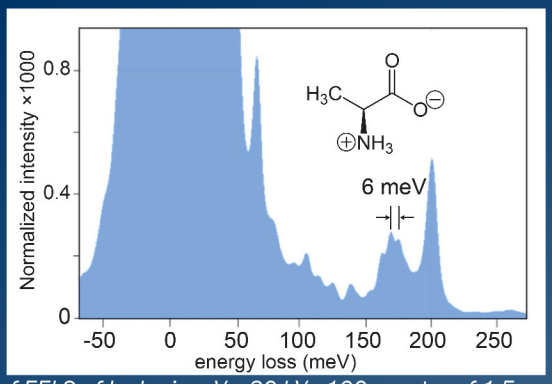
www.hummingbirdscientific.com

Innovation - Experience - Response

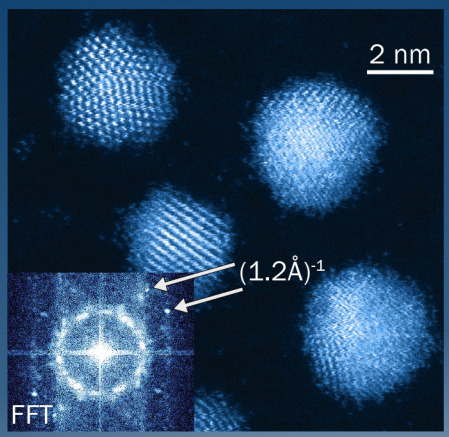


Nion U-HERMES™-S

Ultra-High Energy Resolution Monochromated EELS-STEM with Side-entry stage



Aloof EELS of L-alanine. V_0=30 kV. 100 spectra of 1.5s each, aligned and summed. Hachtel et al., Science (2019).



HAADF STEM image of Au nanoparticles at liquid N_2 temp. 200 kV. No cryofinger was used. Typical ice contamination rate is <1 monolayer/hr.

Ultra-high performance:

- 0.6 Å spatial resolution at 200 kV / 1.07 Å at 30 kV
- <5 meV energy resolution at 30 kV / 7 meV at 60 kV
- cooling, heating holders
- ultra-stable EELS

nion

Visit us at booth 1102