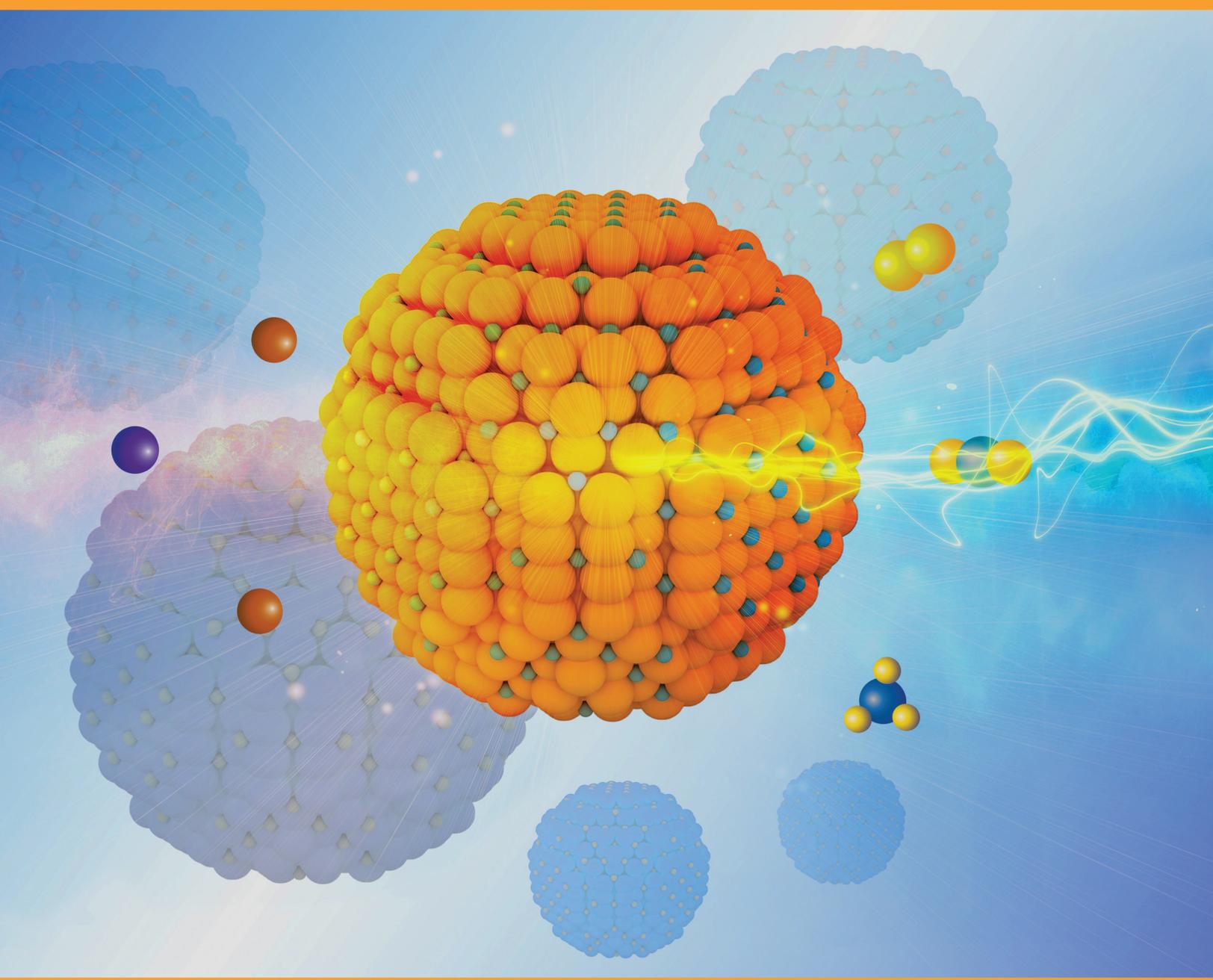


# BASIC RESEARCH NEEDS FOR **Innovation and Discovery of Transformative Experimental Tools**



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science



On the cover: An artist's depiction of transformative experimental tools — including techniques that combine multiple probes such as X-rays, visible or infrared light, electrons, or chemical species — to simultaneously observe, measure, and control energy processes in systems functioning in "real-world" environments. Cover art courtesy of Lawrence Berkeley National Laboratory.



# BASIC RESEARCH NEEDS FOR Innovation and Discovery of Transformative Experimental Tools

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## Chair:

**Ali Belkacem**, Lawrence Berkeley National Laboratory

## Co-Chairs:

**Cynthia Friend**, Harvard University  
**Yimei Zhu**, Brookhaven National Laboratory

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## Plenary Speakers:

**Simon R. Bare**, SLAC National Accelerator Laboratory

**Sharon Glotzer**, University of Michigan

**Amanda Petford-Long**, Argonne National Laboratory, Northwestern University

**Frances M. Ross**, IBM T. J. Watson Research Center

**Robert Schlögl**, Fritz Haber Institute, Berlin

**James Sethian**, Lawrence Berkeley National Laboratory, University of California, Berkeley

**Eric A. Stach**, Brookhaven National Laboratory

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## Panel Leads:

### *Chemical reactions and transformations in functional environments*

**Peter Crozier**, Arizona State University

**Cynthia Jenks**, Ames Laboratory

### *Challenges of heterogeneity across multiple length and time scales*

**Ralph Nuzzo**, University of Illinois at Urbana-Champaign

**Jennifer Ogilvie**, University of Michigan

### *Imaging materials far away from equilibrium*

**Paul Fenter**, Argonne National Laboratory

**Wayne Hess**, Pacific Northwest National Laboratory

### *Transformational experimental tools through integration of instrumentation with theory and computation*

**Jeff Neaton**, Lawrence Berkeley National Laboratory, University of California, Berkeley

**Monica Olvera de la Cruz**, Northwestern University

---

## Basic Energy Sciences Team & Special Assistance:

### Basic Energy Sciences Team:

Tom Settersten, Bruce Garrett, Linda Horton, Helen Kerch, Jeff Krause, Peter Lee, George Maracas, Gail McLean, Raul Miranda

### Special Assistance:

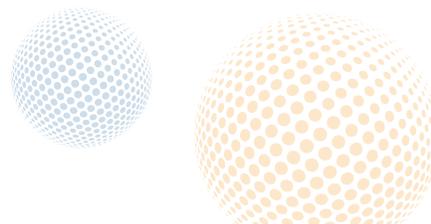
Joshua Haines (administrative), Katie Runkles (administrative)

### Writing and Editing Team:

Melissa Summers, Cheri Hadley, and Jeri Edgar, Lawrence Berkeley National Laboratory

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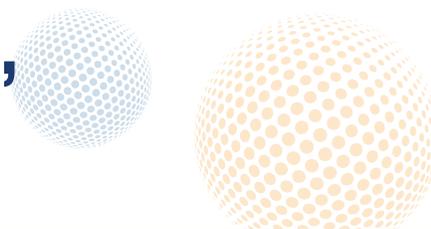


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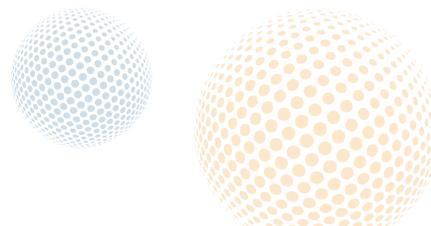
# Abbreviations, Acronyms, and Initialisms



<b>0D</b>	0-dimensional	<b>EPMA</b>	electron probe microanalysis
<b>1D</b>	1-dimensional	<b>EPR</b>	electron paramagnetic resonance
<b>2D</b>	2-dimensional	<b>ESCA</b>	electron spectroscopy for chemical analysis
<b>3D</b>	3-dimensional	<b>ESNet</b>	Energy Sciences Network
<b>4D</b>	4-dimensional	<b>ETEM</b>	environmental transmission electron microscopy
<b>AFM</b>	atomic force microscope/microscopy	<b>EXAFS</b>	extended X-ray absorption fine structure
<b>APT</b>	atom probe tomography	<b>FIB</b>	focused ion beam
<b>ARPES</b>	angle-resolved photoemission spectroscopy	<b>FSI</b>	fluid-solid interface
<b>BES</b>	Office of Basic Energy Sciences	<b>FTIR</b>	Fourier-transform infrared
<b>BESAC</b>	Basic Energy Sciences Advisory Committee	<b>GC-MS</b>	gas chromatography-mass spectrometry
<b>BRN</b>	Basic Research Needs	<b>GD-MS</b>	glow discharge mass spectrometry
<b>CADES</b>	Compute and Data Environment for Science	<b>GDP</b>	gross domestic product
<b>CAMERA</b>	Center for Applied Mathematics for Energy Research Applications	<b>GISAXS</b>	grazing incidence small-angle X-ray scattering
<b>CARS</b>	coherent anti-stokes Raman spectroscopy	<b>GIWAXS</b>	grazing incidence wide-angle X-ray scattering
<b>CDSAXS</b>	critical dimension small-angle X-ray scattering	<b>GPU</b>	graphics processing unit
<b>CPU</b>	central processing unit	<b>GPGPU<sub>s</sub></b>	general purpose graphics processing units
<b>CS</b>	compressive sensing	<b>HF</b>	high frequency
<b>CV</b>	cyclic voltammetry	<b>HFIR</b>	High Flux Isotope Reactor
<b>DC</b>	direct current	<b>HDF5</b>	hierarchical data format 5
<b>DFT</b>	density functional theory	<b>HipGISAXS</b>	high performance grazing incidence small-angle X-ray scattering
<b>DNP</b>	dynamic nuclear polarization	<b>HPC</b>	high-performance computing
<b>DOE</b>	Department of Energy	<b>HP-STM</b>	high pressure scanning tunneling microscopy
<b>DSC</b>	differential scanning calorimetry	<b>ICP</b>	inductively coupled plasma
<b>DTA</b>	differential thermal analysis	<b>IGA</b>	instrumental gas analysis
<b>DTEM</b>	dynamic transmission electron microscopy	<b>IR</b>	infrared
<b>EBIC</b>	electron beam-induced current	<b>LA-ICPMS</b>	laser ablation inductively coupled plasma mass spectrometry
<b>EC-STM</b>	electrochemical scanning tunneling microscopy	<b>LCLS</b>	Linac Coherent Light Source
<b>EDL</b>	electrical double layer	<b>LCLS-II</b>	Linac Coherent Light Source II
<b>EDS/EDX</b>	energy dispersive X-ray spectroscopy	<b>LEXES</b>	low energy electron-induced X-ray emission spectrometry
<b>EELS</b>	electron energy-loss spectroscopy		

<b>LFP</b>	lithium iron phosphate	<b>SERS</b>	surface-enhanced Raman spectroscopy
<b>LSM</b>	(La,Sr)MnO <sub>3</sub>	<b>SECM</b>	scanning electrochemical microscopy
<b>MAS NMR</b>	magic-angle spinning nuclear magnetic resonance	<b>SFG</b>	sum frequency generation
<b>MD</b>	molecular dynamics	<b>SHG</b>	second harmonic generation
<b>MEMs</b>	microelectromechanical systems	<b>SIMS</b>	secondary ion mass spectrometry
<b>micro-IR</b>	micro infrared spectroscopy	<b>SLIM</b>	spatial light impedance spectroscopy
<b>MIDI-STEM</b>	matched illumination and detector interferometry scanning transmission electron microscopy	<b>SNOM</b>	scanning near-field optical microscopy
<b>MIEC</b>	mixed ionic and electronic conductivity	<b>SOFCs</b>	solid oxide fuel cells
<b>MOF</b>	metal-organic framework	<b>SPM</b>	scanning probe microscope/microscopy
<b>MWNT</b>	multi-walled nanotube	<b>SRS</b>	stimulated Raman scattering
<b>NanoSIMS</b>	nanoscale secondary ion mass spectrometry	<b>SSNMR</b>	solid-state nuclear magnetic resonance
<b>NCNR</b>	NIST Center for Neutron Resesarch	<b>STEM</b>	scanning transmission electron microscopy
<b>NCT</b>	neutron computed tomography	<b>STM</b>	scanning tunneling microscope/microscopy
<b>NERSC</b>	National Energy Research Scientific Computing Center	<b>STXM</b>	scanning transmission X-ray microscopy
<b>NetCDF</b>	Network Common Data Form	<b>TEM</b>	transmission electron microscope/microscopy
<b>NIST</b>	National Institute of Standards and Technology	<b>TERS</b>	tip-enhanced Raman spectroscopy
<b>NMR</b>	nuclear magnetic resonance	<b>TGA</b>	thermogravimetric analysis
<b>NV</b>	nitrogen vacancy	<b>TICG</b>	theoretically informed coarse-grained
<b>OEC</b>	oxygen evolution catalyst	<b>ToF-SIMS</b>	time of flight secondary ion mass spectrometry
<b>OER</b>	oxygen evolution reaction	<b>TXM</b>	transmission X-ray microscopy
<b>OPV</b>	organic photovoltaic	<b>TXRF</b>	total reflection X-ray fluorecence
<b>ORNL</b>	Oak Ridge National Laboratory	<b>UED</b>	ultrafast electron diffraction
<b>ORR</b>	oxygen reduction reaction	<b>UHV</b>	ultra-high vacuum
<b>PCE</b>	power conversion efficiency	<b>U-SPM</b>	ultrafast scanning probe microscopy
<b>PEEM</b>	photoemission electron microscopy	<b>UV</b>	ultraviolet
<b>PiFM</b>	photo-induced force microscopy	<b>UV-vis</b>	ultraviolet-visible spectroscopy
<b>PLIF</b>	planar laser-induced fluorescence	<b>WAXS</b>	wide-angle X-ray scattering
<b>POMs</b>	polyoxometalates	<b>XAFS</b>	X-ray absorption fine structure
<b>PRD</b>	Priority Research Direction	<b>XAS</b>	X-ray absorption spectroscopy
<b>PSI</b>	photosystem I	<b>XES</b>	X-ray emission spectroscopy
<b>QM/MM</b>	quantum mechanics/molecular mechanics	<b>XFEL</b>	X-ray free-electron laser
<b>RBS</b>	Rutherford backscattering spectrometry	<b>XML</b>	eXtensible markup language
<b>R2R</b>	roll-to-roll	<b>XPS</b>	X-ray photoelectron spectroscopy
<b>RTX</b>	real-time X-ray	<b>XRD</b>	X-ray diffraction
<b>SAXS</b>	small-angle X-ray scattering	<b>XRF</b>	X-ray fluorescence
<b>SCRP</b>	spin-correlated radical pair	<b>XRR</b>	X-ray reflectivity
<b>SEI</b>	solid-electrolyte interphase	<b>YSZ</b>	yttria-stabilized zirconia
		<b>ZSM-5</b>	Zeolite Socony Mobile-5

# Executive Summary



The scientific discoveries that expand the frontiers of human understanding, and that lead to the innovations of our technological world, require scientific tools and instrumentation to enable observation and manipulation of the physical world. As science advances, so too must its tools; the quest for deeper scientific insights and the drive to control chemistry and materials at the atomic and molecular levels require increasingly powerful and sophisticated instruments.

A secure energy future requires technologies that use existing resources more efficiently, harness renewable resources, and efficiently store energy. The urgent demand for new energy technologies has ushered in a new era in scientific pursuit to decipher the complexity found at the core of chemical and materials processes, as articulated by the basic energy science research community in its series of Basic Research Needs (BRN) workshops. Historically, novel experimental tools and methods have been foundational in both scientific and technological advances — ranging from high-resolution microscopes that “see” atomic structures, to lithography that has enabled advances in semiconductors and computing. Today, expanding the frontiers of basic research requires new generations of instrumentation to reveal the intricacies of complex materials and chemical systems; energy systems in realistic working environments; and systems that are dynamical, far from equilibrium, and extremely heterogeneous. A concerted effort to invent, design, and build scientific instrumentation will enable new scientific breakthroughs and transformative technologies to address the most pressing energy challenges of the 21st century.

To identify the highest priorities for the instrumentation innovation and development needed to address grand challenges in energy sciences, the U.S. Department of Energy’s Office of Basic Energy Sciences sponsored a workshop entitled, “Basic Research Needs for Innovation and Discovery of Transformative Experimental Tools” on June 1–3, 2016 near Washington, D.C. The workshop was attended by approximately 100 leading national and international scientific experts representing areas of basic energy sciences in chemistry, materials, physics, and biology, and included a mix of experimentalists and theorists.

Four priority research directions (PRDs) in instrumentation development were identified in the workshop.

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## **PRD 1: Establish new frontiers in time, space, and energy resolution for characterization and control**

To peer ever further into the complexity of matter and chemical transformations, it is necessary to invent new instruments and methods that break through the current resolution limits of state-of-the-art instrumentation. These capabilities will enable detailed characterization, ultimately leading to exquisite control of chemical and materials systems at the finest length, time, and energy scales.

## **PRD 2: Create innovative experimental methods for investigating “real-world” systems**

The invention and development of novel methods and instruments are critically needed to accelerate discoveries in basic science and advance critical knowledge of fundamental processes in “real-world” systems. These tools, operating at conditions as close as possible to those of functioning materials and chemical systems, will provide fundamental insight into the key processes that control synthesis and the complex chemical transformations found in real systems.

## **PRD 3: Simultaneously interrogate form and function, bridging time, length, and energy scales**

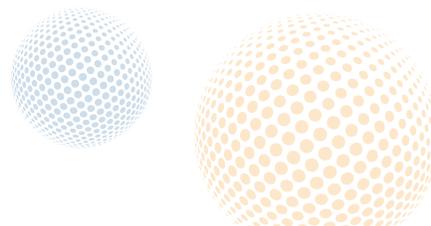
To gain unprecedented insight into complex materials and chemical systems, it is necessary to develop and implement experimental approaches that combine and integrate complementary tools to simultaneously characterize the most critical properties of these systems. The integration of multiple tools into multimodal platforms to interrogate a single functioning system will connect the underlying atomic, molecular, and nanoscale processes of these systems with their macroscopic behavior.

## **PRD 4: Drive a new paradigm for instrumentation design through integration of experiment, theory, and computation**

Integrating experimentation with computational modeling and theory at the outset of the design of an experiment or the development of a new instrument will provide entirely new platforms that enable the extraction of salient physical insights not previously attainable. Such an approach has the potential to greatly accelerate materials and chemical discovery, paving the way to next-generation energy technologies that exploit new understanding of fundamental materials and chemical processes.

Investments in the above PRDs in instrumentation, innovation, and development will yield breakthroughs in our ability to characterize, understand, and control critical energy processes. The PRDs will each have a transformative impact and will help fulfill the opportunities discussed in the 2007 “Directing Matter and Energy: Five Challenges for Science and the Imagination” and the 2015 “Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science” reports issued by the Basic Energy Sciences Advisory Committee.<sup>1-2</sup>

# I. Introduction



Grand challenges in science drive the development of new tools, and conversely, new tools enable the expansion of human knowledge into previously unimaginable areas of science. This interconnected relationship between scientific discovery and tools has been present from the beginning of modern science, when Galileo Galilei returned again and again to the design of his telescopes, striving to increase their magnifying power to reveal more of the features he was discovering on the moon and planets.<sup>3</sup>

Human ingenuity enables paradigm shifts in experimental research, and propels the creation of new instruments to advance science. To continue to accelerate scientific discovery, we must, in the words of Galileo, “*Measure what can be measured, and make measurable what cannot be measured.*” Likewise, a desire to manipulate and control chemical and materials processes at the atomic level has long been a quest in science. In his famous 1959 lecture “There’s Plenty of Room at the Bottom,” Richard Feynman asked, “*What would happen if we could arrange the atoms one by one the way we want them?*” This question captured the imagination of generations of scientists, and foretold many advances in nanoscience and modern materials synthesis.

Today, what cannot be measured but must be measured is chemical and material behavior in “real-life” energy systems that tend to be highly complex and structurally disordered. In contrast to the conventional approach in which each experiment measures a single property of an idealized system, often near equilibrium, the new frontier in instrumentation for energy sciences will be defined by innovative tools that can observe, understand, and control complex, disordered, and hierarchical chemical and materials processes. The scientific challenges ahead all point to the need for basic research involving complex materials and chemical systems, energy systems in realistic environments, and systems that are dynamical and extremely heterogeneous. Basic research provides critical insight into the fundamental processes that drive the functionality of key chemical, materials, and biological systems. These fundamental processes include: chemical reactions in liquids and at interfaces; correlation of charge in materials; molecular assembly and nucleation; electron solvation; ion transport; lattice, orbital, and spin dynamics; and the interactions of these processes on a variety of length scales. Most often they occur far away from equilibrium — meaning that the state of the system changes with time.

Experimental tools are at the heart of discovery science. The ability to invent and develop transformative tools that enable unprecedented insight into energy systems and control of the structure of materials will be a game changer across many fields of scientific research, including catalysis, physical chemistry, materials synthesis and characterization, functional materials, materials chemistry, biology, geochemistry, and geophysics. The Office of Basic Energy Sciences Advisory Committee (BESAC) articulated five new opportunities that have the potential to transform many of today’s energy-related technologies in a 2015 report entitled, “Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science.”<sup>2</sup> The report highlighted the overarching need for instrumentation development to enable transformational scientific advances. In addition, three opportunities identified in the report— 1) Mastering hierarchical architectures and beyond-equilibrium matter; 2) Beyond ideal materials and systems: understanding the critical roles of heterogeneity, interfaces, and disorder; and 3) Harnessing coherence in light and matter — directly relate to the critical chemical and materials processes in complex energy systems.

The need to drive major advances in discovery science requires transformative instruments. An untapped opportunity is afforded by the combined impact of recent advances in science and technology, such as the ability to control fundamental interactions of photons and electrons with matter; state-of-the-art user facilities and increasingly powerful bench-top sources; major advances in computational capabilities; and technological innovations such as nanofabrication, additive manufacturing, and the ability to manipulate single atoms and nanostructures.

In recognition of this opportunity and the close link between instrumentation innovation and the acceleration of discovery in energy sciences, the U.S. Department of Energy's Office of Science, Office of Basic Energy Sciences (BES) sponsored a "Basic Research Needs Workshop for Innovation and Discovery of Transformative Experimental Tools: Solving Grand Challenges in the Energy Sciences." The workshop was held near Washington D.C. on June 1–3, 2016. The goals of the workshop were to identify out-of-reach scientific opportunities related to complex energy systems and the associated instrumentation advances required to enable this research; to report the status and limitations of experimental research and state-of-the-art instrumentation; and to explore opportunities that will enable breakthrough advances through novel and transformative instrumentation.

The workshop addressed the instrumentation needs that derive from the BESAC report, "Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science," discussed above. The workshop was divided into four panels with themes that corresponded to the most prominent scientific research areas discussed in the BESAC report:

**Panel 1: Chemical reactions and transformations in functional environments**

**Panel 2: Imaging materials far away from equilibrium**

**Panel 3: Challenges of heterogeneity across multiple length scales and multiple time scales**

**Panel 4: Transformational experimental tools through integration of instrumentation with theory and computation**

The first three panels addressed the critical instrumentation needs for breakthrough advances in our understanding of chemical, physical, material, and biological processes in environments that are realistic or modeled in such a way that the knowledge gained in basic sciences directly informs the direction of future energy technologies. The fourth panel stems from the scientific community's recognition that a close integration of experimentation, theory, modeling, and computation will drive the development of powerful and transformative tools to enable major advances in energy sciences, in ways that could not be contemplated previously.

The workshop participants identified four priority research directions (PRDs) to create the tools, instruments, and methods needed to tackle these emerging directions in basic research. The PRDs emerged from crosscutting themes in the panel reports, and therefore do not have a one-to-one correspondence with the panels themselves.

### **PRD 1: Establish new frontiers in time, space, and energy resolution for characterization and control**

In order to make progress in our ability to probe local functionality, there is a need to invent new methods that surpass the resolution limits of the current state of the art, in terms of space, time, energy, and other physical parameters. There is a need to develop probes that have high levels of discrimination in order to precisely target a local phenomenon embedded in a complex environment. New methods are needed that defeat natural limits — such as diffraction-driven and space-time uncertainty-driven limits — using innovative approaches or by developing non-invasive or non-destructive methods. These capabilities will enable detailed characterization and control of the structures and chemical processes underlying the functionality of complex energy systems.

### **PRD 2: Create innovative experimental methods for investigating "real-world" systems**

Direct insights into the processes that control the performance and function of real-world energy technologies require that measurements be performed under relevant real-world conditions while the processes occur. Current practice often involves measurements performed on model systems under experimentally accessible conditions that are not directly relevant to a functioning system, with insights obtained by extrapolation. Consequently, the invention and development of instruments that enable *in situ* and *operando* measurements under real-world conditions represent a

significant opportunity. In particular, techniques are needed that can adapt to extremes in temperature, pressure, and chemical environments, and operate without disturbing the inherent functionality of the system. Such tools will provide fundamental insights that enable accelerated development of novel energy technologies.

### **PRD 3: Simultaneously interrogate form and function, bridging time, length, and energy scales**

Complex, hierarchical systems are frequently associated with the most promising emerging energy technologies and require, by definition, a detailed characterization of structure and function across a wide range of length and time scales. Given the inherent complexity of heterogeneous energy systems, there is a need to develop integrated instruments that both exploit and extend recent advances in imaging and spectroscopy across multiple length and time scales. The resulting instruments must also be able to adapt to measure different components of the system at length and time scales relevant to processes of interest. To fully characterize, understand, and ultimately control complex heterogeneous functional materials, it is necessary to develop multimodal platforms that simultaneously measure and combine multiple analytical and physical characterization modes that target the important attributes of the system under study in a correlated way. Connecting underlying atomic/molecular /nanoscale processes with macroscopic processes that are collective outcomes of large ensembles of these individual events requires multimodal tools that bridge both temporal and spatial scales. Implementation of multimodal platforms will revolutionize basic energy research in fundamental areas, including catalysis and materials synthesis.

### **PRD 4: Drive a new paradigm for instrumentation design through integration of experiment, theory, and computation**

The integration of experimentation and computational modeling and theory is essential to the future of science, and major technical advances in these traditionally separate areas of scientific research now present an opportunity to combine these elements at the outset of the design of an experiment or a new instrument. In many experiments, there is a strong link between instrumentation, data acquisition, and signal processing; and there is considerable opportunity to deepen these links to further integrate theory, computation, and novel mathematical approaches. As an example, data analytical techniques can help to extract progressively more refined information from experiments with increasing complexity or increasing size. However, in most cases there is no intrinsic feedback loop that identifies critical information in real time and redirects the subsequent measurement so that the salient information is obtained efficiently. The purposeful integration of these complementary facets of experimentation and theory from the outset will create a new paradigm of scientific instrumentation design and use in basic energy sciences. This will enable accelerated progress in understanding and exploiting the fundamental chemical and materials processes characteristic of complex energy technologies for the 21st century.

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Detailed discussions of the four PRDs are provided in Section II of this report. Section III includes the background information on instrumentation needs for prominent scientific research areas — developed as part of the workshop — and the scientific opportunities enabled by the PRDs.

## II. Priority Research Directions



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To address the grand challenges articulated in the 2007 *Grand Challenges* and the 2015 *Transformative Opportunities* reports,<sup>1-2</sup> four distinct yet complementary PRDs for instrumentation innovation and development were identified in the workshop. These PRDs address the following questions: i) How can instrumentation break through current resolution barriers to characterize and control chemical and material systems at the finest time, length, and energy scales? ii) What revolutionary new approaches are needed to provide insights into materials synthesis and complex chemical transformations of functioning systems in “real-world” environments that go beyond the use of model systems in idealized environments? iii) How can methods be integrated to simultaneously interrogate a material or chemical system to understand, control, and correlate collective behavior and properties across all relevant time, length, and energy scales? iv) How can computational modeling/theory be integrated in the design of an experiment or a new instrument to optimize measurements and enable physical insights not previously attainable?

Four panels of experts discussed specific examples of scientific challenges, the limitations of current instrumentation to address these challenges and the opportunities that will be enabled by the invention and discovery of transformative experimental tools. The reports of each of these four panels are given in Section III. The content of the reports was used to identify recurring themes for instrumentation innovation that cut across all relevant areas of basic research in materials and chemistry. These are articulated in the following PRDs.

## 2.1 PRD 1: ESTABLISH NEW FRONTIERS IN TIME, SPACE, AND ENERGY RESOLUTION FOR CHARACTERIZATION AND CONTROL

*How can instrumentation break through current resolution barriers to characterize and control chemical and material systems at the finest time, length, and energy scales?*

Atomic-scale and near-atomic-scale phenomena and structure are often critical in determining the properties of materials and the outcomes of chemical processes. Likewise, the critical steps in the evolution of structures and chemistries can take place over extraordinarily short timescales — but also need to be understood as they subsequently evolve over longer timescales. Many current experimental tools lack sufficient resolution and sensitivity to reveal structure and chemical events at short length and timescales, resulting in bulk or ensemble-averaged measurements. High temporal and energy resolution, as well as spatial resolution down to single-molecule and single-atom scales, coupled with high sensitivity, are necessary to fully understand chemical and physical processes, including chemical reactions, structural transformations, materials synthesis, and energy flow.

It is necessary to invent new instruments and methods that go beyond the current limitations of state-of-the-art instrumentation. These limitations include: energy, spatial, and temporal resolutions; probe sensitivity and degree of discrimination; probes that are invasive, disruptive, and destructive probes; and rare-event detection. The development of transformational experimental tools and novel approaches that overcome natural limits associated with the diffraction barrier, energy-time uncertainty, and other resolution barriers are important cases.

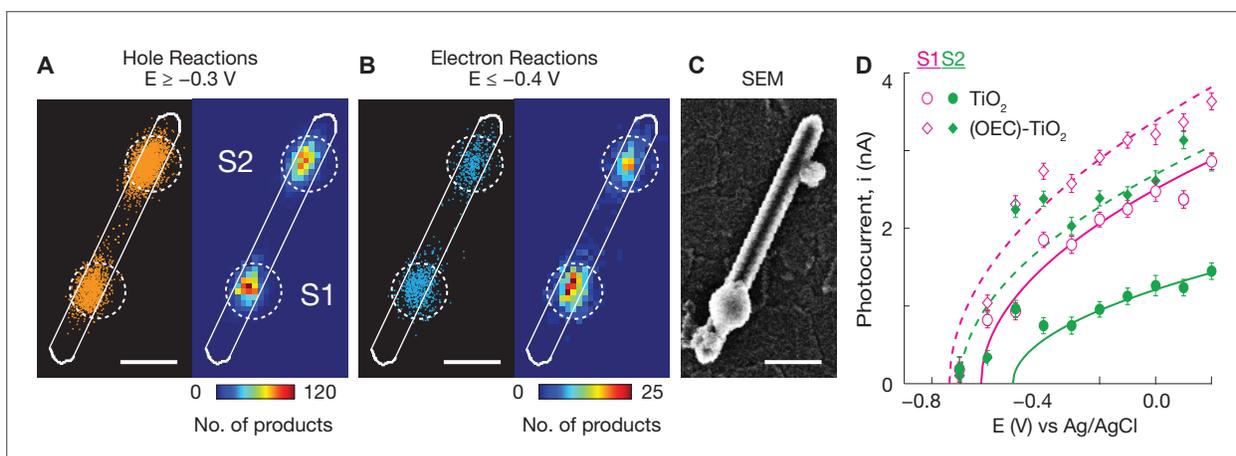
### 2.1.1 Ultrafast and Atomically Resolved Methods

Recent advances in ultrafast scanning probe microscopies, ultrafast tabletop X-ray and non-linear laser spectroscopies, and other high-resolution methods hold great promise for unraveling the governing dynamics of complex chemical transformations. Notable advances in this direction include: sub-molecular, spatially resolved electroluminescence;<sup>4-5</sup> tip-enhanced Raman spectroscopy with sub-molecular resolution;<sup>6</sup> ultrafast time-resolved vibrational spectroscopy with single-molecule sensitivity;<sup>7</sup> combined nano-pico spatiotemporal resolution through ambient photo-induced force microscopy (PiFM);<sup>8</sup> and closely related opto-thermal imaging.<sup>9</sup> Photoelectron emission microscopy (PEEM), reaches sub-femtosecond time<sup>10</sup> and nanometer spatial resolution, sufficient to characterize the time evolution of plasmons — from quantum coherent oscillations, to dephasing, to formation of hot electrons and their injection across interfaces.<sup>11</sup>

Despite major advances, these experimental tools have limitations. For example, the spatial resolution of traditional infrared (IR) microscopy is restricted by the diffraction limit to the micrometer range. Some vibrational methods, such as tip- and surface-enhanced Raman spectroscopies, overcome these limits and can image reactions at high spatial resolution. These techniques do not, however, provide structural information, and scanning may compromise the time resolution. On the other hand, aberration-corrected electron microscopes can achieve sub-angstrom spatial resolution and are routinely used to measure the atomic structures of heterogeneous materials, but are often inadequate for measuring the time and momentum space of the same systems to reveal the origin of their intriguing quantum behavior. In recent years, both X-rays<sup>12</sup> and electrons<sup>13</sup> have emerged as promising ultrafast probes to reveal atomic-level structural dynamics in real time. These techniques and other experimental methods have made progress, but are not yet approaching the required spatial, temporal, and energy resolutions to transform energy research. New methods that break through existing resolution barriers are needed. Advances and discoveries in the basic science of instrumentation innovation will enable these breakthroughs.

### 2.1.2 Local and Transient Functionality

Probes that target and quantify events and sites with high time and spatial resolution will avoid the indiscriminate effects of signal averaging, and will thus reveal the origin of local functionality. Measurements of local functionality



**Figure 2.1.1:** Single-molecule super-resolution fluorescence imaging of charge carrier reactions on a single-nanorod photoanode under photoelectrochemical water oxidation conditions (A, B), combined with local photocurrent vs. potential measurements before and after deposition of an oxygen evolution catalyst (OEC) (D), which is visualized via scanning electron microscopy (SEM) (C).

can involve quantification of reaction kinetics, electrochemical currents, light absorption, charge-carrier generation, charge transfer, or photoemission. Methods are also needed for real-time measurements of transient or rare events — for example those relevant to restructuring, poisoning, passivation, and deactivation in catalytic transformations.

New high-resolution imaging and spectroscopic tools are probing and quantifying key functionalities that are important for energy research. In addition, advances in spatially resolved spectroscopies, such as those discussed in the previous section, and established imaging tools, such as atomic force microscopy (AFM), scanning tunneling microscopy (STM) at ambient pressure, transmission electron microscopy (TEM), and secondary ion mass spectrometry (SIMS) have also been used to interrogate complex materials, and continue to be adapted and modified to incorporate additional modes and capabilities.

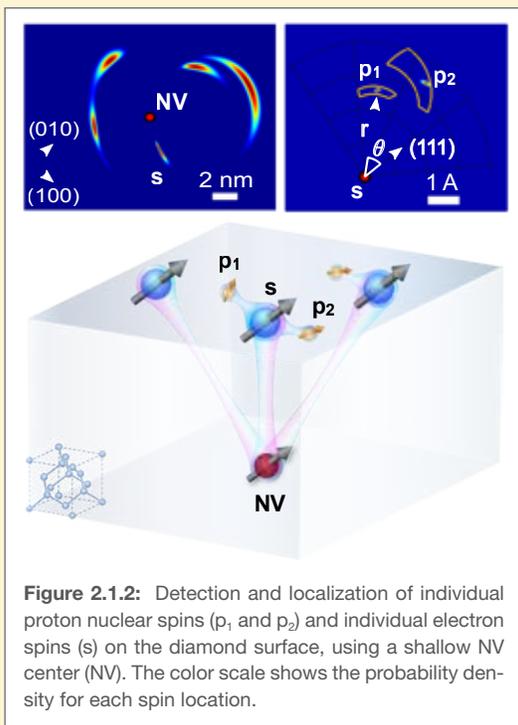
As discussed in the previous section, vibrational imaging can map functionalities such as reactions at high spatial resolution, yielding rich local chemical information regarding the reacting molecules.<sup>4</sup> Vibrational nanospectroscopy based on IR scanning near-field optical microscopy (IR-SNOM) accesses the spectral signals of molecular species and phonon modes of active phases, discriminated with nanometer spatial resolution via the strong localized fields produced at the apex of an AFM tip. New developments in monochromated scanning transmission electron microscopy (STEM) also permit mapping of molecular species and phonon modes at the tens-of-nanometers resolution. Advances in these directions could provide instrumentation with sub-nanometer resolution to probe local functionality using vibrational nanospectroscopy.

Single-molecule, super-resolution fluorescence microscopy can now image (photo)(electro)catalytic reactions and quantify the reaction kinetics of individual catalyst particles in real time, with single-turnover reaction resolution and tens-of-nanometers spatial resolution (Figure 2.1.1).<sup>14-17</sup> But these experiments are limited to the solution phase, involve fluorescent molecules, and do not provide direct, local structural information on the molecular or nanoscale objects. The next frontier is to build on all of the above and similar methods to probe local and transient functionality embedded in complex systems.

### 2.1.3 Spin and Quantum Interactions

The development of a transformative understanding of quantum phenomena — and the discovery of novel materials — face extraordinary instrumentation challenges at the frontiers of time, space, and energy resolution. Physical and chemical phenomena — such as metal-insulator transitions driven by electron correlation and catalytic behavior in exotic material systems — are often exhibited by materials with extreme sensitivity to small perturbations. Therefore, the challenges lie in: a) the detection of individual charges, orbital electrons, spins, and atoms; b) the visualization of charge density waves and spin waves, both in static and dynamic form; and c) the accurate measurement of the physical and

## MAKING USE OF QUANTUM TECHNOLOGY TO DEVELOP NOVEL NANOSCALE PROBES



**Figure 2.1.2:** Detection and localization of individual proton nuclear spins ( $p_1$  and  $p_2$ ) and individual electron spins ( $s$ ) on the diamond surface, using a shallow NV center (NV). The color scale shows the probability density for each spin location.

New precision measurement tools are at the root of transformative advances in science and technology. The recent progress in the field of quantum information science enables novel quantum-optimized nanoscale probes, giving rise to leaps in measurement capabilities. One such quantum probe is based on the nitrogen-vacancy (NV) center in diamond, used as an atom-sized sensor of magnetic fields, electric fields, and temperature.<sup>19</sup> NV centers have enabled a dramatic improvement in the sensitivity and resolution of nuclear magnetic resonance (NMR), detecting and localizing single nuclear spins and single electron spins under ambient conditions, with angstrom-level resolution.<sup>20</sup> (Figure 2.1.2) Using quantum logic to further improve sensitivity, NMR spectra of single protein molecules have been detected, with spectral features revealing information about their chemical composition.<sup>21</sup>

Several technical advances are needed to turn this approach into a truly multi-functional tool for studying heterogeneous systems and materials at the nanoscale. The NV-based sensors have to be integrated with a wide range of material systems and conditions (temperature, pressure, chemical environments); the physical and chemical stability of diamond makes this a promising way forward. Heterogeneity necessitates access to a broad range of spatial and temporal scales, which can be

achieved by going beyond a single-NV sensor to construct and make use of arrays and networks of sensors, making use of coherence and/or entanglement.

NV center-based nanoscale-NMR is a novel experimental method that operates under ambient conditions and without high-field magnets, which makes it a versatile and portable tool, ideally suited for university-laboratory-scale investigation, bringing together methods and ideas from a wide range of disciplines, including precision metrology, quantum science, and materials science.

chemical nature of atomic-sized defects and impurities, not only on a sample surface, but also embedded in bulk and in heterostructures and in three dimensions. An example in improving detection sensitivity is the recent breakthrough in measuring single nuclear spins using a quantum probe based on the nitrogen-vacancy center in diamond, as illustrated in the sidebar.

Utilizing quantum effects for next-generation materials and information technologies requires knowledge of the interactions and competing degrees of freedom of charge, orbital, spin, and lattice. Quantum effects include: coherence and entanglement of electrons and photons, often subtle forms of emergent and topological order, and antisymmetric spin-orbit couplings. The progress of the field calls for novel ideas in instrumentation and methodology development, including utilizing the very quantum mechanical nature of the interference of optical waves, not only in ambient environments, but also at low temperature and under pressure. Scanning tunneling spectroscopy, high-resolution electron tomography, spin-polarized scanning probes, and angle-resolved photoemission spectroscopy are just a few techniques at the forefront. The developments needed include brighter sources, novel optics, innovative detectors, and imaging and spectroscopy instruments with extreme stability for unprecedented spatial, energy, and time resolutions that can offer game changing advances in the field.

Tools to probe the range and topology of the underlying quantum entanglement of quantum materials are needed. Though it is apparent that entanglement is an important feature of quantum materials, no experimental method is

currently available to probe it. Innovative new methods are needed — perhaps involving entangled photons, entangled neutrons, or quantum coherent light sources. The scientific drivers for novel instrumentation related to this topic are presented in the recent Quantum Materials Basic Research Needs report.<sup>18</sup>

## **SCIENTIFIC ADVANCES ENABLED BY THE PRD**

Advances in instrumentation resolution and sensitivity will enable major progress in a wide range of energy sciences. For example, progress in solar chemical conversion will require mastery of dynamical processes that proceed on multiple timescales on heterostructures with structural features that range from molecular to macroscopic. Elementary steps such as photoinduced charge separation occur on femtosecond timescales with charge injection rates and efficiencies that depend on interfacial structure, most likely at the atomic scale. To make meaningful progress, it is essential to understand the governing heterogeneous structural and dynamical processes on the space and time scales of relevance. Among the emerging directions of research, plasmonically driven heterogeneous catalysis provides particularly rich new opportunities. Plasmonic nanostructures serve as nanoantennas to couple far-field radiation into molecules. Theoretically guided design and fabrication will be required to design/engineer structures dedicated to enhancing photocatalysis of key reactions, such as water splitting. More exact characterization through further development of temporally and spatially resolved spectroscopies will enable the controlling science to better inform the design of such functional materials.

## 2.2 PRD 2: CREATE INNOVATIVE EXPERIMENTAL METHODS FOR INVESTIGATING “REAL-WORLD” SYSTEMS

*What revolutionary new approaches are needed to provide insights into materials synthesis and complex chemical transformations of functioning systems in “real-world” environments that go beyond the use of model systems in idealized environments?*

Much of what we know about the fundamental chemical and material phenomena that underlie current energy technologies derives from the use of model systems and *ex situ* observations. While this has been a successful approach for understanding many processes, the complexity of the functional environments of many energy systems gives rise to structures and processes that are both complex and dynamic, and therefore cannot be evaluated by current approaches. Examples of such energy processes include: materials synthesis, materials degradation, chemical transformations, electrochemical conversion, as well as ion and electron transport across functional interfaces. Researchers have long recognized the need for characterization and control of these processes in their intended operating conditions, but the challenges are significant. Recreating real-world conditions in the confines of a laboratory setting is a formidable challenge, especially characteristics that include high temperatures and pressures, corrosive or contaminating fluids and gases, and highly heterogeneous sample environments. A new generation of scientific instrumentation is required to investigate operating energy systems in a non-destructive manner without either disturbing the process of interest or compromising the nominal resolution of the technique.<sup>22</sup>

This priority research direction is intended to accelerate progress toward *in situ* and *operando* measurements over a broad range of chemical and material processes of relevance to energy sciences. The developments of *in situ* and *operando* capabilities are needed across the disciplines of materials, chemistry, and biology (specific examples can be found in Section III of this report). Progress is needed in two broad areas: the development of novel reactors, *in situ* devices and chambers, and windowless cells that reliably reproduce functional conditions under which energy processes can be investigated; and the development of novel methods or instruments that operate at conditions as close as possible to those of the functioning material or process.

### 2.2.1 *In situ* and *Operando* Characterization of Active Sites and Intermediates in Complex Transformations

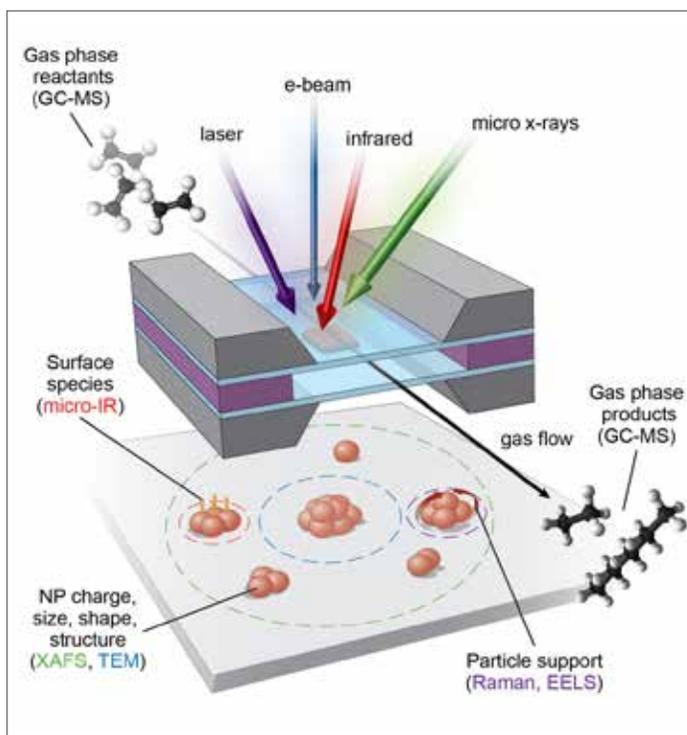
The challenges to identify, measure, and quantify the active sites and intermediates that control complex chemical transformation processes at relevant spatial and time scales in functional environments are tremendous. The recent surge in *in situ* and *operando* research on chemical transformation and conversion processes of energy materials reflects the need for such capabilities and their promise to yield important new discoveries. However, acquisition of brand-new physical and chemical information requires a substantial investment in the development of novel methods and instrumentation to facilitate the understanding of functional systems. For instance, today time-resolved X-ray spectroscopy can be used to investigate the migrating electron during photo-induced interfacial charge transfer or to identify transient molecular configurations in the transition-state region of a surface-catalyzed chemical reaction (Figure 2.2.1).<sup>22</sup> The materials of interest, nevertheless, cannot be studied under *operando* conditions that ultimately provide the direct link between fundamental insights and application-relevant processes. Furthermore, fully understanding energy-related chemical transformations involves three-dimensional characterization of reactants and products that may be in the solid, liquid, or vapor state, or as minor components of a complex mixture. Current state-of-the-art experimental tools, optical methods, electron microscopy, X-ray spectroscopy, and scanning probes do not provide the needed spatial, temporal, or energy resolution in functional environments.<sup>23</sup> There is a strong need for novel instrumentation that measures the real-time dynamics of excitation or electron transfer, bond breaking and formation, the formation of transient chemical intermediates, restructuring, poisoning, passivation, and deactivation, all in “real world” functioning environments.

## 2.2.2 Characterization, Manipulation, and Control of Organization, Structure, Defects, and Interfaces

“Real world” materials are often far from perfect, and contain defects and interfaces that give rise to intriguing properties. Local disorder and defects can significantly modify desired electronic properties and behavior such as enhanced electron scattering or exciton recombination. Characterizing and manipulating these defects and interfaces, as well as molecular assembly and organization in multiple dimensions, enables us to understand, control, and improve overall material functionalities. Measurements of materials in their “real world” environments will allow transformative science and technology discovery and innovation. These environments include solid-solid interfaces during materials growth, liquid-liquid and liquid-vapor interfaces during fuel combustion, and liquid-solid interfaces in corrosion prevention and energy storage applications, to name a few.<sup>24-25</sup> Achieving the required temporal, spatial, and energy resolution simultaneously in such measurements requires the invention and development of groundbreaking experimental tools.

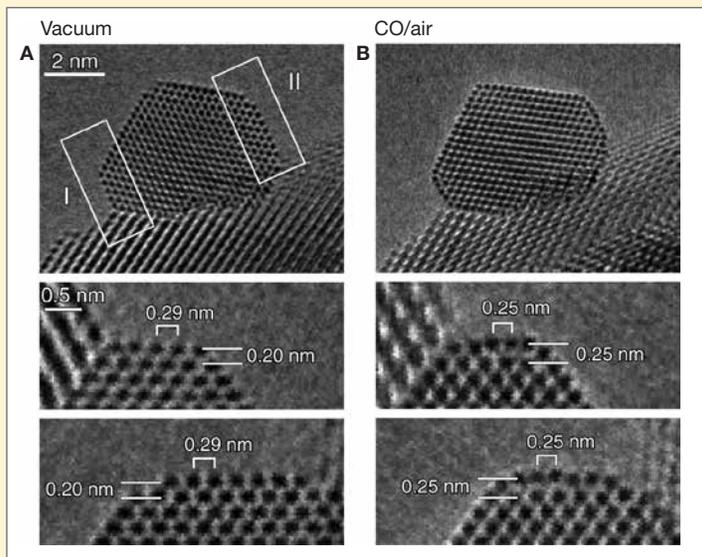
Transmission electron microscopy (TEM) is widely used to study individual defects and interfaces in materials. Its current state of the art can image individual defects and solid-solid interfaces at atomic resolution, and in some ideal cases of thin samples, even in three dimensions. Future TEM techniques must be able to image atoms and molecules and their electronic states, not only on surfaces (using secondary electrons), but also in the bulk (using transmitted electrons) and in liquid and gas environments; the innovative design of liquid and gas cells for electron microscopy is crucial. Techniques based on X-ray scattering are arguably the most used approach to study materials in complex liquid and gas environments due to the large penetration depth of photons. Optical methods such as ballistic imaging,<sup>26-27</sup> shadowgraphy<sup>28</sup> and X-ray fluorescence<sup>29</sup> are being used to study solid-liquid-vapor interfaces, but each has limitations in terms of spatial resolution and/or image size and temporal resolution. For example, in studying the process of corrosion, the liquid constantly changes the measurement of the liquid/solid interface, requiring control of the liquid in ways that are not generally available at present. Well-defined flow patterns that take advantage of microfluidic technology will allow the delivery of reactants to be controlled. Breakthroughs in this area would have broader implications for energy research, such as revealing the catalysis process for electrochemical water splitting, the evolution of processes at solid-electrolyte interfaces in batteries, and the mechanism of atom-by-atom growth during materials synthesis. The characterization, manipulation, and control of specific properties under functional conditions of individual defects, interfaces, and their assemblies in energy systems are not currently within our grasp because of their dynamic nature.

Understanding how metastable defect and interface structures develop under far-from-equilibrium driving forces is a challenge due to increased dynamic rates. A clear opportunity is to develop low-dose imaging capabilities with atomic or molecular spatial resolution, relevant temporal resolution, and meV-energy resolution, to determine



**Figure 2.2.1:** Schematic of a catalytic microreactor that is capable of being probed by photons and electrons, allowing correlative experimentation through *operando* characterization. The various probes and the resulting information that can be gleaned from the data are indicated in the figure, with techniques that include gas chromatography-mass spectrometry (GC-MS), micro infrared spectroscopy (micro-IR), X-ray absorption fine structure spectroscopy (XAFS), and electron energy-loss spectroscopy (EELS).

## CHALLENGES OF CHARACTERIZING REACTING SYSTEMS



**Figure 2.2.2:** TEM images of the surface structure of a gold nanoparticle in (A) vacuum, showing predominantly a bulk terminated structure, and (B) in presence of CO, showing outward relaxation of top (100) layer. The two lower figures for A) and B) are higher magnification images from the boxed regions showing changes in plane spacing as a result of changes in the reactive gas.

As an example of an *in situ* study, high-resolution transmission electron microscopy (TEM) has been used to characterize the change in gold nanoparticle surface structure with changing gas atmospheres relevant to CO oxidation. As shown in Figure 2.2.2,<sup>32</sup> gold nanoparticles in vacuum exhibit a mainly bulk terminated structure, whereas outward relaxation of the surface is observed in the presence of CO.

Recent years have seen dramatic improvements in the ability to characterize the electronic and geometric structure of the resting state of inorganic materials. There have also been significant advancements in X-ray-based absorption spectroscopy techniques, which allow for *operando* measurements; however, these measurements yield information about the average behavior of systems without providing spatially resolved information. Similarly, enzymatic and cellular systems are now being studied using

electrochemical, microscopic, and traditional spectroscopic techniques at electrode interfaces. However, the measured observables (interfacial rates, redox potentials) generally do not unravel the molecular charge transport pathways and resolve the timescales of elementary charge-transfer steps by which individual subunits communicate with each other. Additional limitations stem from the lack of information about the chemical state (e.g. oxidation state, local chemical composition) of the active centers, particularly at the functional interfaces.

Advancements in techniques that shed light on spatial heterogeneity and temporal evolution of the functioning systems are required to develop truly predictive energy-related systems and technologies. It is imperative that these techniques operate at conditions as close as possible to the functioning process conditions. To address inorganic catalytic materials, interface-sensitive techniques are required, much like surface-enhanced Raman and infrared spectroscopies, but with optimized spatial and temporal resolution. Overcoming the limitations in bioelectrocatalytic systems will require the development of *in situ* non-invasive instrumentation that integrates electrochemical techniques, beyond-diffraction-limit microscopy (e.g. super-resolution optical or scanning probe), and multidimensional and surface-sensitive spectroscopies to capture the heterogeneity of rates, molecular makeup, and chemical environment supporting interfacial charge transfer.

which interactions are dominant and how they progress in a changing reaction environment. The study of mixed liquid-vapor-solid states poses an even greater challenge. Corrosion-related materials degradation, for example, is characterized by the concurrent transport of mass and charge across the solution/metal interface, where anodic and cathodic processes can occur simultaneously at different sites of the same material. Currently, fundamental knowledge about the chemical bonding of inhibitor molecules to metal surfaces — as well as the exact nature of the metal surface in contact with the solution and the inhibitor molecules — is lacking. Thus, our ultimate understanding and control of corrosion processes is limited. The development of instrumentation that can elucidate the molecular-scale mechanism of corrosion inhibition will revolutionize the field across a wide range of metals and metal alloys. Further, most of the current characterization methods to locally probe materials in electrochemical cells depend on destructive analysis, recovery of the electrodes, and analysis of the surfaces by spectroscopic techniques such as Raman, fluorescence, and infrared spectroscopy. Pushing the current limits of *in situ* and *operando* techniques would enable

non-destructive characterization of these materials to gain direct insight into the key processes of chemical reaction mechanisms, which could lead to opportunities to design better energy materials and inhibit or prevent degradation of materials.

## SCIENTIFIC ADVANCES ENABLED BY THE PRD

Understanding the critical roles of heterogeneity, interfaces, and disorder, as well as the critical chemical and materials processes in complex functional energy systems, are BES Grand Challenges. Advances in this PRD will accelerate progress toward the ability to perform measurements in realistic functioning environments over a broad range of chemical transformations and material processes of relevance to energy technologies. It will also enrich our knowledge of “real world” materials that are complex and contain defects, grain-boundaries, and interfaces, as well as structural, chemical, and electronic disorder. Direct insights into the most important processes that control the performance and function of real-world energy technologies require making measurements, such as detection of all chemical species and their electronic states on the surface, at the interfaces, and in the bulk, under relevant conditions as the processes occur. Interrogation of materials in functioning liquid and gas environment at atomic and molecular scale will transform our understanding of, for instance, catalysis mechanisms for facilitating energy conversion, ionic transport for improved battery performance, and fuel sprays in combustion for optimizing engine efficiency.<sup>30-31</sup>

The challenges to visualize, measure, and quantify the process of physical and chemical transformation and conversion under “real-world” environments also bring tremendous opportunities that might help us one day to control synthesis and chemical reactions, optimize energy generation and storage, and prevent degradation in materials performance. Using catalysis as an example, local structures typically transform under reaction conditions in the presence of reactants, intermediates, and products. Such transformations are important to advance energy technologies. Nanoparticles and porous materials used for catalysis contain highly reactive under-coordinated active sites that are dynamically transformed by their interaction with reactants. Measurements of local functionality can involve quantification of reaction kinetics, motions of large molecules, electrochemical currents, light absorption, charge carrier generation, charge transfer, or photoemission.

Novel materials synthesis and control is another forefront of energy science and technology research. Phase transformation and atom-by-atom growth are non-equilibrium processes. Innovative *in situ* tools are needed to synthesize, characterize, manipulate, and control complex nanostructured materials and molecular assemblies with desired purities and controlled defects and dopants. Success in this research and development area would advance the field of materials by design to determine, understand, and control the process and pathway of reaction, deposition, and assembly for metastable, thermodynamically permissible, and kinetically stabilized phases of high-value energy materials. It is critical to understand the constituent atomic and molecular species, correlations, and dynamics at the growth front as a function of time, advancing the state-of-the-art in *in situ* characterization of liquid and vapor phases. The development of innovative experimental methods and instrumentation for investigating “real world” materials systems will yield revolutionary advances in our ability to characterize, understand, and control energy processes under functioning environments at the full complement of relevant time, energy, and length scales.

## 2.3 PRD 3: SIMULTANEOUSLY INTERROGATE FORM AND FUNCTION, BRIDGING TIME, LENGTH, AND ENERGY SCALES

*How can methods be integrated to simultaneously interrogate a material or chemical system to understand, control, and correlate collective behavior and properties across the relevant time, length, and energy scales?*

The current state of the art for characterizing heterogeneous materials includes a wealth of techniques — including physical and spectroscopic measurements — that have significant individual strengths. It is now possible to obtain atomic-resolution images with chemical information. Scattering techniques yield detailed structural information from ensembles of molecules and systems with translational symmetry.<sup>33</sup> Spectroscopic approaches, such as those built on advances in phase-stabilized ultrafast lasers, provide local electronic structure and chemical dynamics information with elemental specificity and femtosecond resolution. Overall, we have made great strides to characterize the resting state of materials in terms of their electronic and atomic structure with high spatial resolution.<sup>34-36</sup> Ultrafast and time-resolved measurements are often performed on single components extracted from heterogeneous functional materials.

To understand and control heterogeneity, characterization methods are needed that are responsive to multiple physical properties at different length and time scales. The ideal case is complete probing of the spatial distribution of relevant chemical speciation, physical properties, and excitation dynamics on all relevant length and time scales with multiple modalities. In some cases, measurements of transient states could provide important insight into materials functionality.

There are several broad categories of the limitations of current techniques for characterizing the full interrelationships of the properties, structures, and dynamics of complex heterogeneous systems. For some cases, it is still not possible to resolve the natural spatial and time scales of key processes, but increased resolution, for the most part, is no longer what prevents techniques from addressing multi-scale heterogeneity. In order to characterize the impact of heterogeneity on physical processes, it is not enough to simply measure heterogeneous spatial or temporal distributions of individual properties — we must be able to correlate different properties that affect each other. For example, state-of-the-art characterization methods for materials growth coupled with local probes of magnetic and electric properties would represent a major advance in materials design. Overcoming current limitations will require the development of *in situ* non-invasive instrumentation that integrates atomic resolution imaging techniques, electrochemical techniques, beyond-diffraction-limit microscopy, and multidimensional and surface-sensitive spectroscopies to capture the heterogeneity of rates, structural makeup, and chemical environments.<sup>37</sup> Correlation of such observations becomes substantially more difficult when the system is dynamic or transient. As a result, one frontier in instrumentation is simultaneity — implementing multiple types of probes at the same time on the same sample.

### 2.3.1 Multimodal Probing of Heterogeneous Systems with Complementary and Correlated Measurements

Multiple modes do exist in advanced imaging systems, notably those based on electron microscopy, albeit with limited capacities to broadly span the full range of the spatial, time and energy “five-dimensional” scaling needed to fully understand the role of heterogeneity. Typical characterization protocols currently utilize only a few techniques, and these methods are usually applied sequentially. Sequential approaches have the potential to miss complex interactions in the material. As such, there is an opportunity for the development and implementation of tools for simultaneous multimodal characterization of the most critical features of composition, bonding, dynamics, and electronic structure that define the varied natures of multi-scale heterogeneity in complex material and chemical systems.<sup>38</sup> Novel X-ray free-electron laser sources enable new approaches for time-resolved simultaneous and even coincident imaging and spectroscopy approaches, for example of the water oxidation step of natural photosynthesis.<sup>39</sup> So far, the developments are still in their infancy and restricted to model systems, but further advances may enable groundbreaking coherent X-ray spectroscopy

methods, for example.<sup>12</sup> To fully characterize, understand, and ultimately control complex heterogeneous functioning materials, it is necessary to develop platforms of multimodal methods of analytical measurements and physical characterization that target the important attributes of the system under study in a correlated way. The realization of these platforms will require the invention of new approaches that can overcome the physical restrictions or incompatibilities of different instruments or probes, e.g. combining high magnetic field NMR with low-energy electron detection methods such as angle resolved photoelectron spectroscopy (ARPES).

A major advance in our understanding of phenomena such as charge-carrier dynamics would be achieved if simultaneous measurements were carried out in the time domain, to image the charge-trapping process in real time, e.g. via time-resolved scanning tunneling spectro-microscopy, to simultaneously characterize structure, energetics determined by local electronic states, and the governing mechanism of charge-trapping.<sup>40</sup> The principal instrumentation advance required to achieve this science is the integration of tools — e.g., integration of ultrafast laser capabilities with scan probes — for joint imaging of spectral, spatial, and temporal dimensions. Integration of characterization methods such as mass spectrometry, UV-vis, IR, NMR, X-ray spectroscopies, or electron microscopies has the potential to illuminate previously unobservable aspects of materials synthesis or chemical transformations in complex environments. A priority is to develop platforms that integrate some of these instruments and methods — as well as other important tools used in basic energy research — by overcoming their incompatibilities.

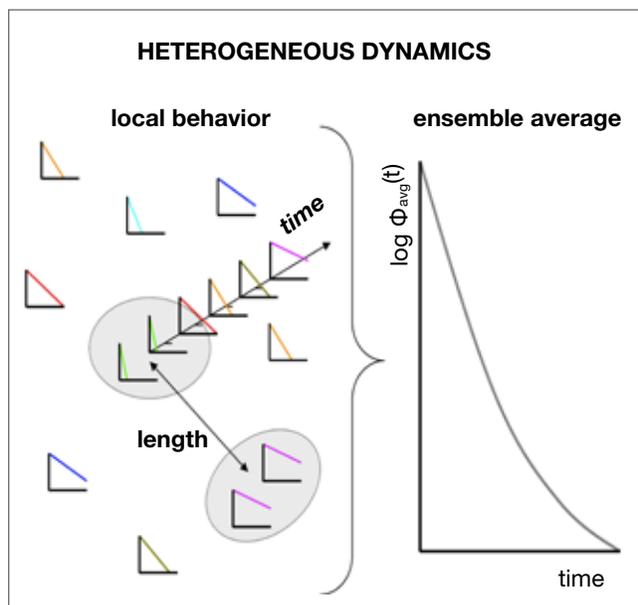
### 2.3.2 Probing Functionality Across Multiple Time Scales and Length Scales

Complex functional systems are often dynamical and/or extremely hierarchical, and detailed characterization of their structure and function requires the invention of novel experimental tools that seamlessly bridge length and time scales. A high priority target is the development of instrumentation that provides spatial resolution across all relevant length scales and that correlate the atomic or nanoscale structural or dynamical behavior of materials to their macroscopic function. Such instrumentation should provide atomic resolution, both on surfaces and in bulk, while enabling full structural and chemical characterization that spans the atomic to ~micron or larger length scales. The instrumentation must enable measurements that are rapid enough to characterize the structural changes occurring in energy materials during both their synthesis and use.

Another high priority target is the development of non-invasive instrumentation that provides temporal resolution across all timescales relevant to the function of the material. Attosecond spectroscopies can follow the motion of electrons, and the technology continues to develop rapidly.<sup>41-44</sup> Spectroscopic approaches capable of characterizing ultrafast processes such as energy transport and charge separation are typically limited in spatial resolution and sensitivity.<sup>45</sup> These measurements usually focus only on specific events rather than the entire evolution of the material or chemical system. There is a need to develop transformative tools to enable high resolution, high sensitivity, spatially-resolved, and multidimensional optical and X-ray measurements. Such measurements should combine frequency regimes to provide complementary electronic and vibrational structure and dynamics over several timescales relevant to material function and evolution of the material during operation. Developing instruments that can characterize and control the essential attributes of spatiotemporal heterogeneity will provide an opportunity for breakthrough advances in energy research.

## SCIENTIFIC ADVANCES ENABLED BY THE PRD

Heterogeneity is an inherent attribute of all energy systems and processes of interest in energy technologies. The degree of heterogeneity, and to what extent it occurs either spatially or temporally, varies significantly from system to system. When observed for varying extents of time or ranges of distance, the properties of heterogeneity in materials and chemical systems may disappear in one regime only to reappear in another, where dominating influences on structures, mechanisms of action, and forms of transformation are seen (Figure 2.3.1).<sup>46</sup> In some of the most prominent energy conversion systems, the dynamical and structural heterogeneities are inextricably mixed, and therefore require coupled resolution in both space and time.<sup>47-48</sup> This PRD will enable this coupled characterization both in space and time in these complex systems. Such complexity underpins frontier interdisciplinary problems spanning the physical (physics, chemistry, materials), natural (biology, atmospheric and geological), engineering and mathematical sciences.



**Figure 2.3.1:** An illustration of how heterogeneous dynamics in pure viscous liquids (a non-exponential approach to equilibrium known for more than 150 years) can arise from a distribution of microdomains, each of which relaxes exponentially (local relaxation), i.e., there is an underlying spatial heterogeneity that is much more difficult to observe. The ensemble average,  $\Phi_{\text{avg}}(t)$ , is the superposition of these exponential processes.

behavior. The first class involves the temporal evolution of materials that is driven by an explicit thermodynamic driving force. The second class involves non-equilibrium configurations of matter that can be used to produce novel functional properties (metastability). In both areas, most research has relied on the observation of materials in “frozen” states, or the measurement of spatially or temporally averaged behavior. These approaches fail to capture the inherent dynamics associated with non-equilibrium states as they develop — including processes by which nanostructured materials can be assembled — as well as the complex evolution of these non-equilibrium materials under operating conditions. The development of novel time-domain characterization tools that bridge several interrelated time scales described in the PRDs of this report offer a unique opportunity to discover the emergent properties of materials. This can be done by tuning excitation energy via transient photo-doping, vibrational or electronic pumping, spin excitation, and other thermodynamical excitation drivers, and watching the evolution of the characteristic parameters of the energy system as a function of time. Similarly, this PRD will enable the creation of novel persistent metastable materials with unique functionalities through observation and control of the dynamical assembly of matter in real-time with chemical specificity.

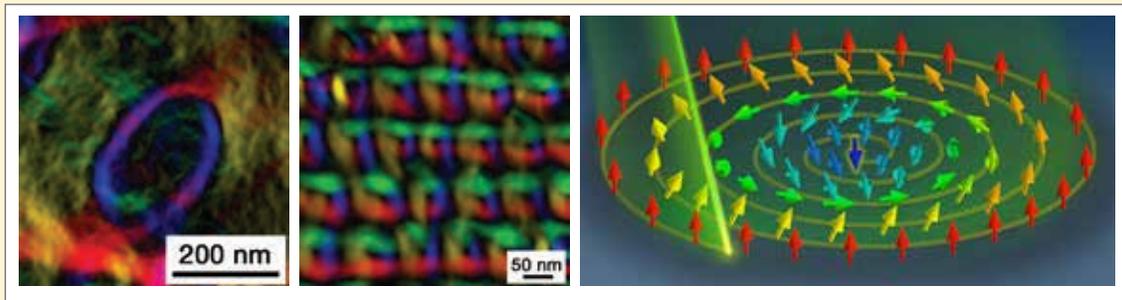
To make meaningful progress in solar energy conversion and storage, it is essential to understand the governing structural and dynamical processes over multiple time and length scales of relevance. The elementary step of photo-induced charge separation occurs on femtosecond timescales with charge injection rates and efficiency that presumably depend on interfacial structure, most likely atomic scales. Charge transport, which is often the rate-limiting step and the source of inefficiency via charge trapping, involves multiple spatiotemporal scales. Carrier, delocalization, tunneling, migration, and self-trapping remain ill characterized, hindering the determination of reliable design principles required to make significant advances. This PRD will provide the experimental tools that will enable breakthrough advances in solar energy conversion and storage research by revealing the key properties across time and length scales.

Spatial heterogeneity is essential to the effectiveness of materials for relevant processes including energy harvesting, conversion, and storage. For example, the nucleation of particles from an initially homogeneous solution, and their subsequent growth and aggregation, are central processes to a wide range of energy-relevant applications and are primary dynamical features of the chemical synthesis of nanomaterials.<sup>49</sup> These can lead to complex dispersions of nanomaterial sizes and composition, such as those seen in supported heterogeneous catalysts, for example. Spatial heterogeneity occurs in systems of mixed material phases, but can also be important within a single phase, for example in compositional and temperature gradients coupled to chemical transformations in a turbulent combustion environment.<sup>50-52</sup> An additional example involving spatial heterogeneity in quantum materials is illustrated in the side bar.

Temporal heterogeneity is inherent in many important natural and technological phenomena that occur away from equilibrium. The role of non-equilibrium processes is manifested in two broad classes of

## MULTISCALE IMAGING FOR QUANTUM MATERIALS

In this “big data” era, the quest for next generation energy-efficient information technology has encouraged research in quantum materials at the nanoscale. One concrete example is the potential to exploit skyrmions as information carriers. A skyrmion is a topological spin texture whose spins point in all directions wrapping a sphere, with the spins at the skyrmion core and at the outer edge pointing out-of-plane in opposite directions. Technologically, it has been predicted that skyrmions can be efficiently controlled using spin transfer-torque effects, thus requiring very low electric current to drive their motion. In spite of recent progress, there are still severe limitations in our ability to harness the fundamental physics of skyrmions, and emergent phenomena in quantum materials in general, for device applications. There is a need for improving the sensitivity and resolution of existing characterization tools, for developing new non-invasive tools, and for combining complementary tools. These tools need to operate over a wide range of spatial resolution to understand how local properties affect global characteristics, to understand the effect of disorder and heterogeneity on functionality, and to access and control order that emerges on different length scales. For example, in thin-film skyrmion devices, we need to correlate atomic-scale structure (interface roughness, structural defects) with the three-dimensional spin structure at the nanometer scale and the desired transport behavior at the mesoscale, requiring the development of novel nanoscale magnetic probes, integrated with the application of stimuli and appropriate time resolution (Figure 2.3.2).<sup>53-54</sup>



**Figure 2.3.2:** Specialized transmission electron microscopy of magnetism, in combination with simulations, allows observation of skyrmion formation, behavior, and stability. A skyrmion is a topological magnetic structure with spin directions (imagine tiny North-South magnetic poles) that are twisted in an axially symmetric vortex-like geometry such that the spin arrangement is not easily perturbed. Skyrmions have potential uses in transporting information because they are tiny, stable, and easily controlled with very low electric currents.

## 2.4 PRD 4: DRIVE A NEW PARADIGM FOR INSTRUMENTATION DESIGN THROUGH INTEGRATION OF EXPERIMENT, THEORY, AND COMPUTATION

*How can computational modeling/theory be integrated in the design of an experiment or new instrument to optimize measurements and enable physical insights not previously attainable?*

Integration of experimentation with computational modeling and theory at the outset of the design of an experiment or the development of a new instrument will provide entirely new instrumentation platforms that optimize measurements to enable the extraction of salient physical insights not previously attainable. This Priority Research Direction expresses the paradigm shift in scientific investigation by the design and integration of all experimental components with theory and simulation. To meet challenges associated with the co-design of instruments with theoretical input and data, new computational methods, applied mathematics, and hardware are required that will maximize the information extracted from multidimensional real-time datasets, improve interpretation of experimental results, and provide on-demand analysis as information is being generated at unprecedented rates.

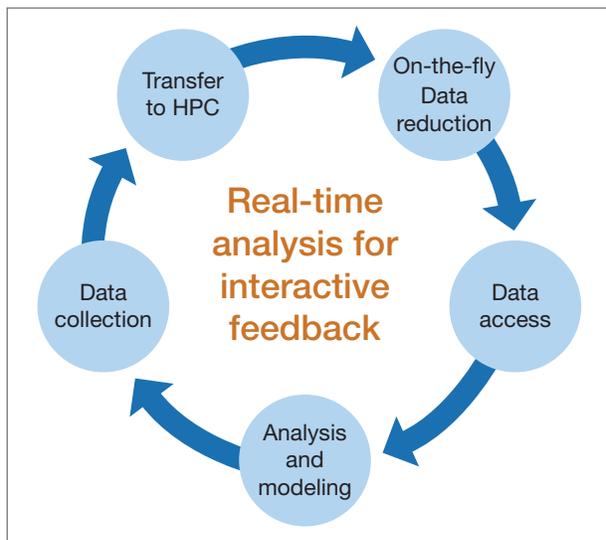
Substantial parallel advances in instrumentation science, theoretical modeling, and applied mathematics have advanced our understanding of energy materials and chemical processes. Rapid advances in instrumentation for imaging, spectroscopy, and measurement of materials function have led to an explosion of new data. In parallel, new theoretical models, new algorithms for data analysis, and methods for archiving and analysis of large data sets are separately being developed. Together, experiments, theory, and new mathematical methods can have a major impact of our understanding of critical functionality. The existing paradigm for combining experiment and simulation for discovery and development of new materials and processes has already led to advances in energy sciences. However, it is most often linear/sequential, in the sense that experiment precedes modeling or vice versa, instead of occurring in a parallel and integrated manner, building on information generated during an experiment, and therefore is slow and inefficient. In addition, it is frequently limited by inadequate methods and instrumentation with insufficient resolution. In most cases, neither the computational methods nor instruments take advantage of existing data or data generated on the fly. In short, the current paradigm does not achieve the full potential of these powerful tools. There is a need to drive a new paradigm for instrumentation design through full integration of experiment, theory, computation, and data.

### 2.4.1 Real-Time Analysis and Control to Optimize Experimental Output and to Guide Subsequent Experiments

Current state-of-the-art experiments involving complex systems relate measured parameters to the system's function only after the experiment is completed. This experimental approach severely limits the ability to rapidly analyze, redesign, and redirect critical energy processes such as material synthesis or complex chemical transformations. There is an opportunity to develop a comprehensive and integrated approach in which experiments are guided on the fly with adaptive multi-physics models that provide feedback on real-time data (Figure 2.4.1). Such an approach has the potential to greatly accelerate materials discovery and understanding, and enhance our ability to make use of new phenomena in complex materials for energy applications. Achieving this goal requires advances in theory, simulation, and modeling across vast length and time scales, as well as new paradigms in algorithms aimed at data analytics and machine learning. These new approaches will be required to take advantage of concurrent revolutions in instrumentation, such as the development of faster, higher-resolution detectors; the advent of robotics capable of high-precision automated multistep protocols and workflows; and the rise of multimodal measurements, generating disparate yet correlated multidimensional datasets on the same sample. Truly capitalizing on these advances in instrumentation will necessitate new approaches to data collection, archival storage, and provenance. Taking a step further, integration of adaptive models, analytics, and real-time feedback with these new experimental tools will facilitate real-time, autonomous extraction of information from heterogeneous datasets and provide direct feedback to experiments. Importantly, this approach will accelerate the development of predictive simulation of experimental observables with the goal of reducing the number of trial-and-error measurements and enhancing the pace of discovery and the depth of understanding.

A wide range of computing resources and new algorithms will be required to fully capture and analyze the volume of data involved. This includes new methods to triage, accelerate, and scale up the analysis of data to provide real-time feedback for researchers. These methods also offer radically new experimental approaches driven by machine learning, for example, where random sightings of a freely evolving system replace traditional tightly controlled experiments.

Advances in the science of data organization, visualization, and analysis are also required to fully exploit the information in massive complex datasets. To that end, dedicated coupled data visualization, mining, and analysis approaches must be developed. One such example is SpectraMiner,<sup>55</sup> bespoke software that enables the handling of data of properties of millions of catalytic particles, while avoiding loss of information. When combined with GPU-accelerated incremental correlation clustering,<sup>56</sup> it provides the user with a visually driven and intuitive interface to easily access and explore the data on millions of particles in real time. Thus, redundant data points are detected and eliminated so as to identify a few “golden nuggets” in vast amounts of data.



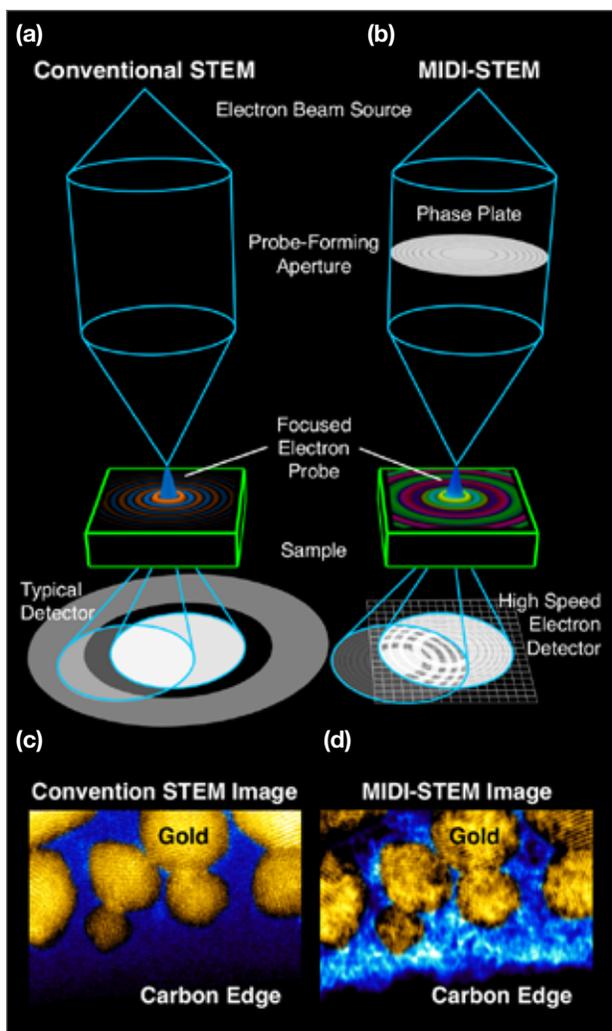
**Figure 2.4.1:** Schematic of implementation of real-time analysis for interactive feedback to experiments. Co-design of instrumentation, theory, algorithms, and data flow is required, including transfer to high-performance computing (HPC).

## 2.4.2 Assimilation, Analysis, and Integration of Complementary Data from Multiple Experiments

As summarized in PRD 3, the complex nature of heterogeneous systems requires complementary measurements from a spectrum of different experiments that must be analyzed as a whole. Understanding correlations among disparate data sets is a challenge that, if met, will be game-changing for the understanding and design of functional materials and chemical systems. Recent breakthroughs in high-resolution imaging and spectroscopy have opened the floodgates of high-velocity information in the form of multidimensional data sets. The resultant high-resolution images contain important, as-yet undiscovered correlations between, e.g., atomic positions and local properties and function, as well as the evolution of these correlations with time, environmental conditions, and external fields.

An illustration of a new imaging mode developed recently is matched illumination and detector interferometry (MIDI)-STEM.<sup>57</sup> This method combines structured illumination with full-field scattering data, and uses a computer algorithm to recover the sample structure. The MIDI-STEM method was enabled by the introduction of high-speed direct electron detectors that enable four-dimensional (4D) imaging of materials. These new detectors record large fields-of-view at rates of hundreds or even thousands of frames per second. These extremely high detector speeds enable entirely new operational modes going beyond the conventional “image of atoms” paradigm to treat the microscope as a multifunctional scattering tool where all scattering events are simultaneously recorded. The capability of the detector can only be fully exploited with development of efficient automated algorithms for analysis. If the probe is scanned over a two-dimensional (2D) grid and a full 2D image of the diffraction pattern is recorded at each position, the experimental dataset consists of a very large 4D array, requiring terabytes of storage for the raw information. Processing and analyzing this type of microscopy data requires efficient automated algorithms for extracting physical parameters. Despite the difficulties associated with conducting these 4D-STEM experiments, the new imaging modes they allow can substantially improve on existing methods.

A comparison between this new linear method and conventional nonlinear STEM imaging illustrates that the low atomic number carbon regions of the sample however are imaged with far higher contrast in MIDI-STEM than in the conventional STEM imaging mode (Figure 2.4.2). The MIDI-STEM method was developed entirely using analytic models and theoretical calculations before being implemented experimentally. This example illustrates the power of new techniques for quantitative atomic structure determination, but the full-field reciprocal space data also



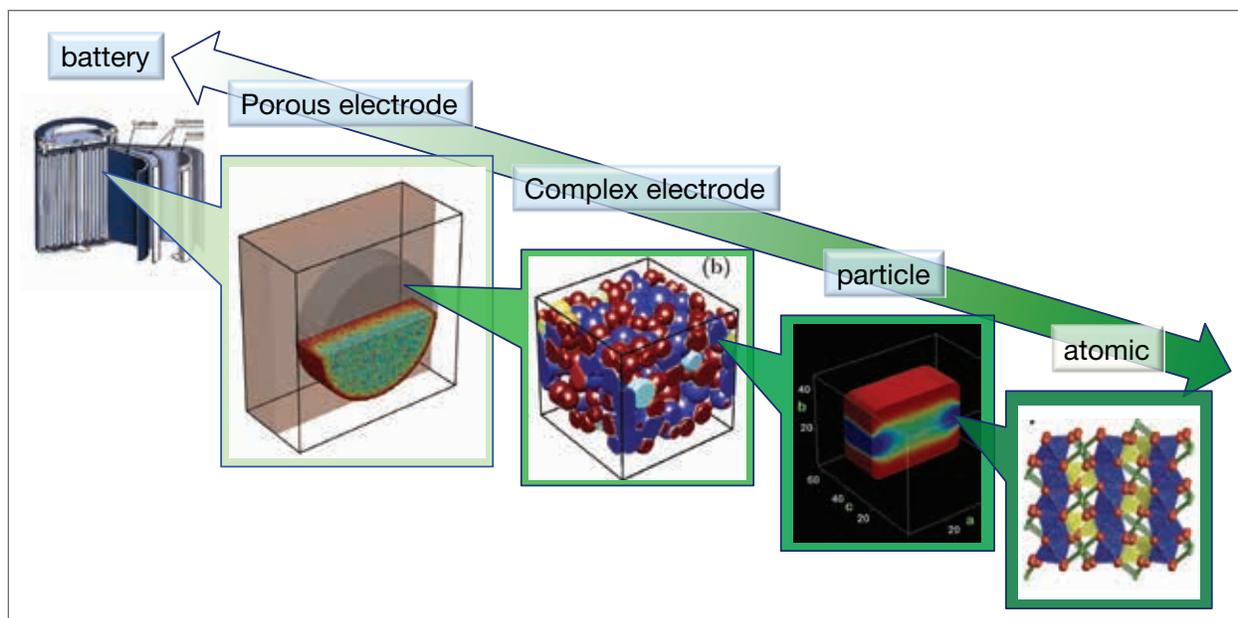
**Figure 2.4.2:** Comparison between conventional STEM microscopy and MIDI-STEM microscopy. Imaging geometry of (a) conventional experiment where 1-2 values are recorded at each probe position, and (b) a MIDI-STEM experiment with structured illumination and a high speed electron detector to record a full image of the diffracted probe at each position. A comparison between (c) conventional and (d) MIDI-STEM imaging for a sample consisting of gold nanoparticles on an ultrathin carbon support, corresponding to (a) and (b) respectively. Note that false-coloring was added to distinguish gold from carbon.

contains localized information on sample structure, composition, three-dimensional defect crystallography and hence, can simultaneously generate 2D maps of strain, polarization, local distortion and electric fields of materials at unit cell resolution ( $<1$  nm). Extracting and deconvoluting these simultaneous signals presents a large challenge to data processing algorithms on multi-terabyte datasets, and will require future developments in on-the-fly processing coupled with machine learning to return nanoscale property maps in real time.

Advances in coupling multidimensional characterization and approaches for data visualization and analysis have been made recently in single-particle characterization, illustrating the challenge of interpreting disparate data sets.<sup>55</sup> The functionality of small catalytic particles depends on a multitude of their coupled properties, and on their environment. The size, composition, phase, density, shape, mass, morphology, fractal dimension, volatility, optical properties, interactions with gas-phase all play a role. By necessity, this multidimensional single-particle characterization produces vast amounts of high dimensionality data, the visualization, mining, and analysis of which calls for unconventional methods that must draw on statistical methods, while preserving the wealth and depth of information. Moreover, analysis should be based on all relevant data generated by different instruments and should include their temporal evolution and the relationships between them. New methods are needed that can build faster and more accurate mathematical algorithms to extract and correlate information from disparate data sets from different experiments or from multimodal platforms. Development of universal integrated workflows that allow seamless data and knowledge exchange is a key aspect of the implementation of the co-design approach.

### 2.4.3 Validating Theories and Integrating Simulations into Novel Instrumentation and Designed Experiments

In the previous decade, atomistic simulations have become central computational tools for energy sciences. They have provided prediction from first principles, ranging from quantum-level understanding of materials to data that could be mined for hundreds of thousands of materials. However, there is often a gap between experimentally-observable quantities and these predictions. Mesoscale modeling is a powerful approach that maps these data onto experimentally observable length and time scales (Figure 2.4.3).<sup>58</sup> While capturing only the essence of the underlying electronic and atomic structures that are relevant to a specific problem, it enables predictions of nano- and micro-scale phenomena on time scales associated with experiments, which can be seconds and even hours. These simulations, in turn, can inform continuum-scale models that would predict device scale phenomena. Such frameworks involve electronic/atomic-scale calculations via, for example, density functional theory, Monte Carlo/kinetic Monte Carlo models, and molecular dynamics simulations that can provide input to mesoscale models including phase-field models and dynamics at single-particle and multi-particle levels.

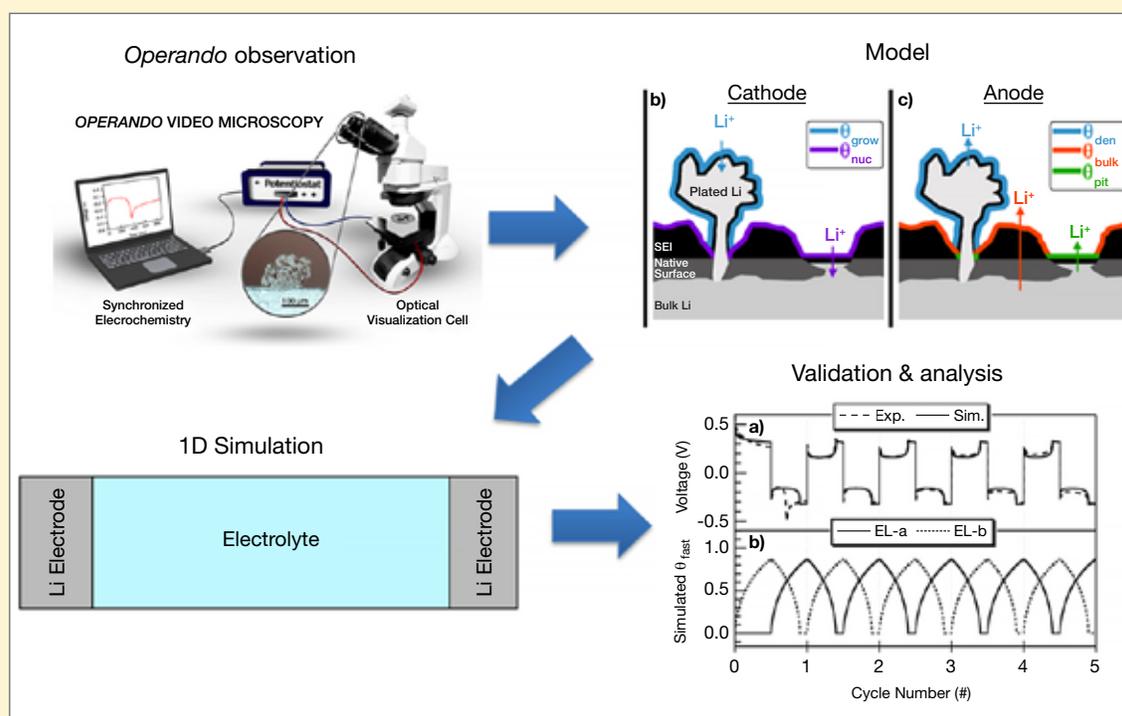


**Figure 2.4.3:** Illustration of hierarchical integration of multiple simulation tools across the length and time scales. Atomistic models are restricted to very small length scales and time scales (or information pertaining only to equilibrium). The dynamics over times scales relevant to experiments can be achieved by mesoscale simulation tools such as the phase field models and the smoothed boundary method electrochemical dynamics.

Experimental tool development and instrument design has always been done with the collection and analysis of datasets in mind. However, given the magnitude of the datasets, developing experimental tools needs to be intimately connected to the latest advances in data analytics, theory, and computation to better incorporate information about phenomena at various time and length scales into our observations. At the same time, for many observables of interest, new predictive theories and simulation paradigms are needed, particularly those spanning length and time scales. The development of such theories and methods will be accelerated by access to multidimensional experimental data collected across time and length scales. For many problems, for example understanding the electrochemical processes illustrated in the sidebar Figure 2.4.4, such data are unavailable or incomplete at a given length or time scale for assessing a set of approximations or a multiscale approach. Access to this data will help evaluate the models, and in doing so, provide feedback on the experiments, with the long-term goal of integrating both. In this manner, this PRD addresses a significant opportunity to advance both instruments and theory through co-development, leading to new integrated experimental tools and approaches.

## SIMULATIONS OF ELECTRO-DEPOSITION AND DISSOLUTION

A major opportunity in the integration of instrumentation and theory is to develop robust, reduced-order models that can be parameterized by mesoscale and atomistic simulations so as to provide the capability for interactive, real-time prediction. Recently, a first step in this direction has been demonstrated for *operando* microscopy of lithium electrochemical processes—both electro-deposition and dissolution. In this work, one-dimensional simulations were able to predict the essential features of a complex morphology that develops when the applied voltage is cycled up and down to induce deposition and dissolution (Figure 2.4.4).<sup>59</sup> The predicted voltage as a function of time agreed well with the experimentally measured value. Furthermore, the simulations yielded understanding of the mechanisms that give rise to the features observed in the voltage stemming from the presence of heterogeneous surfaces formed during electro-deposition and dissolution. Such one-dimensional simulations can be parameterized either by experiments or by more detailed simulations yielding macroscopic observable predictions. Such parameterization reduces the computation time considerably—from days on hundreds or thousands of CPUs to seconds on a single CPU. This “coarse graining” approach, thus, potentially enables real-time feedback to experiments.<sup>60</sup>



**Figure 2.4.4:** Based on *operando* observations of Li dendrite growth, a model of electrodeposition with the effect of nucleation and surface morphology changes was included. Experiments and simulations were in nearly perfect agreement (except for the first cycle involving pitting, which was not considered in the model), demonstrating that computationally efficient one-dimensional simulation can provide robust predictions when it is parameterized properly.

# III. Survey of Scientific Challenges and Opportunities Enabled by Transformative Experimental Tools



The urgent demand for new energy technologies in the 21st century has ushered a new era in experimental investigation where complexity is at the core of chemical and materials processes. A series of Basic Research Needs (BRN) reports [<https://science.energy.gov/bes/community-resources/reports/>] on a range of critical topics, including energy storage, conversion of sunlight to fuel, quantum materials, materials synthesis, and catalysis, have articulated specific scientific challenges where complexity plays a vital role. As clear needs for basic research have been identified, the scientific community has leveraged existing and developed new instrumentation and experimental approaches to address pressing scientific questions. The U.S. has developed and deployed the world's most powerful collection of tools for the synthesis, processing, and characterization of materials and chemical systems that span length scales from atoms to macroscopic assemblies and time scales from attoseconds to that of the human biological clock. These tools include user-facility scale and university-laboratory-scale capabilities. For example, in recent decades, scientists developed capabilities to peer into the smallest reaches of matter, resolving individual atoms in crystalline lattices using powerful microscopes, with the goal of understanding, designing and synthesizing materials of increasing complexity and architecture with targeted functionality. Chemical reactions and transformations, assembly, nucleation, electron solvation, ion transport in liquids and at interfaces, photon energy, thermal energy, and electronic excitation are all at the heart of energy processes. Studying energy systems under functional conditions, and observing, measuring, and quantifying parameters simultaneously pose a serious challenge. Limited progress has been made over the decades due to the limitations associated with the various instrumentation and probes. Delivering on the energy science of the 21st century requires addressing the challenges of experimental approaches involving functional energy systems.

Processes that occur far away from equilibrium — meaning that the state of the system changes with time — are central to most areas of energy science. Most of the progress to date in understanding these phenomena has been made through the observation of materials in “frozen” states represented by spatially or temporally averaged structures. This approach inherently does not capture the dynamic nature and complex properties of materials far away from equilibrium. Here, the development of ultrafast approaches such as photon and electron diffraction, imaging, and spectroscopy represents another grand challenge for modern chemical imaging, while offering a unique opportunity for understanding structural dynamics and the behavior of matter under conditions far away from equilibrium. Delivering on the energy science of the 21st century requires addressing the challenges of experimental approaches involving the time domain.

The ability to study heterogeneous materials systems and chemical reactions in space and time and under functional conditions is one of the biggest challenges in energy sciences. A fundamental obstacle remains to bridge the spatial, temporal and thermodynamic scales that are simultaneously relevant for the outcome of chemical, physical, and/or biological processes. An example would be a hierarchical architecture where the inherent physical or chemical processes in the molecular levels correlate in a complex way with emergent phenomena associated with higher length scales. Another example is a catalytic network formed through an assembly of organic, inorganic, and biological catalysts that work in concert like a living cell. The invention of experimental tools that connect the materials and chemical behavior of “real world” energy systems across multiple time scales and multiple length scales, while preserving the high resolution where needed will have a transformative impact on energy sciences. Delivering on the energy science of the 21st century requires addressing the challenges of heterogeneity across multiple length scales and time scales.

In most experiments, instrumentation, data acquisition, signal processing, theory, and computation with novel mathematical approaches are intimately linked to enable scientific insight. Traditionally, these different components are invented or developed independently from each other and brought together for specific experimental methods. As an example, data science helps to extract successively more refined information from experiments with increasing complexity or increasing size. To meet the spatiotemporal heterogeneity challenge in energy sciences there is a critical need to integrate instrumentation, innovative algorithms, theory and applied mathematics. Delivering on the energy science of the 21st century requires full integration of experimental methods with theory and computation.

The following sections contain the survey reports compiled by each of the four workshop panels. While not intended to be exhaustive, these surveys contain background information on instrumentation needs for several key scientific areas as well as the scientific opportunities that the Priority Research Directions will enable.

## 3.1 PANEL 1: CHEMICAL REACTIONS AND TRANSFORMATIONS IN FUNCTIONAL ENVIRONMENTS

Chemical reactions and phase transformations, along with assembly, nucleation, electron solvation, ion transport at interfaces, photon energy, thermal energy, and electronic excitation are at the heart of energy processes. The challenges to observe, measure, and quantify these processes simultaneously in functional environments are tremendous. Major progress has been made understanding fundamental chemical and material processes using relevant model systems. However, the complexity and heterogeneity of important energy systems can give rise to major changes in the behavior or evolution of these processes in their functional environment. Characterization of chemical and materials processes in functional environments is challenging due to the limitations associated with current instrumentation and probes. Examples of critical technologies that require in-depth understanding are electrochemical energy storage and conversion, efficient production of fuels and chemicals using heterogeneous catalysis, and solar energy conversion to chemicals or electricity. For example, the presence of reactive intermediates in catalysis can be revealed by kinetic studies. However, standard spectral characterization methods cannot reveal the structures and electronic properties of these intermediates in most cases because their populations are too small to be measured. Experimental methods are critically needed to directly detect rare events that lead to reaction intermediates, and that lead these intermediates to generate reaction products. Because of the disparate chemical and structural characteristics of hard materials, soft materials, and liquids, no single class of spectroscopy, diffraction, or imaging can be effectively used to study simultaneously the structure, bonding, and composition at critical interfaces. A common characteristic of these complex systems involves coupled physical and chemical processes that occur in multiple phases and at their interfaces. For example, in engineered materials, heterogeneity, interfaces, local structural deviation, physical confinement, reduced dimensionality, and directionality of energy and electronic flow drive behavior and function.

The ability to probe physical and chemical properties in multiple dimensions is critical to gaining a complete understanding of materials behavior. This ability includes a 3-dimensional (3D) spatial perspective expanded to energy and momentum space, interfacial structural and chemical bonding dynamics, and photonic response at the molecular and atomic levels of real materials systems under functional conditions. The realization of *in situ* and *operando* methods that produce sets of correlated chemical and physical information that spans the heterogeneity of functional systems will revolutionize the understanding of interfacial processes across a wide range of disciplines.

The challenges to observe, measure, and control processes relevant to energy technologies such as catalytic conversion, electrochemical generation and energy storage, and the broadly relevant category of interfacial processes simultaneously under typical operating conditions are tremendous. The need to observe functional materials and conversion processes in their intended operating conditions has been recognized for decades, with recent times seeing a significant increase in such studies due in large part to the development of new tools, instruments, and methods. This is an exciting trend that needs to be pushed further. The following sections examine some of the important scientific questions that underlie energy related chemical transformations involving reactant and products that may be in solid, liquid and vapor states. Catalysis is a critical process for many chemical energy conversion processes and essentially serves as a kinetic switch, accelerating desirable reactions and inhibiting less desirable reactions. Key instrumentation challenges are outlined in Section 3.1.1. Transformational processes that rely on the nature of interfacial liquid layers may be the least understood and most scientifically challenging to investigate. Our knowledge of the structure and composition of the liquid phase within 1 nm of the solid-liquid or liquid vapor interface is extremely limited and a selection of important research questions are articulated in Section 3.1.2. Many energy technologies, such as batteries, fuel cell and membranes require charge and mass transport through materials and materials interfaces. These diffusion or conduction processes often involve transport of ions and electrons and the resulting energy technologies often rely on components that selectively transport one charge species. Challenges related to these processes are described in Section 3.1.3.

### 3.1.1 Catalysis

#### SCIENTIFIC CHALLENGES FOR INSTRUMENTATION: CATALYSIS

An important and pervasive question in heterogeneous catalysis is understanding the fundamental relationship between catalyst structure and reactivity. What structural motifs play a critical role in lowering the activation barriers of the rate limiting step for converting reactants into desirable products? Elucidating the reaction pathways and corresponding reaction coordinates for key processes is essential if complex catalytic systems are to be understood and controlled. The ability to understand catalytic reactions is hampered by the presence of a complex variety of atomic structures and compositions on the surface. For example, in the case of late transition metal nanoparticles supported on an oxide surface, even if it were possible to prepare the nanoparticles with a uniformity approaching molecular specificity (e.g. with atomically uniform sizes and shapes) the nanoparticles contain a variety of local, surface atomic geometries and environments. These geometries and environments include terraces, steps, kinks, and proximity to the interface with the support. Another common class of catalyst material consists of a metal oxide monolayer covering an inert support. This supported oxide material typically consists of multiple molecular structures, each of which may contribute to catalytic function to an unknown degree. Porous materials, including metal organic frameworks (MOFs), mesoporous carbon, porous silica and zeolites, offer opportunities to develop new fundamental understanding of local environment effects on catalytic reactions. If it were possible to prepare and stabilize supported catalytic nanoparticles, oxide species, and porous catalytic materials with absolute atomic uniformity under reaction conditions, our capability to define their catalytic properties at the atomic scale as well as provide reference materials for the interpretation of spectroscopic results would be dramatically improved. While there are limitations in our ability to probe local functionality at high resolution, being able to interrogate that functionality over a large area of a catalyst is also necessary to understand local versus collective phenomena.

The inherent disorder in all catalysts and changes in the disorder as reactions proceed may play a critical role and is not well understood. For example, defects sites are known to play a key role in many catalytic reactions either by enhancing catalytic rates at those sites or by providing sites where unwanted side reactions can occur that lead to selectivity problems. Additionally, the ability to probe multifunctional catalysts to enable conversion of mixtures of reactants would be beneficial.

Local structures typically transform under reaction conditions in the presence of reactants, intermediates, and products. Such transformations are important to understand as a foundation for processing technologies. For example, metal nanoparticles change shape and supported oxides change speciation. Nanoparticles and porous materials used for catalysis contain highly reactive under-coordinated sites that are dynamically transformed by their interaction with reactants under *operando* conditions. Adsorbed species act as ligands, generating local structures of changing chemical state and morphology under *operando* conditions. In addition there is a key need to understand the active phases of catalysts, active sites within them, and transient chemical intermediates involved in the catalytic reactions using *in situ* and *operando* methods. The detection of weakly adsorbed surface species or reactive intermediates generated only in the presence of reactants is crucial to allow the comparison of experimental results with first principle modeling of specific reaction mechanisms. The need to interrogate thermo-catalysts, photo-catalysts, and electro-catalysts in functional environments cannot be overstated.

Adding to the complexity is the design of new chemical conversion catalysts that incorporate multifunctional active sites and manipulate the 3D environment in which these sites reside. A convincing, detailed molecular picture of these multifunctional catalysts based on experimental observations is still missing. Differing local reaction sites and their arrangement is not well understood at high resolution. Being able to track the impact of confinement on the transport of reactants and products within these porous materials would provide new understanding of how to design and control the synthesis of these materials. Furthermore, understanding how the local arrangement within porous confined spaces is impacted under reaction conditions would provide new insights into how to design these types of catalysts. Differentiating localized internal versus external processes for porous materials adds an additional level of complexity and difficulty for some current instruments. The Panel 3 Survey provides further examples of chemical reaction systems that are also difficult to characterize, including multi-step redox enzymatic processes.

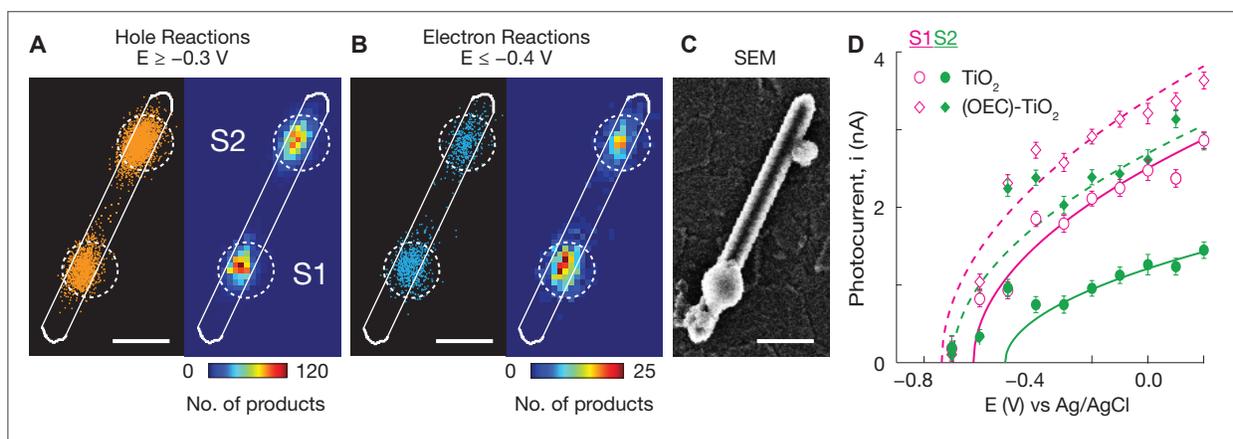
The heterogeneity of catalysts over a range of length and time scales is also critically important to their function. Heterogeneity within reactants also impacts catalysis; within chemical processes important to industry, understanding side reactions is important. Trace impurities within reactants can lead to many unforeseen problems at large scale and thus there is a serious need to understand how reactive sites interact with impurities. Indeed the importance of understanding the fundamental mechanisms driving catalyst deactivation cannot be overstated for technological application. Deactivation mechanisms include selective poisoning, particle coarsening, phase transformation, corrosion and photo-corrosion. Understanding the underlying kinetic and thermodynamic driving forces responsible for these degradation process is essential and will ultimately lead to improved performance. The Panel 3 Survey (Section 3.3.2) provides further examples of chemical reaction systems that operate over a wide range of coupled length and time scales, requiring multiple simultaneous measurements to understand them mechanistically.

### STATUS AND BREAKTHROUGH NEEDS FOR INSTRUMENTATION: CATALYSIS

Modern techniques have brought a new era in interrogating the local activity and structure of catalysts. To bring catalysis science to the next level, improved approaches are needed to probe the local activity of catalysts in terms of spatial resolution, chemical specificity, and applicability in diverse functional environments. Correlating local activity with local structure would be another key frontier, as structural methods alone do not provide activity information. However, this correlation requires multimodal approaches, which brings challenges in sample compatibility with the methods discussed below, especially under *in situ* and *operando* conditions.

Vibrational spectra of catalytic systems using Fourier transform infrared spectroscopy (FTIR) or Raman spectroscopy are diagnostic of the atomic structure and composition of the molecular, solid, and surface species in the system. Spectra can routinely be obtained with a resolution of ca.  $1\text{ cm}^{-1}$ . This is sufficient to discriminate between different molecular species, solid phases, or surface layers according to the positions of measured bands. Even species with similar structures can be distinguished by small shifts in the bands. Infrared and Raman techniques are limited by their sensitivity to minority species or surface species, by interference from fluid or bulk solid phases in the system, and by uncertainty in band assignments. For a solid catalyst surface in contact with a high-pressure gas or a liquid, absorption by the gas or liquid phase can make the solid material undetectable. This is a particular problem for spectroscopy when the vapor or fluid phase contains a strong absorber, such as water. Another source of interference for IR is blackbody emission from the sample at the high temperatures used for many catalytic reactions. Raman spectroscopy is less susceptible to absorption interference since the excitation laser wavelength can be selected in a spectral region where the gas or liquid phase is transparent. However, Raman signals are often weak and can easily be obscured by laser-induced sample fluorescence. A standard practice for the interpretation of measured spectra in terms of atomic structures or molecular assignments is by comparison to measurements on reference materials. Alternatively, the spectral features may be assigned by comparison to density functional theory calculations. For many solid catalyst systems it would be desirable, and in principle possible, to discriminate between species with similar structures. Band assignments between similar structures are limited by the availability of reference materials that represent the scope of the systems under study. For supported oxide catalysts, one of the major categories, suitable reference materials that reflect the structural features of interest do not exist. Likewise, the accuracy of calculated band positions is typically insufficient for band assignments. Moreover, when the material of interest is inhomogeneous and complex, the overlap of vibrational bands increases the uncertainty of spectral assignments.

The assignment of vibrational bands from complex systems would be greatly facilitated by the ability to prepare similar but more uniform materials where knowledge of the preparation chemistry narrows the range of possible structures and species. Another strategy makes use of resonance enhanced Raman spectroscopy where only a subset of species in a mixture is enhanced at the laser excitation wavelength. By measuring Raman spectra at a variety of wavelengths within the region of sample absorption, it may be possible to sample and discriminate among all of the species present. At present both of these strategies are somewhat laborious. Methods for preparing more uniform sample materials are personnel intensive, often requiring days to weeks for a single preparation. Resonance-enhanced Raman measurements at multiple excitation wavelengths are similarly time-intensive. In addition, for many of the catalyst systems of interest, the absorption bands occur in the ultraviolet, necessitating Raman excitation in



**Figure 3.1.1.1:** Single-molecule super-resolution fluorescence imaging of charge carrier reactions on a single-nanorod photoanode under photoelectrochemical water oxidation conditions (A, B), combined with local photocurrent vs. potential measurements before and after deposition of an oxygen evolution catalyst (OEC) (D), which is visualized via SEM (C).

the ultraviolet, where there are fewer available laser wavelengths and the optical properties of windows, lenses and mirrors are mediocre. Computation models linked with instrumentation would be beneficial to speed up and improve assignments.

The spatial resolution of traditional IR-microscopy is restricted by the diffraction limit to the micrometer range. Using synchrotron light and a microscope, the polymerization of an adsorbate on a H-ZSM-5 zeolite single crystal catalyst has been mapped out with a pixel resolution of 3 micrometers, near the diffraction limit, thereby revealing that the reactions occur preferentially only in the straight channels of ZSM-5.<sup>61</sup>

Single-molecule, super-resolution fluorescence microscopy can now image (photo)(electro)catalytic reactions and quantify the reaction kinetics on individual catalyst particles in real time, with single-turnover reaction resolution and tens of nanometer spatial resolution under *operando* conditions (Figure 3.1.1.1 A–B).<sup>14, 62</sup> But the experiments there are limited to the solution phase, involve fluorescent molecules, and do not provide direct, local structural information on the catalyst. Vibrational imaging, in particular tip-enhanced Raman spectroscopy and surface enhanced Raman spectroscopy, can image reactions at high spatial resolution down to single-molecule sensitivity and with rich chemical information on the reacting molecules,<sup>63</sup> but these techniques do not provide structural information on the catalysts, they require a plasmonic probe, and lose time resolution with spectral scanning.<sup>23</sup> Electrochemical current measurements, powerful in quantifying the overall interfacial charge transfer reaction kinetics in electrocatalysis and photoelectrocatalysis, can now be done at sub-catalyst-particle level (Figure 3.1.1.1 D)<sup>14</sup> but the spatial resolution is limited by either optical diffraction (e.g., in laser-guided photocurrent measurements; Figure 3.1.1.1 D) or probe size (e.g., in scanning electrochemical microscopy or fabricated nanoelectrodes). Localized surface plasmon resonance microscopy can probe reactions on individual catalyst particles, but quantifying reaction kinetics is challenging.<sup>64</sup>

Vibrational nano-spectroscopy based on IR scanning near-field optical spectroscopy (IR-SNOM) would provide access to the spectral signals of molecular species and phonon modes of active phases discriminated with nanometer spatial resolution via the strong localized fields produced at the tip apex of an atomic force microscope (AFM). The best results reported in the literature for IR-SNOM of phonons on semiconducting surfaces have a spatial resolution of ~10 nm. New developments in monochromated STEM also permit mapping molecular species and phonon modes at resolution in the tens of nanometers.<sup>65-67</sup> Advances in these directions could provide instrumentation with sub-nanometer resolution under *in situ* conditions at elevated pressures and temperatures.

Other techniques offer additional possibilities for characterizing catalysts. Using solid-state NMR (SSNMR), we are able to understand the local bonding environment of adsorbates on catalysts. Batch reaction studies are possible, but the reaction has to be sufficiently slow because of the limited sensitivity of NMR. Using conventional NMR, high

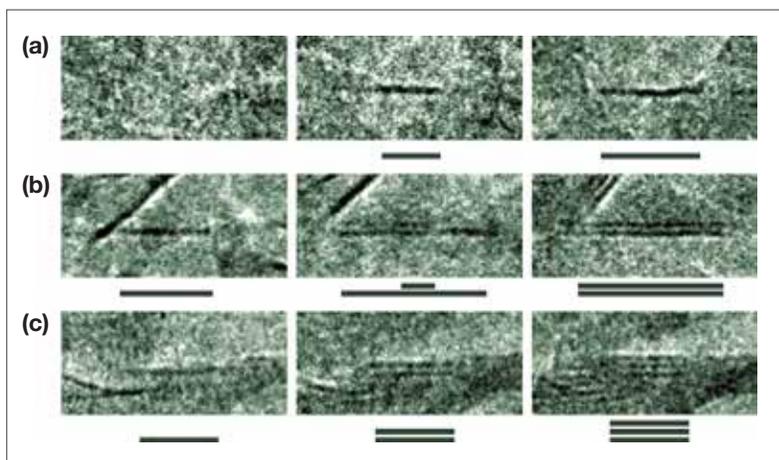
pressure devices have been developed to enable *in situ* measurements including capabilities for variable temperature NMR from 30 K to 1100 K. High-pressure sealed rotors make possible studies at varied pressures, albeit with some limitations including limitations on how fast the samples can be spun and limited sample volume. Spinning samples at the necessary speeds to obtain the resolution needed for analysis has been a significant barrier. Combining temperature and pressure is also now possible. Temperatures of 250 °C combined with pressures of 100 bar have recently been shown to be possible with advances in rotors.<sup>68</sup> The spatial resolution of SSNMR is limited to several hundred microns. Imagine the potential in imaging if this could be improved.

Dynamic nuclear polarization (DNP) NMR allows for unprecedented sensitivity for trace amounts of species with signal increases of 2-3 orders of magnitude over conventional NMR. The impact of DNP NMR on catalytic sciences is expected to be far reaching.<sup>69</sup> Solid-state DNP NMR enables the potential to unambiguously identify surface species from those in the bulk. This technique though is currently limited to studies at 100 K. Advances to enable higher temperature analyses of catalysts would enable *in situ* analysis using DNP NMR. DNP could facilitate the study of changes in local structure as a function of time.

Secondary ion mass spectrometry (SIMS) can be used to look at electrocatalysts, but not with resolution of the local active site. The energy resolution is such that we can differentiate molecular species based on their fragmentation. *In situ* liquid SIMS provides a lateral resolution of ~300–400 nm. Depth resolution for solids can be 1–2 nm, but in liquids it is very difficult because the liquid is mobile and self-renewable. Mass resolution for *in situ* liquid SIMS is about unit mass for the  $m/z$  range of 1–500. New ToF-SIMS instruments can provide much better mass resolution ( $M/\Delta M$  up to 200,000), but only prototypes are available.

An important goal of *in situ/operando* studies of a catalyst is to identify the arrangement of catalyst atoms, adsorbates, or even intermediates on the topmost surface and correlate this structural information with its corresponding catalytic performance. Currently, high pressure scanning tunneling microscopy (HP-STM) and environmental transmission electron microscopy (ETEM) are the two main approaches that can provide structural information at the atomic scale under reaction conditions and during catalysis. Both approaches are somewhat complementary with the STM providing surface structural information on catalyst and adsorbate structure on predominantly flat supports whereas TEM is better suited to high surface area nanomaterials.<sup>70</sup> The development of scanning probe microscopy (SPM) in the 1980s allowed for the first time the atomic level study of surfaces. SPMs such as scanning tunneling microscopy (STM) and atomic force microscopy can be used to obtain chemical specificity at low temperatures and ultrahigh vacuum conditions. The tips used as probes in SPMs reside ~1 nm above the surfaces being tested, and even in the presence of gas or liquid molecules the tunneling currents or forces being measured can still be detected. The challenge is to obtain similar spectroscopic information *in situ* in a reactive environment with elevated temperatures. HP-STM has undergone significant development over recent years and can now image adsorbates at temperature up to 230 °C and pressures of up to 25 Torr. With this approach, adsorbate reconstruction on model catalyst surfaces can be explored as a function of temperature and reaction gas. Recent developments allow surface structure to be observed during the detection of catalytic products such that structure and catalysis can be correlated at the atomic level. There is a strong need to push to higher temperatures and pressures so that a wider range of catalytically relevant conditions can be covered.

TEM is another method to image materials with atomic-scale precision under operating conditions. This approach is able to interrogate high surface area systems and provide detailed information on atomic structure, composition and bonding down to the atomic level. The development of aberration-corrected instruments now makes sub 1 angstrom imaging on nanoparticle surfaces routinely available. Using simultaneously secondary electrons to probe the surface and transmitted electrons to probe the bulk of a sample at atomic resolution in an aberration corrected microscope represents another forefront of characterization of catalysts.<sup>71-72</sup> The enhanced spatial resolution has also improved sensitivity for detecting light atoms such as carbon, nitrogen and oxygen.<sup>73-74</sup> Continued advances in energy dispersive X-ray spectroscopy and electron energy-loss spectroscopy (EELS) make atomic resolution elemental analysis possible. Moreover, the development of monochromators has improved the energy resolution of EELS to close to 10 meV making bonding information accessible through inner-shell, valence-loss or vibrational excitation.<sup>75</sup> *In situ* methods have been developed based on either differential pumping systems or MEMs-based windowed cells. The differentially pump systems



**Figure 3.1.1.2:** Time-resolved *in situ* TEM image series of the growth of nanocrystals consisting of (a) 1L, (b) 2L and (c) 3L MoS<sub>2</sub> slabs. Growth conditions: 0.8 mbar of H<sub>2</sub>S:H<sub>2</sub> = 1:9 at 690 °C. The images represent times of (a) 122 min, 138 min, 152 min, (b) 225 min, 243 min, 257 min, and (c) 178 min, 192 min, 208 min. Sketches are included to guide the eye in identifying the MoS<sub>2</sub> slabs. The frame sizes are 17.3 × 7.9 nm<sup>2</sup>.

are currently limited to a pressure of 20 Torr, but can provide high quality structural information on the surface of nanoparticles. The windowed cells can achieve a pressure of one atmosphere or higher and are compatible with most microscopes. In one example (Figure 3.1.1.2),<sup>76</sup> researchers were able to provide unprecedented insights into the growth mechanism of MoS<sub>2</sub> materials, flowing H<sub>2</sub>S/H<sub>2</sub> across a molybdenum oxide precursor, simultaneously reducing the Mo, sulfidizing it, and crystallizing the material at high temperatures.<sup>76</sup> Such tools can be leveraged to understand both the synthesis of materials as well as their function for intended applications, e.g. catalysis. One particular frontier in this

area is being able to conduct such a study with single-atom sensitivity, a feat that has only been achieved during *ex-situ* conditions.<sup>77</sup>

Detecting catalytic products inside the TEM has now been accomplished with both the windowed cell approach and the differentially pumped designs using both EELS and residual gas analyses.<sup>78-79</sup> The ability to determine reaction kinetics makes *operando* measurements now possible. Combining *in situ* TEM with vibrational spectroscopy would certainly expand the chemical specificity of the electron microscopy approach. Raman spectroscopy has been integrated into a TEM providing high spatial resolution atomic resolution image and vibrational spectroscopy from micron sized areas.<sup>80</sup> The prospect of much more localized probing of vibrational states remains a distinct possibility with electron beam methods by combining monochromation with STEM techniques. The so-called aloof beam approach to EELS, where the electron beam is positioned a few nanometers above the surface, may provide nanometer level probing of adsorbates on individual nanoparticles while minimizing radiation damage effects.

## 3.1.2 Interfaces

### SCIENTIFIC CHALLENGES FOR INSTRUMENTATION: INTERFACES

#### Liquid Interfaces in Combustion

An outstanding challenge in the combustion of fuels is the need to control the atomization and evaporation of the liquid fuel and its mixing with oxygen over a range of optimal times and locations within diesel, gasoline, and gas turbine engines.<sup>81-82</sup> Characterizing these processes is fundamental to maximizing efficiency and minimizing particulate formation. In both reciprocating and turbine engines, the fuel must be transported from the liquid phase to the gas phase in order to combust and convert chemical into mechanical energy. Injection of liquid fuel that breaks up into a spray of micron-sized fuel droplets occurs at temperatures in excess of 400 K and pressures in excess of 20 atmospheres, creating hostile conditions that are characterized by rapid changes in temperature, pressure, and density. Yet we have only poor experimental characterization of the breakup of the liquid fuel spray on the essential length scales of nanometers to millimeters and time scales from nanoseconds to milliseconds. The spatial and temporal range of the breakup of the initial spray into even smaller droplets (atomization) and their evaporation into individual gas molecules depend on the composition of the fuel mixture and the temperature and pressure fields within the engine. The fuel itself spans a wide range of small (high vapor pressure) and large (low vapor pressure) components,<sup>83-85</sup> which evaporate over a range of times and hence distances.<sup>86-87</sup>

To make progress in our basic understanding of fuel sprays under combustion conditions, we must develop tools with high spatial and temporal resolution that can interrogate multi-component gas-liquid interfaces with chemical specificity in extreme temperature and pressure environments. Ideally, these tools will map the history of the shrinking and irregularly shaped droplets as they evaporate under turbulent conditions. To learn how to control the rupture of liquids and their evaporation, we must further elucidate a molecular picture of gas-liquid interfaces under bombardment by hot gas molecules at high fluxes. These rapid and energetic collisions occur on time scales over which molecules leave the surface and therefore may influence the rate and type of molecules that distill from the droplet. Indeed, the gas-phase mean free path is often on the same scale as the interfacial width of the hot droplet, fundamentally altering the way in which fuel and air mix and react.<sup>88</sup> Ultimately, precise control of this fuel-air rapid mixing may provide new routes to minimizing solid particle formation that occurs upon pyrolysis of unburnt fuel and emission of partially burnt hydrocarbons.

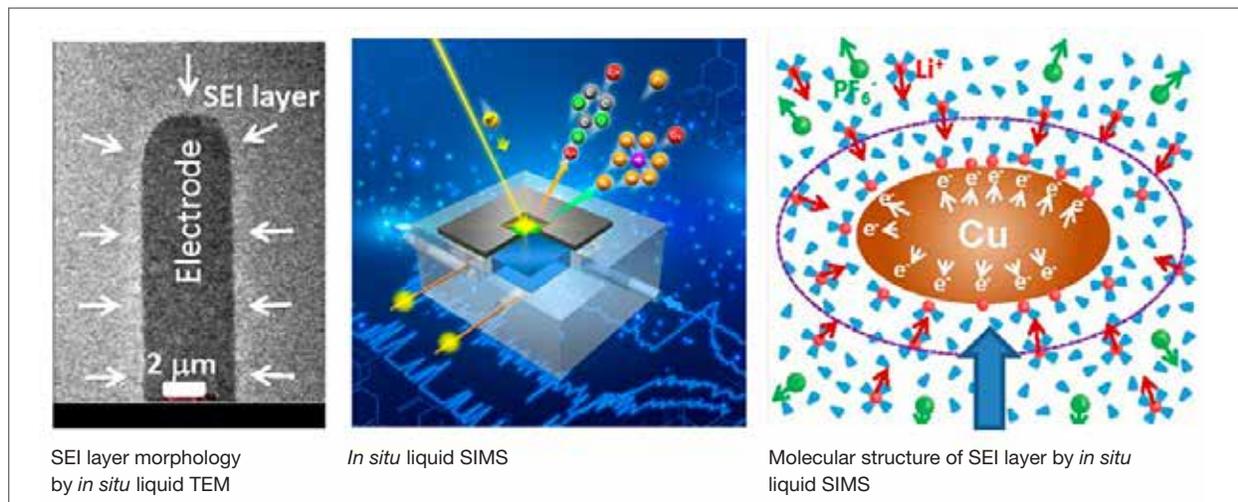
To develop an understanding necessary to predict and optimize engine efficiency, several issues need to be addressed. Reactors must be developed that can safely reproduce the high temperature and pressure environments in actual combustors for injecting sprays into reactive environments. Diagnostic methods also need to be developed that have sufficient spatial and temporal resolution to interrogate the broad temporal and length scales that span spray atomization to combustion. Detailed chemical information concerning the composition of the bulk and interfacial regimes of the droplets and the vapor cloud surrounding them will help to characterize the evaporation process. No single technique can provide a complete picture, mandating that a suite of reactors and diagnostics are developed that together can span combustion conditions.

Liquid fuels are complex mixtures of hundreds of species including alkanes, alkenes, aromatics, cycloalkanes, and oxygenates that enter the gas phase upon evaporation. Prior to ignition, a radical pool must develop in the gas phase whose composition is controlled by the relative evaporation of the different species. This process may be modeled by relying on fuel surrogates and monitoring the liquid and vapor cloud spectroscopically. For example, high resolution chirped pulse microwave spectroscopy is a non-destructive probe<sup>89</sup> that can yield considerable information for a broad range of species simultaneously. If X-ray fluorescent active materials are used, then relative proportions of species in the bulk and vapor phase can be obtained. The interrogation of liquid interfaces at the molecular scale under high temperature and pressure conditions may require extensions of present optical and electron spectroscopies. Imaging the evolving spray structure will optimally involve spatial resolutions ranging from tiny droplets smaller than 10 nm to a wide field of view of the droplet region, with sufficient sensitivity and temporal resolution to capture images without signal averaging.

Incomplete oxidation results in the formation of soot particles which negatively impact the environment and human health. For a realistic measurement of the formation of soot particles in a flame, a spatial resolution of 10x10 micron at a temporal resolution of microseconds is required for atmospheric pressure flames ( $T < 2400$  K). For high pressure flames ( $< 20$  atm; more akin to a combustion reaction) the spatial resolution needs to be increased by at least a factor of 10, although precise estimates are difficult due to the lack of information we have so far on soot formation under these conditions.

### Liquid/Solid Interfaces

Many relevant energy processes take place at the interface between a liquid and a solid. For electrochemical systems, the first step to a better understanding of liquid/solid interfaces at the molecular scale is the 3D imaging of the electric double layer under steady-state conditions (not net transport across the interface). See Figure 3.1.2.1.<sup>90</sup> The emphasis here is on the detection of all chemical species at the interface (both in the solid and liquid phase) with high spatial resolution (tentative goal 0.1 nm perpendicular to interface, 1–10 nm in plane). Questions to be address here are inner vs. outer shell adsorption of solution ions to the interface and their concentration as a function of distance from the interface; the chemical state of the solid substrate; the electrical potential distribution in the electric double layer and in the substrate; and the local pH at the interface. For semiconductor/liquid interfaces, which are of particular interest for alternative energy sources, direct measurements of band bending and the nature of surface states which can



**Figure 3.1.2.1:** Imaging the liquid-solid interfaces using a) liquid cell TEM b) liquid cell time of flight SIMS c) Schematic diagram showing Li deposition on Cu derived from in situ observations. SEI is the solid-electrolyte interphase.

lead to band edge pinning and thus degraded performance of photo-electrochemical devices are paramount. High in-plane resolution is required for the identification of active sites and areas of the sample, as in the case of heterogeneous catalysis.

Arguably no other process at the liquid/solid interface is more difficult to investigate with relevant temporal and spatial resolution than corrosion due to the constantly changing position of the liquid/solid interface. Success in this area paves the way for the characterization of virtually all other phenomena at liquid/solid interfaces. Corrosion is characterized by the concurrent transport of mass and charge across the solution/metal interface, where anodic and cathodic processes can occur simultaneously at different sites of the same material (even for single crystals). An exciting new area of inquiry is the elucidation of the molecular scale mechanism of corrosion inhibition, where fundamental information about the chemical bonding of inhibitor molecules to metal surfaces, as well as the exact nature of the metal surface (e.g., metallic, hydroxylated, or oxidized) in contact with the solution and the inhibitor molecules is lacking and thus limiting the ultimate control of corrosion processes across a wide range of metal and metal alloys.

The chief experimental problem in all these experiments is to enhance the signal from the thin (~nm) interfacial region over that from the adjacent bulk liquid and solid phases. The development of true 3D spatial chemical and potential imaging of the liquid/solid interface with nanometer resolution will revolutionize the understanding of the interfacial physical chemistry across a wide range of disciplines. Determination of the chemical composition, electrical potentials, and mass/charge transport across liquid/solid interfaces under operating conditions requires full spatial and temporal overlap of multiple probes to fully elucidate the properties of the electric double layer (distribution of ions and electric potentials, orientation of dipoles, etc.), the role of defects and grain boundaries in enhancing/limiting transport properties, etc. Spatial and temporal overlap are required due to the inherent inhomogeneities at the interface and the temporal fluctuations of the physical-chemical properties during an electrochemical reaction (e.g., corrosion, electroplating). Emphasis has to be on the direct probing of the interfacial region with high spatial resolution to go beyond the current indirect electrochemical methods (cyclic voltammetry, impedance spectroscopy) used to reveal molecular level processes at liquid/solid interfaces.

## STATUS AND BREAKTHROUGH NEEDS FOR INSTRUMENTATION: LIQUID INTERFACES

### Liquid/Vapor Interfaces of Fuels

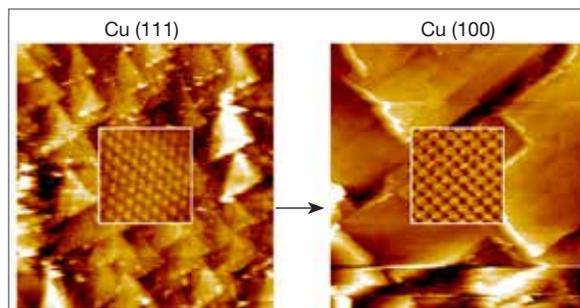
Current X-ray absorption and phase-contrast techniques can produce exquisite images from within the liquid core exiting the injector to the point where the spray is completely developed.<sup>91</sup> However, images with fields of view of only a few mm<sup>2</sup> can be captured at once and the smallest droplets that can be detected are ~10 micron in

diameter. Consequently, raster scan techniques are necessary to span the dimensions of a typical fuel spray. Small angle X-ray scattering, SAXS, can image droplets as small as ~10 nm, but the image size is limited to around 100 x 100 micron, and typically averaging over several tens to hundreds of shots is necessary to achieve sufficient signal-to-noise ratios.<sup>92</sup> Combining information from radiographic and SAXS methods can provide more detail but requires considerable time and the data can currently not be collected simultaneously. X-ray techniques are currently of course not the only methods for investigating physical properties of sprays. Optical methods such as ballistic imaging,<sup>26-27</sup> shadowgraphy<sup>25</sup> and X-ray fluorescence<sup>29</sup> are being used but each has limitations in terms of spatial resolution and/or image size and temporal resolution. A further complication is that fuel sprays in practical combustors are not introduced into quiescent environments but into high temperature and pressure regimes that are likely to become even more extreme in the future. X-ray and optical spray experiments are currently performed at room temperature and elevated pressures primarily due to the challenges of engineering suitable vessels and windows. Furthermore, many spray studies are carried out by spraying fuel into non-reactive gas and do not yield information about the transition from spray to flame, an essential step for predictive simulations and optimization. Although a high temperature, high pressure chamber has been developed which is outfitted with multiple optical diagnostics to probe flame development as well as sprays,<sup>28, 93</sup> at this date, no molecular-based experimental techniques (such as sum frequency generation) have been used to interrogate liquid interfaces under such extreme conditions.

### Liquid/Solid Interfaces

The investigation of liquid/solid interfaces is one of the biggest challenges in interface science in the years ahead.<sup>94</sup> Liquid/solid interfaces are ubiquitous in technological applications, energy generation and storage. Over the past decades a wide array of spectroscopies and microscopies have been developed that can interrogate the liquid/solid interface directly, among them vibrational spectroscopy, sum frequency generation, IR, Raman, second harmonic generation, UV-vis and microscopy (fluorescence, Raman, IR), X-ray based techniques (X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, X-ray diffraction, X-ray reflection, scanning transmission X-ray microscopy), scanning probe microscopy (STM, AFM, scanning electrochemical microscopy), as well as electron microscopies (SEM, TEM).<sup>95</sup> Each technique has provided important information on the chemical state of the liquid/solid interface, but is also limited either in its spatial or temporal resolution by the nature of the interaction of the probe with the interface. For instance, optical techniques are able to penetrate thick layers of aqueous solutions, but are in general not interface-sensitive, except for non-linear optical techniques which nevertheless do not provide information over the extent of the interfacial region that is being probed and cannot detect all components of the interface. Electron or ion-based techniques are in general limited by the strong interaction of the probes with matter, limiting the thickness of the liquid layer that can be penetrated. Scanning probes are able to image liquid/solid interfaces with high spatial but very limited chemical sensitivity. On the theory side, liquid/solid interfaces are much more challenging to model compared to, e.g., solid interfaces with vacuum, owing mostly to the high rate of spatio-temporal fluctuations in the liquid, which requires sampling a large number of configurations.<sup>96</sup>

The current status of our knowledge of liquid/solid interfaces is thus characterized by isolated deep insights into particular aspects of the interfacial properties, without an overarching, experimentally supported picture of the complete chemically and spatially resolved structure of the interface (in particular the structure of the electric double layer), or mass and charge transfer processes across the interface. Electrochemical scanning tunneling microscopy (EC-STM) allows one to image the surface of a material with atomic-scale precision in a true electrochemical environment. In one particular study, a polycrystalline copper electrode was observed at negative potentials in 0.1M KOH; interestingly, over time during this potentiostatic hold, the electrode formed Cu(111) facets on its own, followed by Cu(100) facets (see Figure 3.1.2.2).<sup>97</sup> Observing how a surface reconstructs in its functioning environment (electrochemical or otherwise) is crucial to understanding its performance at the macroscopic scale. Electrochemical STM is able to



**Figure 3.1.2.2:** *Operando* electrochemical scanning tunneling microscopy images in liquid of 0.1M KOH of Cu electrode during CO<sub>2</sub> reduction reaction. The electron transforms from a (111) surface (left) to a (100) surface (right) during the reaction.

image absorption structures of ions on single crystal metal surfaces with atomic resolution with respect to the adsorbate and metal ions, but is not able to resolve the solvation layer around the ions. Standing wave X-ray fluorescence spectroscopy is able to measure the distance of certain ionic species from a single crystal oxide or metal interface with angstrom resolution as a function of pH and potential, but is not sensitive to all components of the interface or the electrical potentials.<sup>98</sup> The most widely used techniques for the characterization of liquid/solid interfaces are electrochemical methods, like cyclic voltammetry and impedance spectroscopy, which do not probe the interface directly, yet currently provide the largest proportion of the data that is used to develop models of the molecular scale structure of the electric double layer and other properties. There is a clear need to develop techniques that directly and noninvasively probe the chemical and potential distribution at the liquid/solid interface with high spatial and temporal resolution.

X-ray methods are particularly amenable for use in functioning environments, due in large part to the high photon energies that can penetrate gases, liquids, and solids, and as such have become one of the most prominent modes of studying materials in operation. Some key methods that have been used for this purpose include X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), transmission X-ray microscopy (TXM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD), among others. In one example,<sup>99</sup> a mixed metal oxide electrocatalyst consisting of MnNiOx, was studied by XAS and XES to observe electronic structure changes simultaneously in both the Mn and Ni as the catalyst oxidized water to produce O<sub>2</sub> (the oxygen evolution reaction, OER). In another example,<sup>100</sup> TXM was employed to understand Fischer-Tropsch catalysts at work. XPS has been employed to study changes in both a material as well as the adsorbed species on that material during operation in an electrochemical cell.<sup>101</sup>

A special and important liquid/solid interface that is present at extreme conditions is that of carbonaceous particles (e.g. soot and nanotubes) that are formed in flames. In particular nascent soot particles are not necessarily solid but can contain a high proportion of liquid hydrocarbons,<sup>102-103</sup> which may be encapsulated or on the surface of the particle. Understanding the particle formation mechanism is critical to controlling pollutant formation and the flame synthesis of high value and bulk materials (e.g. laser jet toners, fumed silicas). Current state of the art methods that yield detailed chemical information require sampling particles from the environment where they are formed, such as in an engine<sup>103-104</sup> and introducing them into some analytical device, such as a mass spectrometer. High resolution TEM images of carbonaceous particles have been invaluable for elucidating soot structures<sup>105-106</sup> but like AFM images are normally obtained by collecting samples through thermophoretic sampling, where a particle is removed from the environment where it is formed and then introduced into an ultra-high vacuum environment for analysis, with the particle nature most likely changing during this process. *In situ* X-ray based scattering methods (wide- and small-angle X-ray scattering, WAXS and SAXS, respectively) have been used in atmospheric pressure flames.<sup>107-108</sup> While good spatial resolution can be obtained (100 by 100 to 600 by 600 micron for SAXS and WAXS respectively), the time required to raster scan an atmospheric pressure flame is on the order of hours. During this period many factors affect the data acquired including drifts in the synchrotron light source energies, flame instabilities, changes in burner properties, drift in detector electronics, etc.

### 3.1.3 Materials for Electrochemical Generation and Storage of Energy

#### SCIENTIFIC CHALLENGES FOR INSTRUMENTATION: MATERIALS FOR ELECTROCHEMICAL GENERATION AND STORAGE OF ENERGY

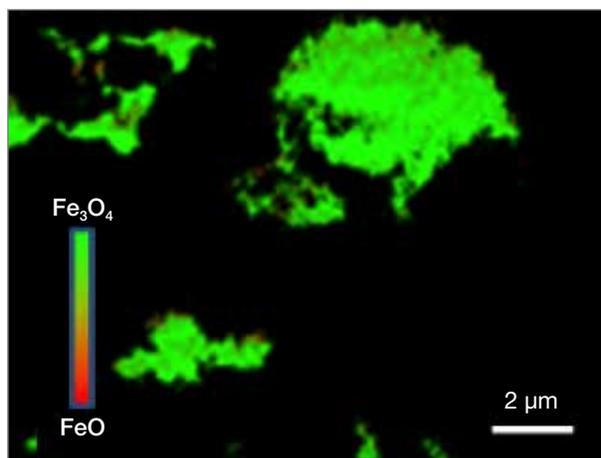
Electrochemical energy conversion and storage devices, such as Li-ion batteries, supercapacitors, fuel cells, electrolyzers, and membranes are complex systems where processes occur on multiple length scales, from angstroms to millimeters. The functionalities involved in these materials are varied and include ionic and electronic transport, oxygen storage and release, and catalysis. For example, in batteries, while the active material governs the fundamental chemistry taking place for energy storage, the architecture of the composite electrode and the transport properties of the separator and the electrolyte, although not chemically active for storing energy, are critical in delivering the energy and power promised by the active material. Therefore, to optimize the performance in an actual electrochemical cell, it is important to understand how reactions progress in or on the surface of electrodes and how they are affected by cell components

associated with transport processes. This requires understanding mass and charge (electronic and ionic) transport through and across the different phases (e.g. electrolyte, multiphase electrodes, and current collectors), and through different pathways within a phase (grain, grain boundaries, dislocations), as well as “side” reactions such as catalyst poisoning and the formation of solid-electrolyte-interphase layers — including their interrelationship and evolution over time. Overarching questions include how local structure regulates transport phenomena at interfaces, surfaces and defects, and how transport phenomena and ultimately, device performance, evolve over time due to changes in the composition and structure of the electrodes and interfaces.

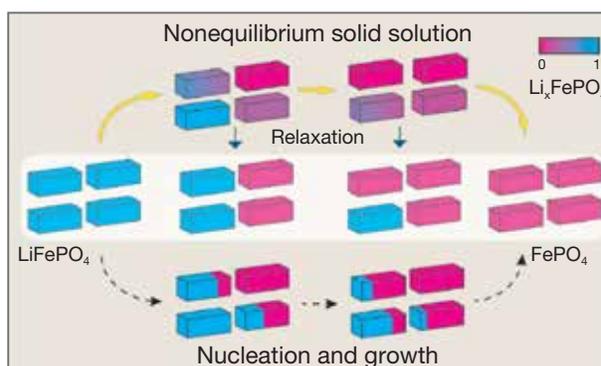
In Li-ion batteries, the active electrode material is embedded in the composite electrode (consisting of electrode particles, carbon particles for enhanced electrical conductivity, and binder). The use of nanomaterials has proven highly effective for energy storage systems to control the path length of lithium ion diffusion. Recent investigations over multiple length scales has demonstrated that local phenomena must be understood as well as the influence of the environment of the active material. For example, the investigation of nanocrystalline  $\text{Fe}_3\text{O}_4$  as a prospective negative electrode material revealed aggregation of the active material within the electrode structure, Figure 3.1.3.1.<sup>109</sup> Prediction of the electrode and material function demanded development of a multiscale model which considered the length scales of the fundamental material particles as well as the size of the aggregate,<sup>110</sup> illustrating the importance of multiple length scales. Nanomaterials offer design tools for tailoring the properties of batteries. Lithium iron phosphate, when produced and utilized at the nanoscale, can proceed through a non-equilibrium solid solution mechanism that provides rapid charging and high power through rapid discharge. This is not possible through the nucleation and growth mechanism of large grains, Figure 3.1.3.2.<sup>111</sup>

Solid oxide fuel cells, permeation membranes and electrolyzers rely on functionalities associated with non-stoichiometric oxides, such as fluorites or perovskites, giving rise to ionic (usually oxygen ions or protons) and electronic conductivity as well as active redox catalytic properties. Most commonly, oxygen ion conduction takes place via a thermally activated vacancy-hopping mechanism with the optimum bulk vacancy concentration achieved by aliovalent cation doping.<sup>112-113</sup>

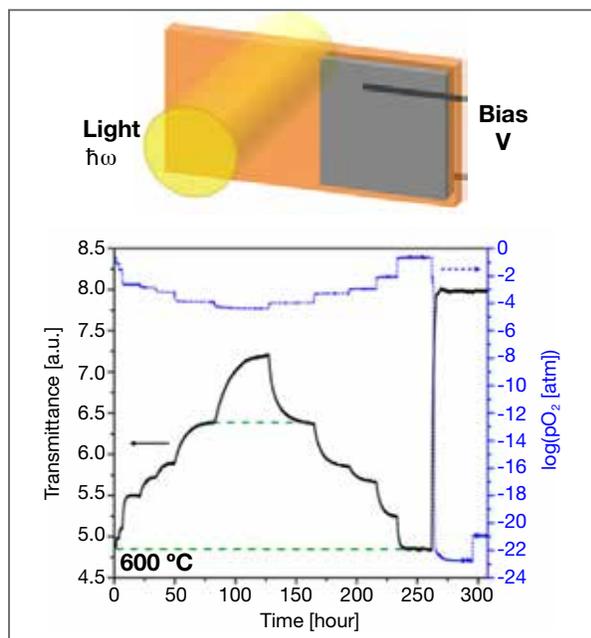
Elucidating the factors that enhance ionic conductivity is a critical challenge for understanding and ultimately designing materials for electrochemical generation and storage of energy. Materials such as yttria stabilized zirconia show high ionic conductivity at temperatures of 700 °C or higher and retain their strictly electrolytic properties under both highly oxidizing and reducing conditions. Developing electrolytes and electrodes that can function at lower temperatures would speed the development of fuel cell and electrolyzer devices at reduced cost and with higher reliability. At lower temperatures, there can be substantial variations in ion conductivity associated with structural heterogeneity such as grain boundaries and strain fields. For example, space charge effects have generally been found to slow ion conduction at grain boundaries in fluorite oxides such as ceria.<sup>114-115</sup> Oxygen diffusion at grain boundaries in (La,Sr)  $\text{MnO}_3$  was recently found to be orders of magnitude higher than in the grains.<sup>116-117</sup> Indeed, the relationship between local conductivity and grain boundary structure and composition is an outstanding question that currently inhibits the



**Figure 3.1.3.1:** Transmission X-ray microscope image of electrode containing  $\text{Fe}_3\text{O}_4$  nanoparticles.



**Figure 3.1.3.2:** Schematic depicting the nucleation and growth mechanism of large grains of  $\text{LiFePO}_4$ .



**Figure 3.1.3.3:** Correlated optical and impedance spectroscopy measurements on  $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  showing increased optical absorption at higher  $p\text{O}_2$  due to increase in the  $\text{Pr}^{4+}$  concentration. This provides a novel approach for *in situ* characterization of variations in transport properties with changes in the ambient oxygen.

rational design of grain boundaries. Even less is known regarding the impact of dislocations on oxygen transport, but as with grain boundaries, there is evidence for the potential for both enhancement and depression of oxygen ion conduction.<sup>118</sup> Chemical looping for processes such as combustion and thermochemical fuel synthesis requires nonstoichiometric oxides which must be able to withstand large changes in oxygen stoichiometry while maintaining structural stability at temperatures up to 1500 °C.<sup>119</sup> The behavior of cation dopant distributions in the presence of defects and their impact on structural stability, ion transport and catalysis at elevated temperature is poorly understood. Novel *in situ* optical approaches have been developed which allow the behavior of dopant cations to be monitored with changes in the ambient oxygen chemical potential (see Figure 3.1.3.3).<sup>120</sup> Furthermore, excursions in oxygen stoichiometry result in corresponding changes in lattice parameters, leading at times to the development of stresses sufficient to induce device cracking. This chemomechanical coupling between the chemical state of a material and its mechanical dilation, also of relevance to lithium battery electrodes and hydrogen storage materials, is characterized by its chemical expansion coefficient, such that minimization limits mechanical

damage. These multidimensional chemomechanical effects deriving from phenomena ranging from the atomic scale (changes in point defect dimensions), to interfacial effects and bulk phase transformations are just now beginning to be investigated in earnest.<sup>121</sup> Mixed ionic and electronic conductivity (MIEC), by offering sites for oxygen incorporation and electronic species for redox reactions, extends the active region of the electrode from the triple phase boundary to the full surface area. This is particularly critical at the cathode where the oxygen reduction reaction is responsible for oxygen exchange at oxide surfaces and becomes kinetically slow at intermediate temperatures (300–500 °C). Establishing the relative roles of bulk ionic and electronic defects vs surface electronic structure and chemistry under varying polarization potentials will point the way forward for tailoring structures to accelerate oxygen transport across the surface. In oxygen permeation membranes, MIEC is essential to support ambipolar diffusion through the membrane as well as the redox reactions at the respective gas/solid interfaces.

Supercapacitors work by storing electrical charge at the interface between an electronic conducting material and an ion conducting electrolyte. Because the capacitance of the system is related to the surface area of the material and inversely related to the distance between the plates, these materials are ideally highly porous, with a high density of micro- and mesopores in the size range 1–10 nm. Generally, activated carbon is the material of choice, but new advances in graphene oxide and activated graphene based materials have demonstrated substantial improvements in overall performance.<sup>122–125</sup> A significant question related to the advancement of progress is understanding how the electrical charge is stored, which requires characterization of the dynamic interaction between the electrolyte and the electrode. Moreover, the mechanisms by which the application of high voltages leads to material breakdown, and the specific role of defects in both of these phenomena still need to be determined.

### STATUS AND BREAKTHROUGH NEEDS FOR INSTRUMENTATION: MATERIALS FOR ELECTROCHEMICAL GENERATION AND STORAGE OF ENERGY

The existing range of structural, spectroscopic and electrochemical tools available for characterizing electroceramics typically provides insights by probing aspects of the chemical, structural, or electronic states. Investigating system structure and dynamics under polarization and under charge and discharge cycling is critical in order to fully understand materials functionalities and declining performance associated with aging due to structural and chemical change.

Only through the development and application of a suite of complementary tools sensitive to dynamics on appropriate scales, can we develop the comprehensive understanding of energy materials needed to design improved systems.

For example, for applications involving nonstoichiometric oxides such as solid oxide fuel cells, oxygen permeation membranes, and sensors, significant changes in oxygen stoichiometry (e.g., changes of  $\delta$  in  $\text{MO}_{2\pm\delta}$ ) occur during operation at elevated temperatures and under reducing/oxidizing conditions that are further impacted under electrochemical polarization conditions. Variations in stoichiometry can result in major changes in electrical, optical, electrochemical, diffusive, and mechanical properties of functional materials, which in turn impacts device performance. *In situ* thermogravimetric analysis, is routinely used to determine stoichiometry but its sensitivity is limited to 1 part per thousand in  $\delta$  and with no ability to probe locally or under electrochemical polarization. Alternative methods based on a number of novel concepts have recently been demonstrated including the use of high temperature compatible crystal resonators, coulometric titration coupled with measurements of chemical capacitance and optical absorption techniques offering many of these desirable features.<sup>120, 126</sup> Extending microscopy approaches, such as *in situ* STEM EELS, which can currently probe local oxidation states not only at elevated temperatures and pressures but also under polarization would be highly desirable. Likewise important are techniques such as scanning tunneling microscopy/spectroscopy that offer high spatial resolution regarding near surface electronic structures under dynamic perturbation under varying conditions of temperature, atmosphere and bias.

In batteries, one challenge has been in the ability to identify metastable intermediates critical to performance that might provide new design rules for enhanced performance. One example of such metastable phenomena is the high rate lithium iron phosphate system (LFP). The nano-LFP system defies prediction, where slow two-phase is predicted, but where high rate is observed due to metastable solid-solution behavior. Metastable phenomena may be more pervasive and not limited to the bulk electrode material, involving for example dissolution and transport of specific chemical species. A life limiting mechanism for several battery systems is cathode solubility resulting in the formation of deposits on the anode surface, resulting in an increased cell impedance.<sup>127</sup> Several materials display dissolution such as  $\text{LiMn}_2\text{O}_4$  cathodes where Mn dissolution leads to compromised cell performance.<sup>127-135</sup> Dissolution of vanadium has also been observed from  $\text{LiV}_3\text{O}_8$  material<sup>136-139</sup> and cobalt dissolution from  $\text{LiCoO}_2$  has also been correlated with capacity fade through cobalt deposition on the anode.<sup>140-143</sup> A major challenge is developing novel tools to characterize organic surfaces that form within a battery.

Most current characterization methods for locally probing interfaces depend on destructive analysis, recovery of the electrodes and analysis of the surfaces by spectroscopic techniques such as Raman, fluorescence, and infrared spectroscopy. However, critical to the success of *operando* measurements is the fidelity of the electrochemical performance of the *operando/in situ* cell and its compatibility with characterization measurements. Further, when combining insights from multiple complementary methodologies, a single cell design offers greater opportunity to correlate findings from different characterization approaches.

Our ability to characterize and describe systems or system components that are less well ordered remains limited. The space group notation is ideal for perfect crystals and reasonable classification systems have been developed to describe “well-defined crystal defects” such as point defects, dislocations and grain boundaries. However, for more disordered systems, the classification such as radial distribution function and pair correlation function is limited and excludes subtle aspects of the system. For example, the carbons used in supercapacitors present substantial challenges for simple structural characterization: they have a hierarchical, 3D porous structure which cannot be readily described in terms of either a fixed crystal structure (Space Group) or as simply “amorphous.”<sup>125, 144-145</sup> They do not possess long-range order in the traditional crystallographic sense, but a simple classification system to describe the folding and defects present in the graphene sheets is not yet available. Other classes of materials, such as carbon nitrides, show similar complexity. We still lack the characterization tools to describe subtle differences in less well ordered systems, an important class of energy materials.

## 3.2 PANEL 2: CHEMICAL IMAGING OF MATERIALS FAR AWAY FROM EQUILIBRIUM

Many important natural and technological phenomena use and rely on disequilibria. The role of non-equilibrium processes is manifested in two broad classes of behavior. The first class involves the explicit temporal evolution of materials that is driven by an explicit electromagnetic or thermodynamic driving force (e.g., dynamics). The second class involves the non-equilibrium (metastable) configurations of matter that can be used to produce novel functional properties. In both areas, most measurements have relied on either probing “frozen” states or spatially and temporally averaged measurements. These approaches however, fail to capture the inherent dynamics associated with the development of non-equilibrium states — including processes by which nanostructured materials can be assembled — as well as the complex evolution of these non-equilibrium materials under operating conditions.

Advances in modern chemical imaging that make use of multimodal approaches are central to the ability to create, understand, and control matter. Here the word “imaging” is used broadly to include the energy landscape of the chemical or material systems. Implicit in this approach is the need to explore the full range of elemental, chemical, and structural sensitivities, along with the relevant spatial and temporal resolutions needed to master materials response and behavior. Chemical imaging provides unique opportunities for understanding the structural dynamics and behavior of matter under conditions far away from equilibrium through the use of ultrafast tools (e.g. pump-probe modalities with picosecond-to-femtosecond temporal resolution) that probe the response of materials to energetic excitations via photon- and electron-based probes (e.g., diffraction, imaging, and spectroscopy). These ultrafast tools offer new opportunities to discover emergent properties of materials by tuning the photon excitation energy via transient photo-doping, vibrational pumping, and spin excitation. Similarly, the creation of metastable materials with novel functionalities requires the ability to observe and direct the dynamical assembly of matter in real-time with chemical specificity. This can be achieved through real-time multimodal chemical imaging using techniques with complementary sensitivities (e.g., using X-ray, electron, optical, and scanning-probe based tools). To this end, the development and deployment of a new generation of multidimensional characterization tools to observe and image the dynamical evolution of structure and function in 3D under various applied stimuli (e.g., temperature, electrochemical potential, and gaseous environment) is essential. Such advances, especially when paired with computational studies of time-dependent material properties and chemical processes, will accelerate materials discovery, especially for hierarchically assembled materials.

### 3.2.1 Energy Processes Across Time Scales and Length Scales

New capabilities to image transformations that combine multiple techniques are required to understand and control complex chemical and material processes. The development of new imaging methods capable of probing the properties of materials, devices, and their chemical activity is required to gain understanding and control over complex chemical structures and processes. By combining multiple imaging modalities, it will be possible to elucidate processes with timescales that can range from attoseconds to milliseconds, and length scales that can range from angstroms to micrometers. The spatial and temporal progression of individual events involved in processes away from equilibrium requires greater dynamic range to interrogate and understand many important problems in materials sciences, biology, chemistry and physics. Methods that operate in the nanoscale and ultrafast domains are essential because these are the scales at which important processes take place. For example, a detailed mechanistic understanding of heterogeneous photocatalysis may require tracking of multi-step chemical reactions under highly dynamic conditions. Knowledge of complex active-site structures (i.e. relative orientation of the support, active catalyst material, and target molecule) as the transition state is traversed, is beyond the combined spatial and temporal limits of current experimental techniques.

Complex materials are comprised of mixtures of different materials classes, such as metals, semiconductors, and insulators, and different phases, such as solids, liquids, and soft materials. Methods are needed that can image multiple material compositions and phases on surfaces and at buried interfaces with depth discrimination. Understanding material compositions on surfaces, in the bulk or at buried interfaces, is critical to following processes such as particle- or photon-induced nucleation or phase transformations. Current approaches to access

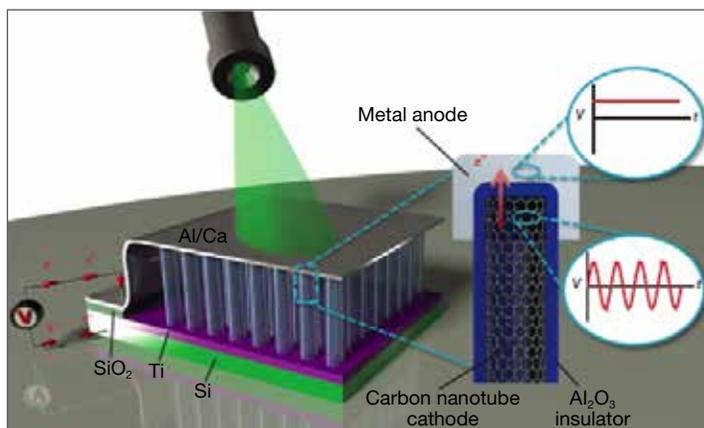
such information require the use of highly subscribed light sources (such as the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory) or rely on techniques with either high spatial resolution (e.g. scanning probes for surfaces; TEM or atom probe tomography for bulk or buried structures) or high temporal resolution such as ultrafast optical techniques. The above examples highlight the need to develop multimodal techniques that provide simultaneous high spatial and temporal resolution. A further challenge is unambiguous chemical identification (i.e., by IR, linear Raman, coherent anti-Stokes Raman, sum frequency generation, or other vibrational imaging techniques) perhaps in combination with these imaging modalities, with molecular-scale spatial resolution at ultrafast timescales. Obtaining such a combined capability would enable the identification of transient species during multistep reactions, and greatly advance a mechanistic understanding of a wide variety of chemical transformations relevant to energy sciences.

A comprehensive understanding of the chemical and structural transformations in complex heterogeneous materials at the inherent spatial and temporal scales of these materials is currently impossible to obtain. The development of robust *in situ* multimodal imaging tools would enable novel capabilities, such as simultaneous synthesis and characterization. Current experimental methodologies have several limitations; for example, single-molecule imaging techniques have difficulty identifying multiple molecular species simultaneously. Furthermore, the need to bridge gaps in spatial resolution between optical, scanning probe, and transmission electron microscopies remains a challenge. While transmission electron microscopy provides exquisite spatial resolution, the field of view is very limited and sample preparation is restrictive. In contrast, optical microscopies provide a wide field of view, and ease of sample preparation, but limited spatial resolution. Many important collective chemical and material processes can be studied at these intermediate length scales. Examples include imaging studies of biological systems, energy storage materials, and persistent metastable materials.

The operation of devices that harvest, store, or deliver energy can lead to substantial perturbations necessitating the control of materials in non-equilibrium conditions. The evolution of materials under these conditions involves a range of significant challenges spanning the full range of spatio-temporal scales. At a fundamental level, non-equilibrium structures involve the development of transient states associated with the accommodation of energy transport through a material. Unlike near-equilibrium materials that adopt crystalline structures with simple faceted morphologies, non-equilibrium materials (i.e., those that exist under conditions of driven transformations defined by external stimuli such as electrochemical potential, temperature, etc.) can be expected to exist in a range of states that may be either disordered or partially ordered. The ability to characterize such structures — in the environment of interest and with relevant resolution and fields of view — generally remains far beyond the reach of current capabilities. A particular challenge is the need to understand such structures consistently at length-scales that range from the molecular/nanoscale dimensions that define the fundamental organization of matter, through the mesoscopic and macroscale organization that controls mass/charge transport relevant at the device scale, or fluid flow within porous reactive matrices in geologic materials. At present, there exist numerous modalities for probing aspects of such structures (e.g., X-ray and electron microscopy and coherent diffraction imaging), each with different ranges of spatial and temporal resolutions. Beyond these structural challenges lies the need to understand the temporal evolution of such systems at the natural response time of the systems, which nevertheless depends critically on the nature of the process, whether controlled by molecular-scale structural reorganization (e.g., bond reorganization), through larger scale collective instabilities, or due to heterogeneous dynamics. Dynamical responses can be measured through techniques such as X-ray photon correlation spectroscopy, albeit over a modest range of temporal scales. The ultimate modality will therefore combine these spatial and temporal sensitivities to image material transformations in real time.

## VISUALIZING ELECTRONIC AND CHEMICAL DYNAMICS

Progress in solar energy conversion (e.g., solar to chemical or solar to direct power generation) will require mastery of dynamical processes that proceed on multiple timescales on hetero-structures with structural details that span from the molecular to device size length scales. The elementary step of photoinduced charge separation occurs on femtosecond timescales with charge injection rate and efficiency that presumably depend on interfacial structure, most likely on atomic scales. Charge transport, which is often the rate-limiting step and the source of inefficiency via charge trapping, involves multiple spatiotemporal scales, and particularly so, in nanocrystalline structures that are among



**Figure 3.2.1.1:** Schematic of the vertically aligned multi-walled carbon nanotube-insulator-metal (MWNT-I-M) optical rectenna. MWNTs are supported on a low-resistivity Si substrate with a back metal (Ti) contact, coated with an insulator ( $\text{Al}_2\text{O}_3$ ) from roots to tips and topped with a 40 nm Ca/20 nm Al semi-transparent electrode. An insulating  $\text{SiO}_x$  layer is deposited between the Ti and top electrode for current and voltage measurements on the area to the left of the MWNTs. The device is illuminated from the top with laser or solar light. The effective diode structure at the tip of a single MWNT is shown to the right of the device. The red arrow indicates the direction of electron emission from the MWNT cathode into the top metal anode. Right: a.c. input voltage signal in the MWNT antenna and DC voltage output signal in the top metal anode after rectification in the diode.

the most efficient cells. Carrier delocalization, tunneling, migration and self-trapping remain sufficiently ill-characterized such that reliable design principles have not emerged. Among the promising new directions on the horizon are: new materials, such as perovskites; improvements through the use of plasmonic nano-antennas to increase collection efficiency; direct solar to chemical energy conversion via plasmonic or hot-electron chemistry; and alternative principles that may prove disruptive, such as direct rectification of light to DC voltage via plasmonic nanotennas (rectenna), see Figure 3.2.1.1,<sup>146</sup> which have higher theoretical efficiency than photovoltaics.<sup>147</sup> To make meaningful progress in solar energy conversion and storage, it is essential to understand the governing heterogeneous structural and dynamical processes on the multiple space and time scales of relevance. Instruments capable of resolving dynamics of nanoscale devices, at femtosecond timescales, and imaging heterogeneous structures at angstrom length scales, are needed.

### SCANNING PROBES OF PLASMON-ENABLED CATALYSIS AND METAMATERIALS

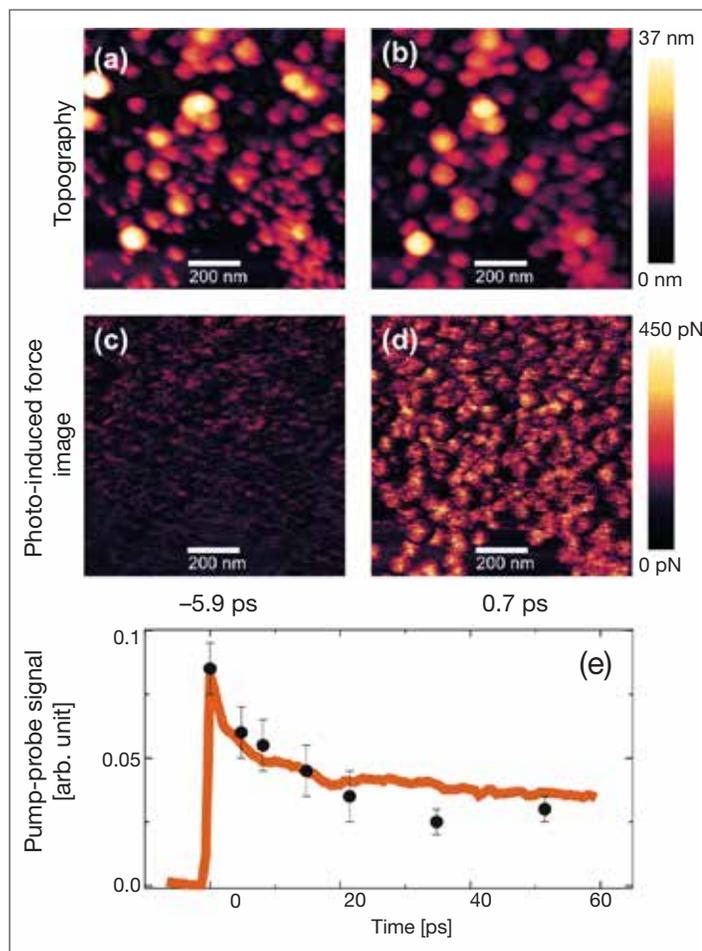
Among the emerging directions of research, plasmonically driven heterogeneous catalysis provides particularly rich new opportunities. Plasmonic nanostructures serve as nanoantennas to couple far-field radiation into molecular receivers, through the quasi-static local field where electric and magnetic fields may be sculpted with few limitations. The gross nanometric structure of the nanantenna, and the extended architecture in the case of nanantenna arrays (metamaterials), dictate the coupling to the far field. It is now increasingly clear that atomistic detail controls the near-field hot spots that drive the chemistry.<sup>148</sup> Theoretically guided design and fabrication with control over atomistic levels of detail will be required to engineer structures dedicated to enhance photocatalysis of selected reactions, such as to split water,<sup>149</sup> or to dramatically enhance photothermal conversion of sunlight.<sup>150</sup> Surface plasmons can potentially control chemistry via field dressed states or selective triplet state chemistry or chiral control. The controlling science, empirical and speculative at present, is ripe for exact characterization through the modern tools of time-resolved spectromicroscopy.

Recent advances in ultrafast time-resolved scan-probe microscopies hold great promise for unraveling the governing dynamics of heterogeneous photocatalysis and its plasmonic variant. Among notable relevant advances are: submolecular spatially resolved electroluminescence<sup>4-5</sup> and tip-enhanced Raman spectroscopy with submolecular resolution;<sup>6</sup> ultrafast time-resolved vibrational spectroscopy with single molecule sensitivity,<sup>7</sup> combined nanometer-picosecond spatiotemporal resolution through ambient photo-induced force microscopy, PiFM,<sup>8</sup> and closely related opto-thermal imaging.<sup>9</sup> As effective is photoelectron emission microscopy (PEEM), which reaches sub-femtosecond time and nanometer spatial resolution, sufficient to characterize the time evolution of plasmons, formation of hot electrons and their injection across interfaces.<sup>11</sup> A major advance in our understanding of carrier dynamics would be scored by imaging the charge trapping process in real time, via time-resolved scanning tunneling microspectroscopy to simultaneously determine structure, energetics characterized by local electronic states, and the governing mechanism of the trapping process. The principle instrumental advance required to conquer this challenge is the integration of tools, for example, ultrafast laser capabilities with scan probes, for joint imaging of spectral, spatial, and temporal dimensions (Figure 3.2.1.2).

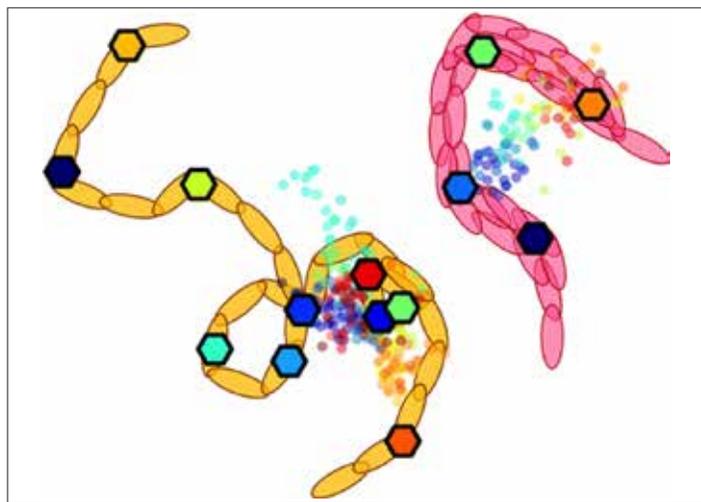
We are at the birth of the broad and exciting field of plasmon-driven catalysis, which encompasses chemistry, physics, photonics, plasmonics, materials, metamaterials, with structural and dynamical inhomogeneity on multiple space and time scales. Rapid progress in this field can be expected given the tools to “see,” with spatio-temporal resolution reaching the angstrom-femtosecond scale. The immediate natural extension to seeing is the adaptation of the same tools to control and manipulate matter with atomistic to nanometric detail. It is not difficult to imagine a lab inside an electron microscope, where theory-inspired systems can be assembled with direct “visual” feedback, the targeted properties can be measured *in situ* through nanoprobe, optical, and scan probe methods, and the structures are refined with direct feedback from theory.

### OPTICAL APPROACHES FOR VISUALIZING ENERGY TRANSPORT IN ORGANIC MATERIALS

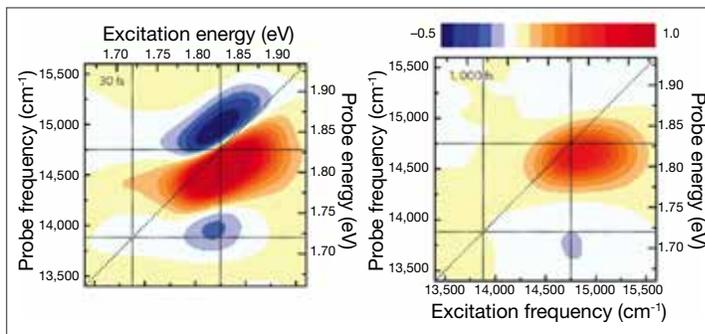
Underlying the ability to design high efficiency photovoltaics is the requirement to understand and direct structure-function relationships at the highest level of detail. In model conjugated polymers, single molecule fluorescence spectroscopy was used with great success to elucidate the relationship between molecular conformation and exciton diffusion and recombination. Recent applications of super-resolution microscopy on such systems show the power to directly map the emission sites along a single molecule (Figure 3.2.1.3).<sup>151</sup> Spectroscopic approaches, meanwhile, have been used to understand at high temporal resolution the photophysical processes in molecules with properties promising for use in high efficiency photovoltaics, including small organic molecules capable of singlet fission, the process by which a single photon produces multiple excitons that may be used to generate charges and create extractable photocurrent. A recent experiment reports real-time observation of multiexcitonic states in pentacene derivatives using two-dimensional coherent ultrafast electronic spectroscopy (Figure 3.2.1.4).<sup>152</sup>



**Figure 3.2.1.2:** Simultaneously recorded topography (a,b) and photo-induced force (c,d), when the probe precedes the pump by 5.9 ps (a,c), when the pump precedes the probe (b,d). The optically recorded pump-probe signal (e, continuous curve) agrees with the PiFM signal (e, discrete points).



**Figure 3.2.1.3:** Results from super-resolution fluorescence imaging of a model conjugated polymer reveal positions of emitting sites with < 5 nm resolution, allowing reconstruction of overall molecular architecture. Similar approaches can simultaneously map spectra of each emitting site along the polymer backbone.



**Figure 3.2.1.4:** Two-dimensional coherent electronic spectroscopy reveals that for short evolution times between a pump and probe, the spectra are dominated by features of the singlet state. At longer times, the response becomes dominated by triplets. Red peaks indicate positive signals (increase in transmission) due to ground-state bleaching and stimulated emission, while blue peaks correspond to absorption. Horizontal and vertical dotted lines show expected singlet and multiexciton energies.

While each of these types of experiments represent state of the art in spatial and temporal resolution achievable using visible light for study of materials relevant to high efficiency optoelectronics, recently there have also been micro-spectroscopic approaches to studying energy transport in these materials, approaches with potential to simultaneously achieve a high degree of spatial and temporal resolution. Such approaches greatly advance understanding of how local changes in molecular conformation and/or organization correlate with photophysical function. One recent implementation of transient absorption microspectroscopy reported direct visualization of exciton transport in single tetracene crystals with 200 fs time resolution and 50 nm spatial precision (Figure 3.2.1.5).<sup>153</sup>

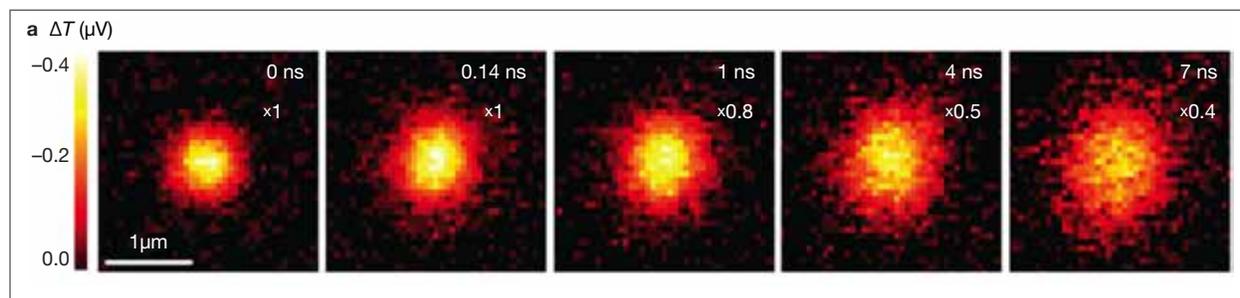
Microspectroscopies hold great promise for elucidating connections between molecular organization in chemical transformations and energy transfer. To push forward in this area, enhanced spatial resolution is needed. This may be achieved by integrating various super-resolution approaches, as are developing in biological imaging, together with time-resolved spectroscopies. These approaches hold promise for achieving spatial resolutions on the order of 5 nm with temporal resolution in the femtosecond range. Understanding with exquisite spatial and temporal resolution the fate of excitations is a critical step towards developing control of energy transfer processes. In the next steps, all-optical approaches to directing bottom-up organization of relevant materials and on-the-fly spectral-spatiotemporal characterization is envisioned.

## X-RAY PROBING OF FUNDAMENTAL INTERFACIAL ELECTRONIC AND CHEMICAL DYNAMICS

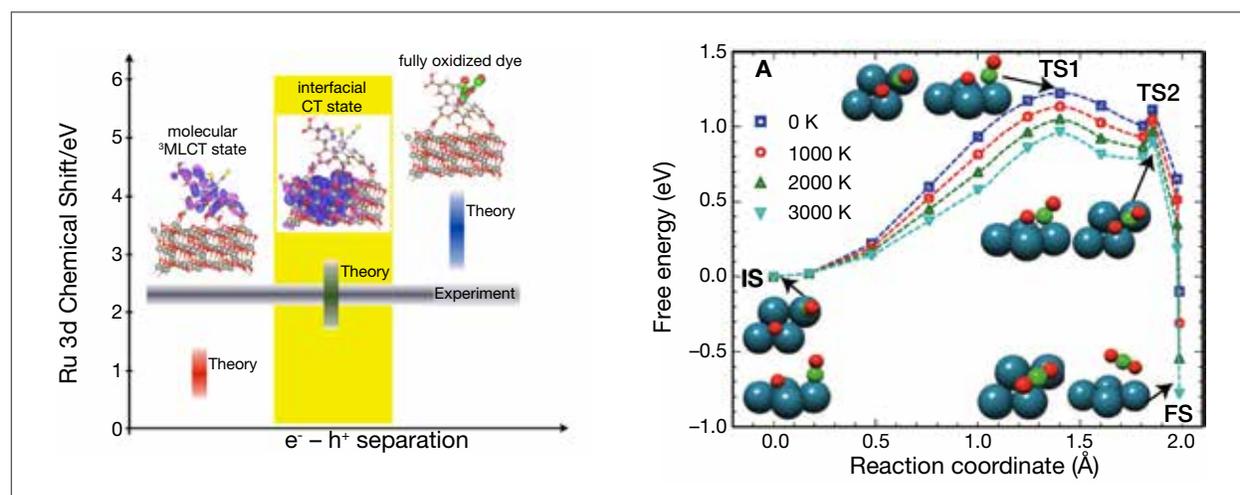
Photo-induced generation, migration, exchange, and trapping of charge carriers at interfaces between solids, molecules, and liquids, and in nanoscale heterojunction structures, are of central importance for the vast majority of emerging solar energy-conversion technologies. Monitoring the evolution of the interfacial electronic structure as it proceeds in real time, under realistic conditions, and with the atomic-site specificity and chemical sensitivity of X-ray spectroscopy holds great promise for improving our fundamental understanding of the reaction mechanisms that underlie the function of such devices. Hybrid systems based on dye-sensitized semiconductor nanostructures, organic/inorganic halide perovskite material combinations, and molecular donor-acceptor blends are attracting particular attention and, at the same time, pose a significant challenge for currently available characterization techniques owing to their inherent spatial and functional heterogeneity.

Soft X-ray spectroscopy techniques are particularly well suited to monitor electronic and chemical states of matter with elemental site-specificity and chemical sensitivity. Currently, these techniques are predominantly applied to study excited state and charge-transfer characteristics under ultrahigh vacuum conditions or of isolated molecules and nanocrystalline semiconductor samples in solution. Extending these methods to non-replenishing condensed phase systems and, ultimately, to operating photochemical devices holds great promise to capture transient electronic and chemical states that may be crucial to understand a material or device function but are too short-lived to be tracked by steady-state spectroscopy techniques.

Next generation X-ray free electron lasers such as the European XFEL and LCLS II will provide femtosecond X-ray pulses at unprecedented pulse repetition rates and average power, making photon-hungry *in situ* and *operando* X-ray spectroscopy techniques a viable option. Diffraction-limited synchrotron radiation sources will provide complementary capabilities in the picosecond domain. A crucial challenge to address, however, is the development of time-resolved



**Figure 3.2.1.5:** Transient absorption images on tetracene crystals pumped at 470 nm and probed at 810 nm to visualize triplet excitons at different pump–probe delays.

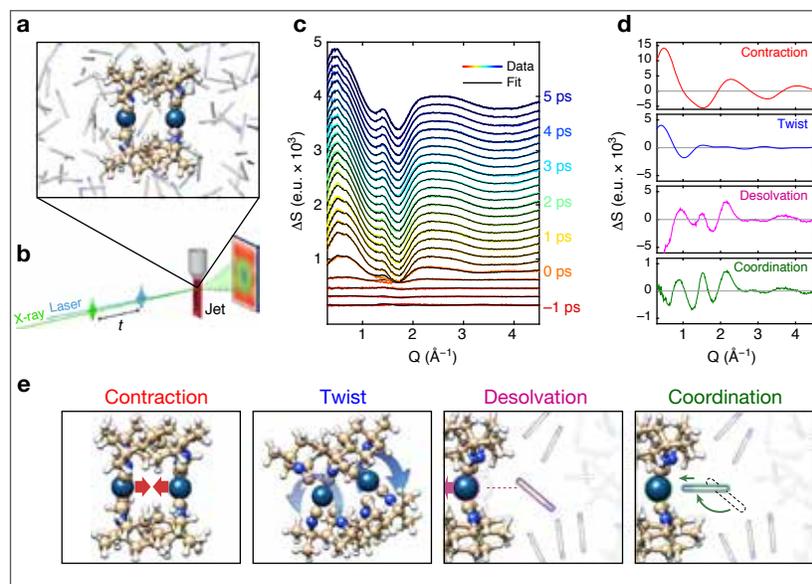


**Figure 3.2.1.6:** Examples of interfacial processes studies by time-domain X-ray spectroscopy: a) Locating a migrating electron during photo-induced molecule–semiconductor charge transfer by femtosecond time-resolved XPS b) Exploring the transition state region of surface-catalyzed CO oxidation on laser-heated Ru(0001).

*operando* X-ray spectroscopy techniques that are capable of taking advantage of these new light sources. In particular, efficient use of high-repetition rate light sources to sample multiple temporal scales in a single experiment will be vital to enable the leap from the study of a few model systems to monitoring reaction pathways under application-relevant conditions.

Ultrafast time-resolved X-ray spectroscopy methods have been used to, for example, localize a migrating electron during photo-induced interfacial charge-transfer and identify transient molecular configurations in the transition state region of a surface-catalyzed chemical reaction (Figure 3.2.1.6). While the atomic site-specificity and chemical sensitivity of X-ray transitions provides an atomic-scale perspective of the ensuing dynamics, current experiments probe either idealized, “clean” interfacial systems<sup>154-155</sup> or isolated nanoscale samples.<sup>156</sup> As such, the field of time-domain X-ray studies of interfacial electronic and chemical dynamics is in a proof-of-concept phase that creates exciting scientific stimuli but is also marked by a significant “reality gap” with respect to the *operando* conditions that ultimately need to be met in order to directly link fundamental insights with application-relevant processes.

Extending the realm of ultrafast X-ray techniques to *in situ* and *operando* conditions will bridge the gap and provide atomic-scale insight into ongoing photovoltaic and photochemical energy conversion processes under application-relevant conditions. Currently available steady-state *operando* X-ray spectroscopy techniques demonstrate the vital importance of “real life” environments to access meaningful fundamental data and point the way toward required tool developments; merging the capabilities of cutting-edge time-domain and *operando* X-ray techniques will open pathways to connect the most fundamental temporal, spatial, and spectral scales with relevant functional scales.



**Figure 3.2.1.7:** (a) Shows a snapshot of  $[\text{Ir}_2(\text{dimen})_4]^{2+}$  in acetonitrile solution from Born-Oppenheimer Molecular Dynamics simulations. (b) Shows the experimental set-up. (c) Shows the recorded difference scattering data and fit, each consecutive curve has been offset by 150 e.u. for visibility. (d) Shows examples of the four components used to fit the data; The contraction signal is simulated for a 4.2 to 2.9 Å contraction of the Ir-Ir distance with no change in the ligand twist. The ligand twist component is simulated for a 0 to 15 degree increase in the N-Ir-Ir-N ligand dihedral twist at an Ir-Ir distance of 2.9 Å. The two solute components are extracted directly from the analysis. (e) Shows a sketch of four dynamics giving rise to the signals presented in (d).

## PROBING TRANSIENT STRUCTURES AT ATOMIC TIME AND LENGTH SCALES USING ULTRAFAST ELECTRON DIFFRACTION

In photochemistry, photosynthesis and photovoltaics, the absorbed photon energy is transformed into chemical, mechanical and electrical energy. Often, this energy conversion is mediated by nuclear motions, such as molecular isomerization, atomic vibration or proton transfer, over time scales ranging from a few tens femtoseconds to microseconds. Capturing these structural changes with atomic resolution and on the relevant timescales will provide fundamental understanding of photoinduced transformations, thus enabling the control necessary to achieve higher energy conversion efficiency.

In recent years, both X-rays and electrons are being developed as

ultrafast tools to reveal the atomic-detail structural dynamics in real time, and both these techniques are approaching the desired atomic spatial and temporal resolution. Ultrafast X-ray structural probes often rely on large national facilities such as the Linac Coherent Light Source (LCLS) at SLAC. In contrast, due to the strong Coulomb's interaction with nuclei, electrons are scattered at least five orders of magnitudes more strongly than X-ray photons and neutrons. This makes electrons more suitable to probe small volume, dilute samples where signals are weak, and also to capture fast events where signal is limited by extremely short duty cycle. Furthermore, being charged particles with light mass, electrons can be readily focused to the sub-angstrom scale through the use of electrostatic and magnetic lenses, and shaped in energy and momentum space. Because of these unique features, electrons allow versatile operation modes for imaging, diffraction, and spectroscopy, with both high spatial and energy resolutions, all in a single instrument.<sup>157</sup> In general, such a facility can fit into a single PI's laboratory.

In a recent gas phase ultrafast electron diffraction (UED) experiment, 0.7 Å and a ~100 fs spatio-temporal resolution has been demonstrated.<sup>158</sup> Acquiring the sub-50 fs time resolution together with the addition of a liquid cell in the UED facility will lift the current limitation and enable a vast array of photoinduced transformations under direct and real time investigation with atomic time and length scales.

An important example is seeking direct structural characterization of photocatalytic reaction mechanisms in bimetallic  $d^8$ - $d^8$  complexes (Figure 3.2.1.7).<sup>156</sup> Transition metal based molecules and materials dominate thermal, electro-, photo-, and bio-catalysts for the transformation of small molecule reactants like  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . The dominance of transition metal catalysts derives from their ability to bind reactants and shuttle the multiple electrons required for bond making and breaking. The inner coordination sphere nuclear structure surrounding catalytic metal is critical to understanding the function of photocatalysts. Two science objectives warrant emphasis. First, characterizing the nuclear structure of the inner coordination sphere would provide a direct probe of how the reactant transforms to product while bound to the metal site. Secondly, understanding how photocatalysts function requires understanding how the nuclear structure surrounding the metal site responds to photoexcitation and how this interplay between the non-equilibrium electronic and nuclear structure influences reactivity.

To understand the coupled motion of electrons and nuclei in isolated quantum systems and proton transfer reactions, a new generation of ultrafast electron diffraction facilities with 10 fs time resolution must be developed. The technical developments required specifically for solution-phase studies include delivery of stable liquid jets of micron thickness and demonstration of the multiple elastic scattering signals with the inelastic scattering interference sufficiently weak for diffuse scattering measurements to be definitively interpreted.

### STUDYING ULTRAFAST PHOTON-LATTICE COUPLING IN PEROVSKITES

In the past several years, lead-halide hybrid perovskites have emerged as disruptive materials for photovoltaics, with power conversion efficiencies now reaching 20%, comparable to polycrystalline silicon (Figure 3.2.1.8).<sup>160</sup> In the prototypical methylammonium lead-halide ( $\text{CH}_3\text{NH}_3\text{PbX}_3$ ,  $\text{X}=\text{I}, \text{Br}, \text{Cl}$ ), charges in polycrystalline films show remarkably long lifetimes ( $>1\mu\text{s}$ ) and, consequently, long diffusion lengths of up to 170  $\mu\text{m}$  in single crystals. Recent studies have suggested that ultrafast dynamical processes following absorption of a photon underlie these efficiencies<sup>161-163</sup> as reflected in unusual hot carrier relaxation dynamics. Additional studies have pointed towards the important role of polaronic distortions in the unique transport properties, which in turn generated proposals that the hybrid organic-inorganic structure leads to greater structural deformability,<sup>164</sup> giant photostriction responses and strong light-matter coupling.<sup>165</sup> Theoretical studies have pointed towards dynamic structural fluctuations as a potential explanation of the long carrier lifetimes and slow recombination rates exhibited by these materials in the presence of significant defects.<sup>166</sup> In summary, there exists an important connection between electronic and structural processes at early time-scales after photoexcitation, processes that determine from a microscopic perspective the efficiency of a photovoltaic device. Direct probes of the coupled optical and structural response that likely underlies these functionalities need to be further developed.

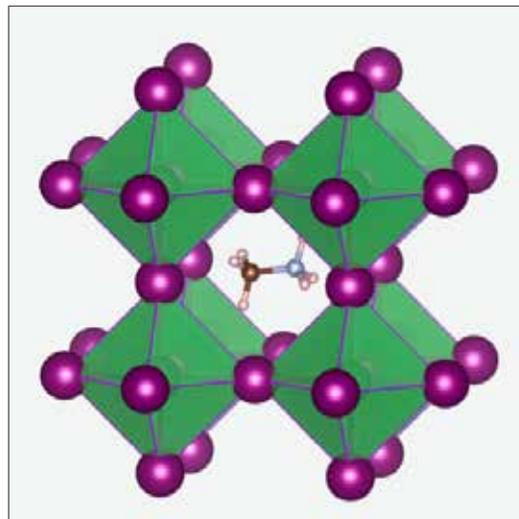


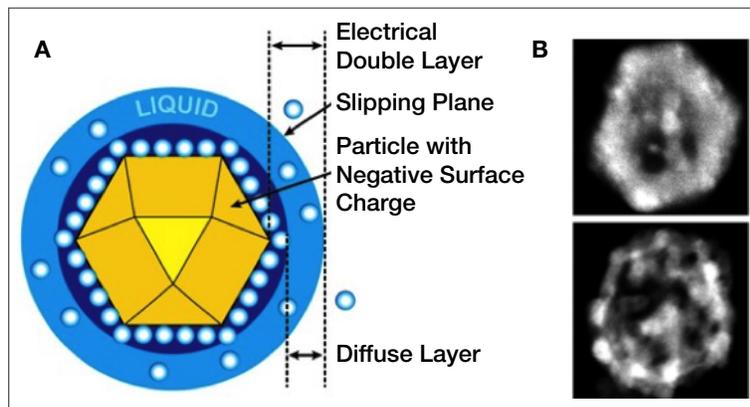
Figure 3.2.1.8: Hybrid perovskite structure.

### COUPLING ALGORITHMS WITH THE HARDWARE TO CONVERT MASSIVE DATA INTO INFORMATION

One of the important methods to track chemistry in time is to monitor evolving vibrational spectra. While this can be effectively accomplished through methods such as time-resolved stimulated Raman spectroscopy and coherent anti-Stokes Raman spectroscopy, including novel schemes for super-resolution to go beyond the diffraction limit,<sup>167</sup> an inherent challenge is that in contrast with ensembles, a single molecule does not have a spectral fingerprint. In single-molecule spectroscopy, light scattering is a strictly tensorial quantity, which depends on molecular orientation relative to local vector fields. The challenge is even greater for electronically excited and transient nonstationary states in heterogeneous environments. The very large data set that can be generated in one measurement that extends from femtoseconds to seconds timescales cannot be fully analyzed or interpreted presently. Advanced mathematical algorithms are necessary to go beyond principle component analysis, to match transient spectra individually. This could take the form of using best-guessed theoretical scattering tensors derived from quantum chemistry calculations, to carry out exhaustive searches of the tensor space to make matches on the fly, and to then adapt the original tensors to identify transient structures. Integration of advanced applied mathematical tools with the hardware will be essential to recognize the information content of massive data sets that can be generated in any of the movies generated through time-resolved microspectroscopy.

## 3.2.2 Non-Equilibrium Structural Evolution and Driven Transformations

Understanding the processes involved in heterogeneous catalysis, nanomaterials synthesis and self-assembly, separations, ion transport in composite membranes, energy storage (e.g., in batteries and capacitors), and materials corrosions are all brought together in a unifying challenge: the imaging of chemical and structural states within



**Figure 3.2.2.1:** (A) At solid-liquid surfaces, the zeta potential is used to understand ionic arrangements at the interface and how this leads to functionality (B) Typical *in situ* TEM image of an Au/Ag nanoparticle during and after completion of an exchange reaction.

and materials synthesis/stability (e.g., electrode-electrolyte interfaces in batteries,<sup>168</sup> nucleation and growth from solution,<sup>169</sup> and corrosion resistance<sup>170</sup>). For all these cases it is known phenomenologically that the interface structure controls the properties of the system as a whole—the concepts of the electrical double layer (EDL)<sup>171</sup> and the Zeta potential<sup>172</sup> are typically invoked to understand function in these systems (Figure 3.2.2.1 A). It is also known that the solid surface can be functionalized to control the solvation/desolvation of ions,<sup>173</sup> either intentionally or as a byproduct of the process itself (e.g., the solid-electrolyte-interphase (SEI) layer in Li-ion batteries<sup>174</sup>). However, the specific properties of individual interfaces and how to control them are not currently within our grasp because of the dynamic nature of the interface. Measuring how the meta-stable interfacial structural dynamics develops, under driving forces far from equilibrium, is an even greater imaging challenge due to the increased speed required (Figure 3.2.2.1 B).<sup>175</sup> We therefore need fast to ultrafast (i.e. microseconds to picoseconds) low-dose imaging capabilities with atomic and molecular spatial resolution and meV energy resolution to determine which interactions are dominant and how they progress in a rapidly changing liquid environment.

As shown in Figure 3.2.2.2, directly imaging nanoparticles using conventional *in situ* transmission electron microscopy (TEM) during a reaction is limited in both spatial resolution (by the liquid) and in temporal resolution (by the source). In addition, the electron beam acts like a catalyst for any chemical reaction and experiments need to be performed under extremely low doses ( $<0.1 \text{ e}/\text{\AA}^2/\text{s}$ ).<sup>176-177</sup> Despite the complexity of the challenge for imaging atomic/molecular processes at solid-liquid interfaces in the TEM, the basic constituents have already been demonstrated: nanostructure dynamics have been observed by aberration corrected TEM,<sup>178</sup> transient microstructures have been observed on the sub-microsecond timescale in the dynamic TEM (DTEM),<sup>179</sup> and molecular species have been identified by electron energy loss spectroscopy (Figure 3.2.2.2).<sup>180</sup> In addition, Compressive Sensing approaches<sup>181-183</sup> for optimized sampling have been demonstrated to increase speed and lower dose for imaging *in situ* reactions and can be implemented within the microscope hardware (also addressing the data challenge for imaging on these time and length scales).<sup>183-184</sup> Combining all of these together requires the use of pulse compression technology to shape the photo-emission pulse of the DTEM in either the spatial, temporal or spectroscopic domain.<sup>185-186</sup> Such capabilities have already been demonstrated for electron diffraction experiments and employing them on a microscope would transform the capabilities of TEM to directly image chemistry — essentially the compression optics add a temporal/spectroscopic lens to the spatial lenses that are routinely used in microscopy today and delivers multimodal imaging capabilities over the molecular to micron length scales.

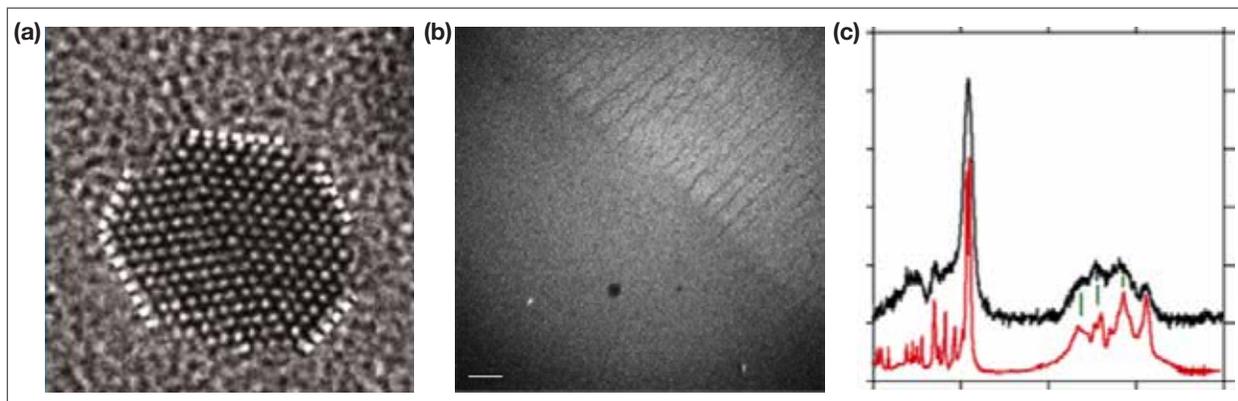
## CORROSION

The cost of the deterioration of materials (e.g., metals) due to chemical reactions with the environment had a net cost within the United States of \$276 billion in 1998, about 3.15% of US GDP. Corrosion is critically important for

a complex functional system with both spatial and temporal resolutions. Here we highlight a few energy-related areas that demonstrate the need for developments in instrumentation and methods for imaging with time resolution to reveal the underlying fundamental science controlling these critical technologies, including batteries, corrosion/oxidation, geologic fluids, and electrochemistry.

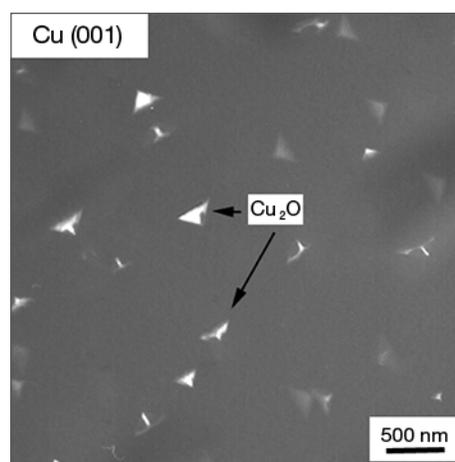
## DIRECT IMAGING OF CHEMICAL REACTIONS AT NANOSCALE SOLID-LIQUID INTERFACES

The solid-liquid interface is key to many functions important for energy storage



**Figure 3.2.2.2:** (a) TEM image of a colloidal nanoparticle inside a graphene liquid cell, (b) DTEM image with ~10 ns temporal resolution showing the presence of a liquid phase at a reaction front in the formation of NiAl intermetallic from Ni and Al multilayers, (c) monochromated EEL spectrum showing vibrational spectroscopy from the surfaces of individual nanoparticles.

applications ranging from microelectronic devices to bridges, oil pipelines and metal implants in humans. Many theories exist to explain corrosion/oxidation mechanisms. However, all classical oxidation theories assume a uniform evolution of the reaction front.<sup>187-189</sup> Structural changes are not considered, in part because of a lack of experimental results that visualize this non-uniform nucleation and growth in conditions that allow for highly controlled surfaces and impurities. Recent *in situ* TEM studies reveal that the initial stage of Cu oxidation is due to surface diffusion of oxygen (Figure 3.2.2.3),<sup>190</sup> providing a clear challenge to the classical oxidation models. A 2011 report, *Research Opportunities in Corrosion Science and Engineering* by the National Research Council, recognized the need to reinvent our understanding of corrosion at the nanoscale. Improvements, especially in temporal and spatial resolution during *in situ* oxidation is needed to benchmark theoretical developments to model oxidation from the early stages to the growth of the microns-thick oxide scale that lead to macroscale corrosion.



**Figure 3.2.2.3:** TEM image of copper oxide islands formed during *in situ* oxidation of Cu thin films.

## GEOCHEMICAL REACTIONS

The interaction and reaction of complex geologic fluids with minerals controls the chemical and transport processes encountered at the Earth's surface and in the subsurface. Despite the extensive length and time scales over which water-rock interactions can occur, there is the inescapable fact that interfacial phenomena — i.e. mineral surfaces as well as buried interfaces such as grain boundaries, fractures and dislocations at the atomic scale — control the exchange of matter and impact the nature of elemental transport, migration, weathering, water chemistry, biological processes and sequestration and remediation schemes.<sup>191-192</sup> A key grand challenge in the earth sciences is to understand the geochemical and geological processes controlling the evolution of porous fluid-rock systems from the nano- to the macro scale.<sup>193</sup> Highly resolved spatial and temporal information is needed to advance our understanding of how these properties change over a wide range of pressure, temperature and composition. Nano- to microscale heterogeneities in the form of surface roughness, crystal size, variable composition, structural ordering and defect content must be understood in order for advancements to be made in predicting the properties and behavior of complex natural materials under varying geochemical environments. Novel methods are required to probe the structure and reactivity of the fluid-solid interface from atomic to the molecular level in real-time at conditions relevant to subsurface energy systems (e.g., gas shale, CO<sub>2</sub> sequestration, geothermal, contaminant sites). New developments in optical, X-ray, and neutron instrumentation are needed to address the following key questions:

- To what extent do atomic- and molecular-scale structural features control the macroscopic properties of complex fluids and minerals?
- How do the specific fluid and mineral properties at fluid/solid interfaces influence mass transfer along and across the interface?
- How do reactive domains develop and evolve at mineral surfaces, and to what extent do porosity generation and fluid confinement influence this process?

## CONTROL OF MICROSTRUCTURE EMERGING FROM NON-EQUILIBRIUM STATES

Lighter and stronger materials are critical components in reducing energy use in a wide range of transportation and energy generation systems. Higher performance materials with unique properties are key to a variety of energy storage and conversion processes. The ability to produce these materials involves controlling transitions through highly non-equilibrium states. For example, many structural metals (e.g. for aircraft) are cast from molten liquids, then processed using sophisticated heat treatments to optimize the microstructure and finally machined into a final form, with further heat treatment to produce the optimal performance that is needed. Modern imaging techniques have great potential to observe the evolution of these non-equilibrium states and to accelerate the development of new processes to create optimized microstructures.

Additive manufacturing, often referred to as 3D printing, builds objects by depositing microscopic amounts of material in specific places with specific properties. The deposited material is then locally processed with, for example, a laser to create the desired microstructure and properties. Since materials are modified locally, properties can be tuned across the object to optimize performance. In addition to creating superior performance, additive manufacturing also allows for rapid prototyping and shorter production times. Additive manufacturing is particularly suited to high value products such as in aerospace components and energy conversion devices where control of porosity and weight is critical. Ultimately, these challenges can only be met with probe tools that are able to spatially and temporally image the interplay of structure, strain, and composition as material is created.

### 3.2.3 Experimental Challenges for High-Resolution *Operando* Measurements

A particular challenge in the use of high resolution measurements for *operando* observations of a device under study is the need to understand which of the relevant transformations need to be resolved within a macroscopic system with inhomogeneity. Consequently, it is necessary to significantly shorten measurement times. These advances will necessarily involve improvements in current detector technology (e.g., sensitivity, dynamic range), but also in methods of data processing to enable “on-the-fly” analysis in order to ascertain the value of a discrete 2D measurement based on the goals of the experiment. Such measurements must also be performed with the ability to apply stimuli to a sample within a wide range of environments (extreme temperatures and pressures).

The design of novel sample cells is needed to enable reliable electrochemical and imaging measurements, especially with soft X-ray and electron based probes where penetration of the probe beam is severely limited. As such, novel methods to control the liquid phase for studies of the solid/liquid interface are needed to accommodate high surface area electrodes where liquid passes through microstructured porous materials. Microfluidic technology can be used to develop well-defined flow patterns, to allow a controlled delivery of reactants during imaging.

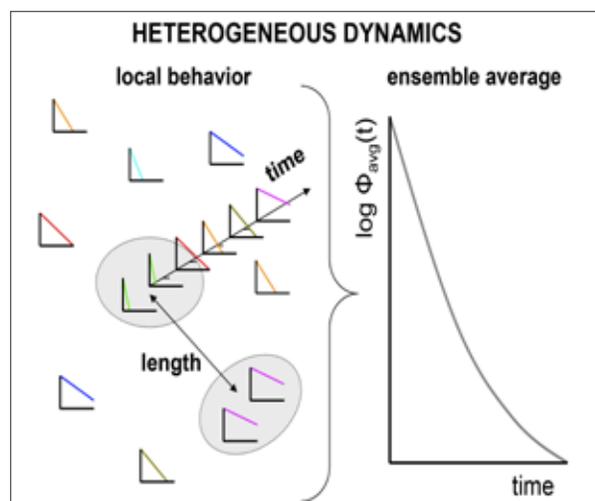
The impact of the imaging probe on the sample is another significant consideration. These studies will inevitably require the exposure of samples to an intense probe beam to image processes in time and space by spectroscopy or diffraction. Mitigating the effects of the probe beam will require multiple approaches. A more robust and quantitative

knowledge of primary and secondary effects of beam perturbations is needed so that experiments can be designed to minimize these effects. While beam-sample interactions are well-studied in relatively simple materials, it is currently very difficult to predict behavior in complex functional materials systems that are of interest. Complementary to this approach is the development of low dose techniques and improved detectors that maintain the information content of the data while limiting damage.

The challenge becomes even more daunting when it comes to understanding rare events (e.g., nucleation), where the time and location of reaction is unknown within a large sample. These studies are often not possible with the current user access mode of synchrotron user facilities. Achieving this objective will require creative approaches in the design of detectors that enable X-ray spectroscopy in laboratory-scale microscopes.

## 3.3 PANEL 3: CHALLENGES OF HETEROGENEITY ACROSS MULTIPLE LENGTH SCALES AND TIME SCALES

Except for perfect single crystals near 0 K, all matter is heterogeneous on some length or timescale. It is inherent in both the structure and the nature of its interactions at even the most elementary levels. The term “heterogeneous” is used in different senses by different communities, and only in mathematics is there a single meaning. For others, the most obvious usage is in the sense of mixtures and composites, where its most dramatic impact on materials properties are manifested. So it is an essential attribute of the natural world, and the complex, highly dynamical systems within it. Superalloy properties depend on it. Such heterogeneity is spatial and may have both compositional and density manifestations on length scales that can vary from nanometers to millimeters. But, quite separately, there is dynamic or temporal heterogeneity that can be observed even in pure monatomic liquids like selenium where the term is used to account for the need for more than one timescale to describe the liquid’s non-exponential approach to equilibrium after perturbation. And there are many other uses of “heterogeneity,” e.g. in chemical reactions, as explained below.



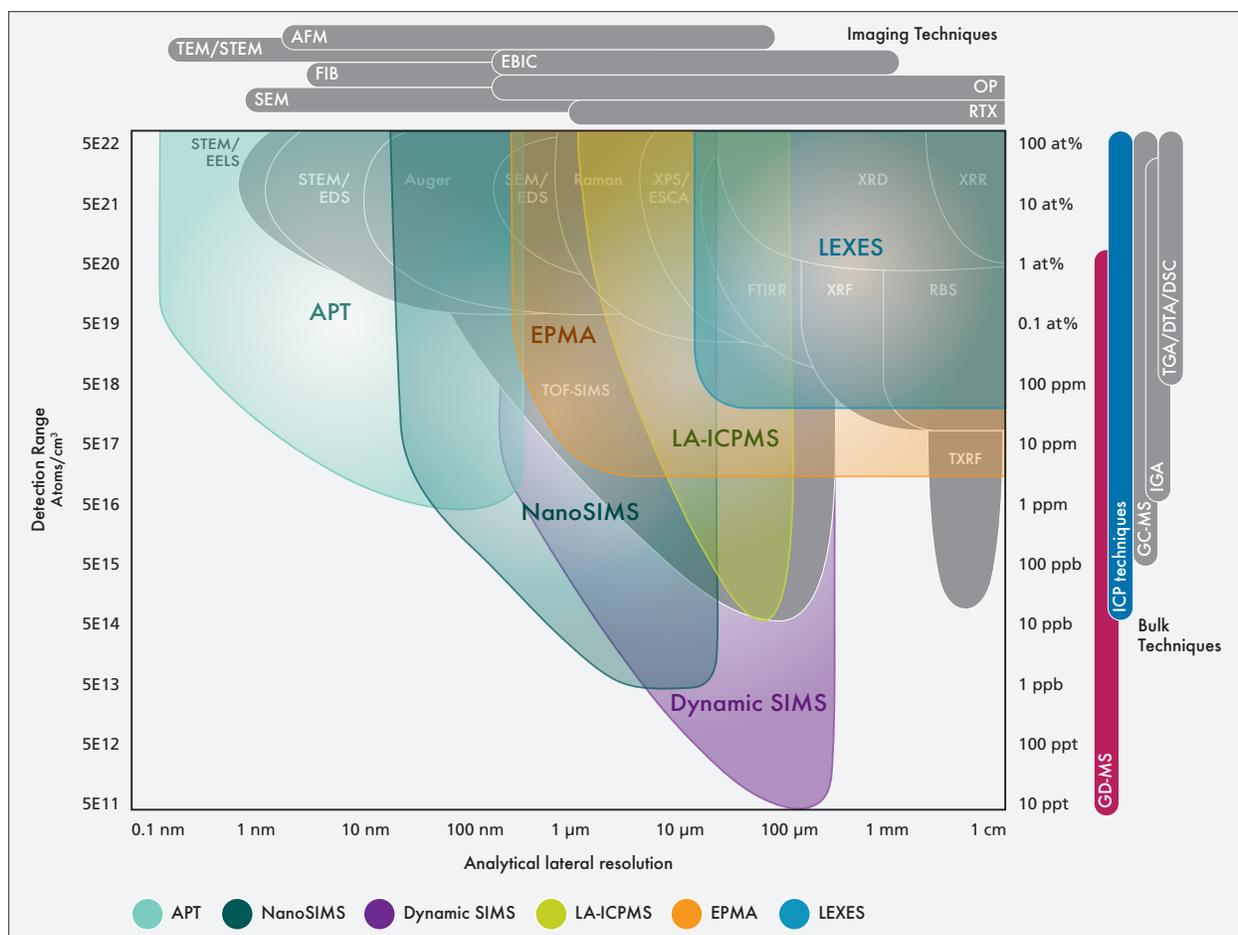
**Figure 3.3.1.1:** An illustration of how heterogeneous dynamics in pure viscous liquids (a non-exponential approach to equilibrium known for more than 150 years) can arise from a distribution of microdomains, each of which relaxes exponentially (local relaxation), i.e., there is an underlying spatial heterogeneity that is much more difficult to observe. The ensemble average,  $\Phi_{\text{avg}}(t)$ , is the superposition of these exponential processes.

When observed for varying extents of time or ranges of distance, the features of this heterogeneity may disappear in one regime only to reappear in another where dominating influences on structures, mechanisms of action, and forms of transformation are seen, as indicated by the time series in Figure 3.3.1.1.<sup>46</sup> The importance of such complexity is a common foundational principle underpinning frontier interdisciplinary problems spanning physical (physics, chemistry, materials), natural (biology, atmospheric and geological), engineering and mathematical sciences. The challenge of characterizing complex systems where essential attributes of spatio-temporal heterogeneity come to play an important role stands as both an impediment and opportunity for progress in research.

that mediate energy transformations integrate processes that occur on broad time scales — spanning ~femtoseconds to seconds, even to millennia — and length scales ranging from angstroms to meters, and well beyond. At the atomic scale, the ultrafast rearrangements of bond breaking and formation and the redistribution of charge are at the heart of energy conversion. These events are coupled at larger spatio-temporal scales by processes such as the diffusion of energy carriers; separation of charged species across interfaces; formation and evolution of reaction intermediates; and interactions of mass/energy-transfer with complex system-level dynamics. These interactions are critical to materials properties and functionality and need to be understood and thus characterized in descriptive/predictive multiscale terms to enable the rational design and improvement of new materials and processes. Fluctuations and disordered states, however, and especially their mutual couplings, are poorly understood in many energy-relevant technologies, and new tools and methods are required to characterize them across relevant spatio-temporal scales.

### 3.3.1 Spatial Heterogeneity

Many critically important energy materials and functional systems exhibit chemical and textural heterogeneities that are linked across disparate time and, in particular, length scales. For example, the nucleation of particles from an initially homogeneous solution, subsequent growth, and aggregation are central to a wide range of energy-centric

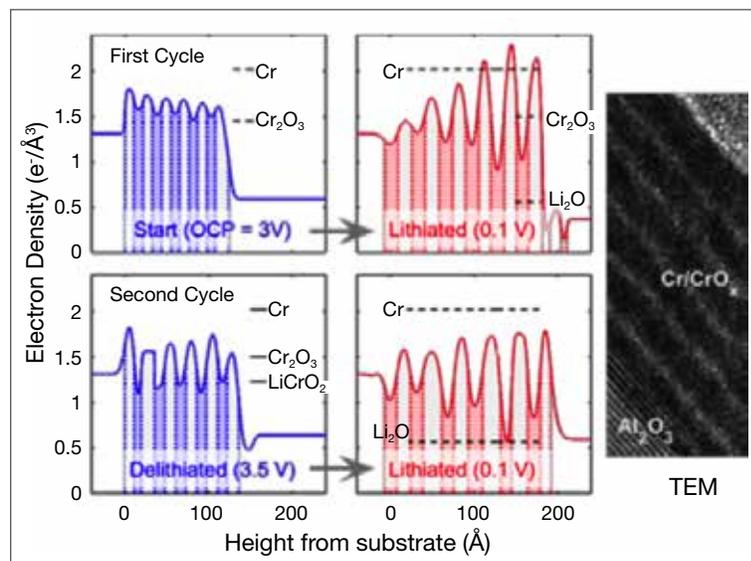


**Figure 3.3.1.2:** Multiple analytical platforms now needed to fully characterize the spatial distributions of atoms in materials by post-mortem studies. Techniques featured in the figure include atom probe tomography (APT), differential scanning calorimetry (DSC), differential thermal analysis (DTA), electron beam-induced current (EBIC), energy dispersive X-ray spectroscopy (EDS), electron probe microanalysis (EPMA), electron spectroscopy for chemical analysis (ESCA), focused ion beam (FIB), glow discharge mass spectrometry (GD-MS), inductively coupled plasma (ICP), instrumental gas analysis (IGA), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), low energy electron-induced X-ray emission spectrometry (LEXES), nanoscale secondary ion mass spectrometry (NanoSIMS) Rutherford back-scattering spectrometry (RBS), real-time X-ray (RTX), total reflection X-ray fluorescence (TXRF), and X-ray fluorescence (XRF). OP refers to optical techniques, and FTIRR to Fourier transform infrared and Raman spectroscopy.

applications, and are the central underlying dynamical features of the chemical synthesis of nanomaterials. The nature of these processes are such that they can lead to complex dispersions of nanomaterial sizes and composition as seen in many industrially important forms of supported heterogeneous catalysts.

Materials for energy harvesting, conversion, and storage display complex morphologies, mixed material phases, interfaces, and heterogeneity that are essential to their effectiveness. Interfacial systems naturally exploit heterogeneity, but spatial heterogeneity can also be important within a single phase. Strong composition and temperature gradients that are coupled to chemical transformation in a reacting flow such as turbulent combustion provide an example. An effective photo-electro-catalyst in its simplest form combines a light harvesting material (e.g., semiconductor) and an electro-catalytic material (e.g., metal nanostructure), and the interface between these two building blocks to a large extent governs the performance of the assembly. These interfaces are complex, exhibiting high degrees of structural non-uniformity and therefore electronic heterogeneity, which directly impacts their interaction with light and their effectiveness in transferring excited charge carriers from the semiconductor to the metal.

Centrally important in understanding the natural or synthetic formation of complex materials, and the relationships between structure and functionality, is the distribution of trace and major elements in materials spanning angstrom to centimeter length scales. Equally important for many functional systems is characterization of the empty or fluid-filled



**Figure 3.3.1.3:** The lithium ion conversion reaction ( $\text{CrO}_x + 2x\text{Li} \rightarrow \text{Cr} + x\text{Li}_2\text{O}$ ) is observed, *in operando* and at sub-nanometer resolution, with *in situ* X-ray reflectivity. The  $\text{Cr}/\text{CrO}_x$  multilayer structure is found to (de)lithiate in a purely 1-D manner, preserving the layered structure.

pores in materials, and their interconnect- edness, which fundamentally controls capacitive electrical energy storage, sub- surface contaminant transport, chemical separations by membranes, and hetero- geneous catalyst performance, to name a few examples. Figure 3.3.1.2 illustrates the current state of the art and limitations on spatially-resolved characterization of the elemental composition of materials. This figure also shows the multiple plat- forms that must be utilized in order to fully characterize the elemental distribu- tions in a complex material, essentially precluding the observation of dynamic elemental redistributions, structural and morphological changes and porosity/ permeability evolution of materials in real time, associated with diffusion, amorphous-crystalline transformations, and many other dynamic materials responses.

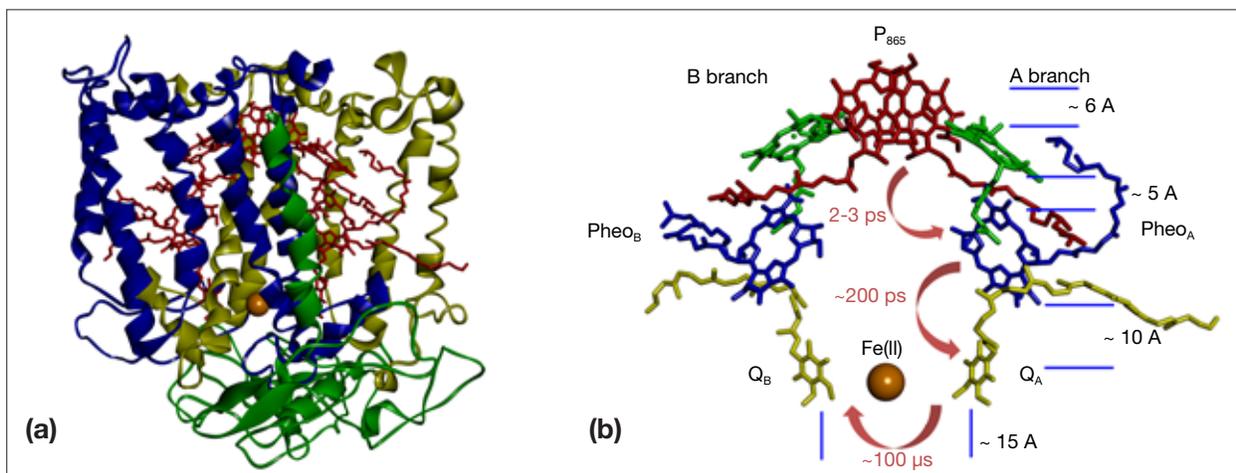
Advanced characterizations are needed of materials structure that spans atomic-to-macroscopic length scales and the dynamics that mediate transformations of these features. Such data are needed to provide understanding of our best existing materials, to establish how they operate over their lifetime in *operando* environments, and to enable theoretical modeling and rational design of improved alternatives.

For example, oxide conversion reactions, which are an alternative approach for high capacity lithium-ion batteries, suffer from structural irreversibility associated with the phase separation and reconstitution of reduced metal species and  $\text{Li}_2\text{O}$ . In particular, the morphology of the reduced metal species plays a critical role in the electrochemical prop- erties of a conversion material. An electrode with alternating layers of chromium and chromium oxide shows these phase changes in real-time and at molecular length scales (Figure 3.3.1.3).<sup>194</sup> The results demonstrate that layers expand and contract with each lithiation and delithiation reaction, improving reversibility.

### 3.3.2 Temporal Heterogeneity

Characterization of the dynamics of energy transport and conversion is needed over a vast range of timescales, from the femtosecond making and breaking of bonds to the many orders of magnitude slower temporal domains of trans- port of charge, production of reaction intermediates and products, as exemplars. A source of substantial complexity is that the timescales are fundamentally coupled. For example, an electrolyte must be capable of facile cation motion so that very little energy is converted to heat by the passage of the current, and a superionic conductor may exhibit multiple timescales related to this transport. There is a long time scale for diffusion of the anions on their lattice sites, a much shorter time scale for the anion spinning on its lattice site and a shorter time scale still for the migration of the cations. To understand and mitigate the relevant factors limiting a material's performance and lifetime, it is nec- essary to monitor long-term degradation. Many important materials systems demonstrate frustration of system level dynamics which lead to trapped states, long relaxation times, metastability, and polymorphism, which in turn lead to transformations within a material that subsequently evolve with marked temporal and structural heterogeneity. The properties of materials operating in extreme/high-radiation environments and the evolution of flow in complex porous or particulate media provide additional examples.

In some of the most prominent energy conversion systems, the dynamical and structural heterogeneities are inextrica- bly mixed and therefore require coupled resolution in both space and time. Dynamical processes on a range of times- cales change spatial distributions, morphologies, and structure of the different chemical constituents in functional



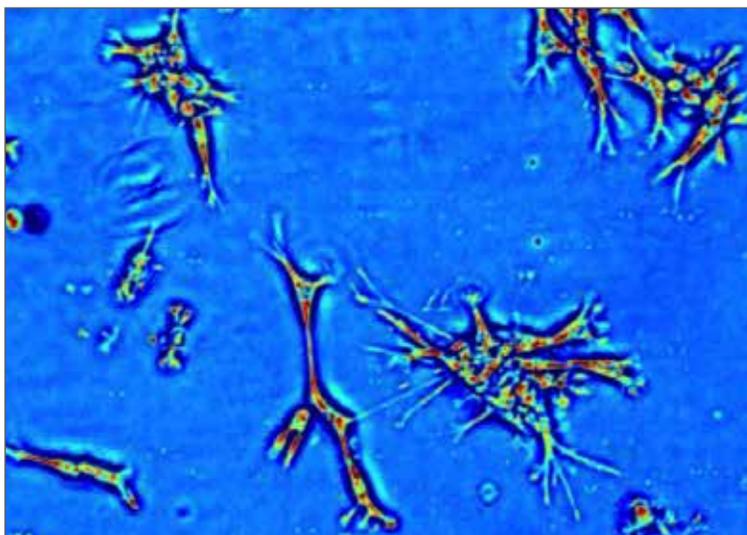
**Figure 3.3.2.1:** (a) The photosynthetic reaction center from the bacterium, *Rb. sphaeroides*. (b) The structural arrangement of the cofactors in the reaction center with the edge-to-edge distances and rates of electron transfer. The cofactors are arranged in two branches, identified as the A and B branches. Each branch contains one of the bacteriochlorophylls (BChl) of the special pair, P865 (red), followed by a BChl monomer (green), a bacteriopheophytin (Bpheo) (blue), and a quinone (yellow).

materials. The associated coupling and resulting functional interaction are defined on length scales determined by electron, vibrational, or structural correlations. In large photosynthetic protein assemblies like photosystem I, photosystem II and the purple bacterial reaction center (shown in Figure 3.3.2.1),<sup>195</sup> the regulation and fine tuning of cofactor properties by the interaction with the protein environment are key to directing the flow of electrons. Through various interactions at interfaces (cofactor-cofactor, cofactor-protein, protein-lipid, etc.), the light reactions of photosynthesis occur in multiscale processes in time and distance, spanning 15 orders of magnitude on the time axis (femtoseconds to minutes) and 3–4 orders of magnitude in distance (from several Å to hundreds of nanometers). Determining the coupling between temporal and spatial inhomogeneity demands multimodal, correlative, and adaptive imaging approaches, because a single electron, X-ray, or optical measurement does not provide complete physical insight.

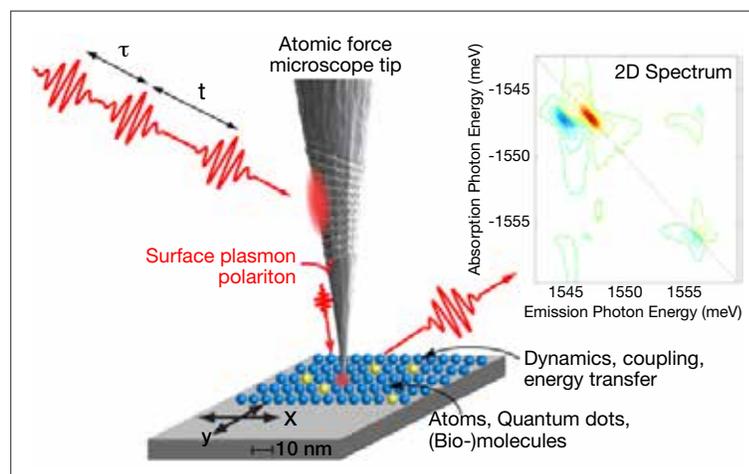
### 3.3.3 Dynamic Heterogeneity

While many energy materials display spatial and temporal heterogeneity, the quantitative nature of its features may also evolve responsively in *operando* conditions over time. For example, catalytic, electro-catalytic, photo-electro-catalytic, and bioelectrocatalytic materials undergo chemical transformations as part of their functional cycle. These transformations most often take place at functional interfaces of solid or soft (synthetic, biological) materials operating in reacting gas or liquid phase environments. These interfaces are characterized by high degrees of spatial heterogeneity, manifested in large numbers of diverse sites which are catalyzing the chemical transformations. Even a simple spherical catalytic metal nanoparticle is characterized by large numbers of diverse surface sites, exhibiting different degrees of surface coordination and different chemical activities. The degree of heterogeneity and complexity is further increased when multiple building blocks are used in the design of materials. For instance, an effective photo-electro-catalyst in its simplest form combines a light harvesting material (e.g., semiconductor) and an electro-catalytic material (e.g., metal nanostructure), and the interface between these two building blocks to a large extent governs the performance of the material. These interfaces are complex exhibiting high degrees of structural non-uniformity and therefore electronic heterogeneity, which directly impacts their interaction with light and their effectiveness in transferring excited charge carriers from the semiconductor to the metal.

With advances in materials synthesis have come significant enhancements of capabilities for providing catalyst nanostructures with complex structural/functional forms — nanocubes, nanocages, nanowires, core-shell nanostructures, as examples — for use in energy-centric catalytic, electro-catalytic, and photo-catalytic processes. The development of biological systems capable of energy exchange with inorganic electrodes has expanded the range of potential electrocatalysts to now include redox proteins that are active at heterogeneous biotic-abiotic interfaces, further increasing the scope and complexity of the heterogeneity present in functioning systems.



**Figure 3.3.3.1:** Spatial light impedance spectroscopy (SLIM) tracking the migration and chemo-mechanical dynamics of live 3T3 (3-day transfer, inoculum  $3 \times 10^5$  cells) fibroblast cells supported on a gradient hydrogel scaffold fabricated by 3D printing.



**Figure 3.3.3.2:** Ultrafast SPM: Femtosecond coherent nonlinear optical scanning probe imaging with nanoscale spatial resolution provides access to coupled degrees of freedom and ultrafast response functions on the characteristic length scales of electron, lattice, and spin excitations. Focusing plasmon polaritons at the apex of a nanometer tip leads to the nonlocal generation of an intense third-order nonlinear response as a local probe for nano-imaging coherent quantum dynamics.

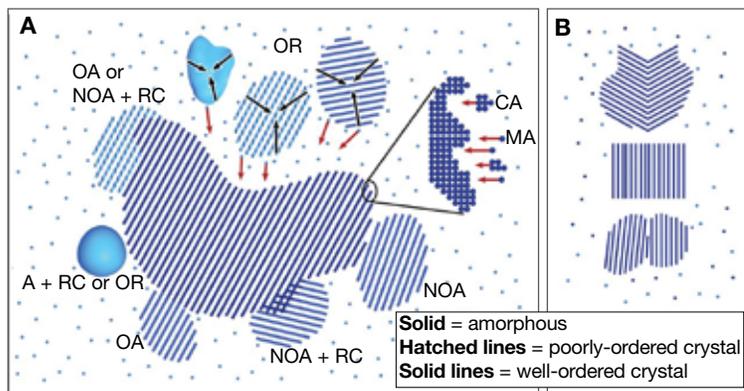
The electronic, magnetic, optical, catalytic, or biological properties of essentially all materials depend on the details of the coupling and interaction of their building blocks on the atomic and molecular scale. Progress has been made in ultrafast spectroscopy of ensembles, molecules, and bulk matter revealing some details of their quantum dynamics, but has generally been limited to mesoscopic length scales. In particular optical multidimensional coherent spectroscopy can reveal coupling by measuring a phase-resolved signal as a function of two time-delays and taking a multidimensional Fourier transform, which reveals correlations between the frequencies present during the time periods. Recently, spectroscopy of single objects has become possible, but not in their interacting environment. Conversely, scanning probe microscopies (STM, TEM, etc.) can image even complex organic and inorganic matter with atomic spatial resolution, yet in general lack spectroscopic insight into the underlying mechanisms that define the materials' properties.

Stepping up further in complexity, biology exemplifies how extreme structural and spatiotemporal heterogeneity can be harnessed towards energy acquisition and conversion. Living cells deploy a wide variety of enzymes with diverse active (redox) centers to drive chemical transformations, sustain their metabolism, affect migration, attachment, proliferation, and ultimately higher levels of organization. Advanced methods of super-resolution, spectroscopic, and chemomechanically responsive live cell imaging (Figure 3.3.3.1)<sup>196</sup> have made it increasingly possible to deduce important new understandings of the complex forms of dynamical heterogeneity present in living systems and continue to motivate efforts to improve multimodal forms of characterization of all forms, especially in terms of handling challenging regimes of dynamic heterogeneity.

### ULTRAFAST SCANNING PROBE MICROSCOPY (U-SPM)

The combination of new concepts in scanning probe microscopy, photonics device engineering, and ultrafast spectroscopy could enable spectroscopic imaging down to atomic spatial and femtosecond temporal resolution. This would allow for probing inorganic, organic, and biological matter at the most fundamental and elementary level that defines its function. This ultimate spectroscopic "eye" could visualize and reveal the coupled quantum dynamics of interatomic processes that are the origin of essentially all properties of heterogeneous matter.

A combination of advanced high spectral and temporal coherent spectroscopy with atomic scale spatial resolution imaging is required to give insight into these underlying mechanisms. This approach of ultrafast scanning probe microscopy (U-SPM) will allow the probing of the dynamics of electronic, spin, and geometric structural properties at the atomic level of atoms and molecules in their interacting and functional environment. This approach, based on light localization at the tip apex, opens a new regime of optical spectroscopy and imaging at deep-sub-wavelength dimensions and with high momentum states of light. In its emergent extension to ultrafast scanning probe microscopy (Figure 3.3.3.2),<sup>197</sup> optical nano-imaging can be implemented in principle in any optical modality, including nonlinear and ultrafast, coupling to a wide range of order parameters and their dynamics. It is compatible with low-temperature, high magnetic fields, or sample bias, also in a multimodal and hybrid imaging approach, complementing recent advances in ultrafast X-ray and electron imaging.



**Figure 3.3.4.1:** Multiple growth mechanisms can occur simultaneously within a single crystallizing system, depending on the values of global parameters such as supersaturation, local factors that include interface curvature, and materials parameters such as phase stability versus particle size.

Developing optical multidimensional coherent nanoscopy promises to address a grand challenge in condensed matter and material science by providing insight into how emergent quantum and biological materials are endowed with functionality. The approach will also facilitate the design of quantum based novel photonic, electronic and bio-inspired technologies.

### 3.3.4 Rare Events

It is often found that critical processes in energy systems are triggered by statistically rare events. For example, the degradation of energy materials occurs over extended periods of time resulting from numerous complex mechanisms involving both slow processes and rare events. A key challenge for improving the performance and longevity of energy materials is to determine mechanistic pathways for their action and transformations occurring within them, to elucidate the nature of interactions that most importantly mediate their degradation, and how all such features contribute to their evolution over time. There exist many frontier challenges in research that would serve to address interests such as these, perhaps none offering more far ranging impacts than that afforded by improved abilities to characterize rare events underpinning complex transformations of material and chemical systems. To characterize, model, and predict the spatio-temporal evolution of structure and function in a material over the lifetime of its functional use—and use such information to inform sustainable/energy efficient designs—requires methods that can capture the specific chemical interactions and physics of events that occur only in the tails of statistical distributions. The events that initiate chemical detonations—the chemistry of hot spots as one exemplar—illustrate an extreme example. The localization of corrosion processes that precipitate gross structural failures due to stress corrosion cracking provide yet another. These statistically rare events do not occur as sole contributors to the degradation of chemical and material systems of importance in energy technologies. Here we find many examples of how new understandings of growth requires a full multiscale integration of components of its chemistry—developing fundamental understanding of the complex physico-chemical processes associated with the nucleation of particles from an initially homogeneous solution (a rare event), the longer timeframe mass-transfer coupled features of their growth, dissolution, and aggregation, along with the diffusional and mass transport mediated properties of their particle suspensions. The understanding of such features, shown schematically in Figure 3.3.4.1,<sup>49</sup> represents a need that is central to a wide range of energy-relevant applications, such as nanomaterials synthesis, heterogeneous catalysis, geologic waste isolation and remediation, biological systems, drug delivery, and redox flow batteries.

### 3.3.5 Current Status and Limitations for Characterization of Heterogeneous Materials

The current state of the art for characterizing heterogeneous materials includes a wealth of techniques—both physical and spectroscopic — that have dramatic individual strength. It is now possible to obtain atomic resolution images with chemical information from surfaces. Scattering techniques yield detailed structural information from ensembles of molecules and systems with translational symmetry. Spectroscopy approaches, such as those built on advances in phase-stabilized ultrafast lasers, supply local electronic structure information and chemical dynamics with element specificity and femtosecond resolution.

Overall we have made great strides in our ability to characterize the resting state of materials in terms of their electronic and geometric structure with high spatial resolution. Conversely, ultrafast and time-resolved measurements are often performed on single components extracted from heterogeneous functional materials.

To understand and control heterogeneity, characterization methods responsive to multiple physical properties at different length scales are needed. The ideal is complete probing of the spatial distribution of relevant chemical speciation, physical properties, and excited state dynamics on all relevant length and time scales with multiple modalities. In some cases, such measurements at different growth stages of the material could provide important insight into functionality. To address inorganic catalytic materials, interface-sensitive techniques are required but with optimized spatial and temporal resolution.

There are several broad categories of the limitations of current techniques for characterizing the full interrelationships of properties, structures, and dynamics of complex heterogeneous systems. For some cases it is still not possible to resolve the natural spatial or time scales of key processes — but increased resolution is for the most part no longer what limits the ability of techniques to address multiscale heterogeneity. Rather it is the capacity for: 1) correlating multiple properties; 2) coordinating behaviors on disparate time or length scales; 3) detecting events or features with sufficient sensitivity; and 4) measuring dynamical or functional behavior under relevant conditions.

In order to characterize the impact of heterogeneity on physical processes, it is not enough to simply measure heterogeneous spatial or temporal distributions of individual properties — it is important to be able to correlate different properties that affect each other. For example, state-of-the-art characterization methods for materials growth coupled with local probes of magnetic and electric properties are needed. Overcoming current limitations will require the development of *in situ* non-invasive instrumentation that integrates atomic resolution imaging techniques, electrochemical techniques, beyond-diffraction-limit microscopy, and multidimensional and surface-sensitive spectroscopies to capture the heterogeneity of rates, structural makeup, and chemical environment. Correlating such observations becomes substantially more difficult when the system is dynamic or transient. As a result, one frontier in instrumentation is in simultaneity — implementing multiple types of probes at the same time on the same sample.

Coordinating behavior across different time or length scales and in multiple dimensions is a manifestation of a similar challenge. Often large-scale changes in structure affect the local environment in which fundamental physical phenomena occur, or rapid processes at an individual atomic level may more slowly coalesce into a collective behavior with a larger spatial extent. A lack of techniques that access multiple scales (in any dimension) on the same sample, or adaptive methods that can tailor resolution based on the specific attributes of interest at a particular position or time is lacking in current methods.

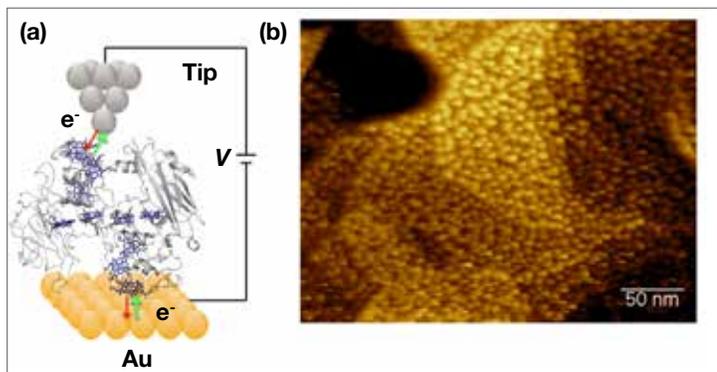
Often techniques are limited by insufficient sensitivity to detect and identify rare events or minority sites or species in the presence of a large background. Challenges due to low electron spin concentrations prevent direct determination of the electronic/geometric structure and dynamics of complex systems with endogenous paramagnetic centers by simultaneous multidimensional pulsed electron paramagnetic resonance (EPR) magic-angle spinning NMR (MAS NMR) measurements. Increased sensitivity in X-ray and electron probe techniques is needed to avoid the stubborn limitations arising from radiation damage.

Finally, it is imperative that these techniques operate at conditions as close as possible to those of the functioning environment. Depending on the particular system of interest, this may mean that the techniques must be adapted to extremes of

temperature and pressure, or may need to operate without disturbing electrical or magnetic field distributions. The compromises needed for *in situ* or *operando* measurements may hinder characterization of inhomogeneity. For example, significant advancements in X-ray based absorption spectroscopy techniques now allow for *operando* measurements, but these measurements yield information about the average behavior of the systems without providing spatially-resolved information.

### CHALLENGES OF CHARACTERIZING REACTING SYSTEMS

Recent years have seen dramatic improvements in our ability to characterize the resting state of inorganic materials in terms of their electronic and geometric structure. Enzymatic and cellular systems are now being studied using electrochemical, microscopy, and traditional spectroscopy techniques at electrode interfaces (Figure 3.3.5.1).<sup>198</sup> However, the measured observables (interfacial rates, redox potentials) generally don't unravel the molecular charge transport pathways and resolve the timescales of elementary charge transfer steps by which individual subunits communicate with each other. Additional limitations stem from the lack of information about the chemical state (e.g. oxidation state, local chemical composition) of the active centers, particularly at the functional interfaces.

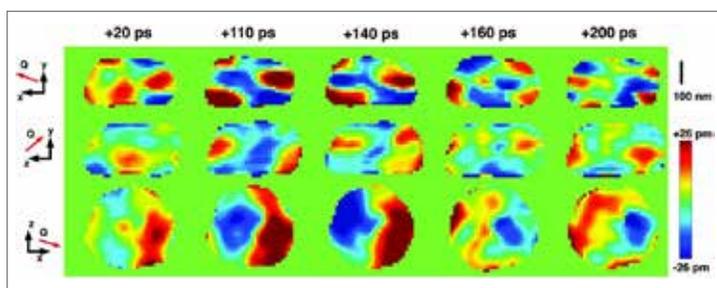


**Figure 3.3.5.1:** Scanning probe (tunneling) microscopy of enzymes containing multiple redox centers on electrode interfaces. The figure illustrates a) a schematic representation of a scanning tunneling microscopy approach to measuring the current-voltage relationship in individual enzyme molecules, and b) a representative image.

Advancements in techniques that shed light on spatial heterogeneity and temporal evolution of the functioning systems are required to develop truly predictive energy-related systems and technologies. It is imperative that these techniques operate at conditions as close as possible to the functioning process conditions. To address inorganic catalytic materials, interface-sensitive techniques are required, much like surface-enhanced Raman and infrared spectroscopies, but with optimized spatial and temporal resolution. Overcoming the limitations in bioelectrocatalytic systems will require the development of *in situ* non-invasive instrumentation that integrates electrochemical techniques, beyond-diffraction-limit microscopy (e.g. super-resolution optical or scanning probe), and multidimensional and surface-sensitive spectroscopies to capture the heterogeneity of rates, molecular makeup, and chemical environment supporting interfacial charge transfer.

### FRONTIERS IN X-RAY-BASED MEASUREMENTS

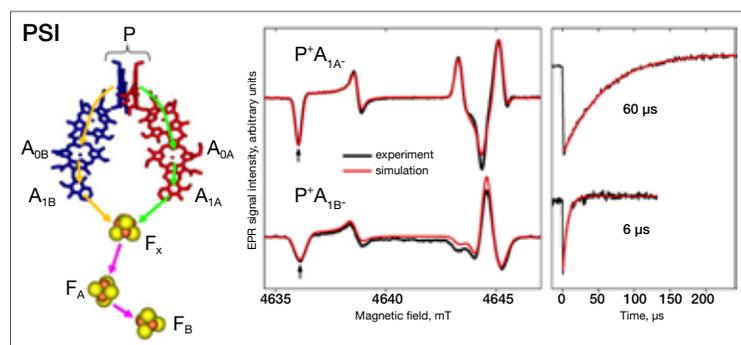
X-rays have developed into a primary tool for materials characterization. Their weak interaction with matter and wavelength dependent penetration depth enables the probing of a large range of material properties from surfaces, to interfaces, to bulk structure. In recent years methodologies were advanced to investigate samples in relevant environments such as proteins under physiological conditions, photoexcited dynamics in solution, materials in extreme environments and catalytic processes in *operando* conditions. The element specificity of X-rays allows targeting specific sites or obtaining chemical information in complex environments. Recent advances in X-ray sciences enabled time-resolved studies over many orders of magnitude from slow to ultrafast processes and visualizing non-equilibrium dynamics with femtosecond temporal and nanometer spatial resolution (Figure 3.3.5.2).<sup>199</sup>



**Figure 3.3.5.2:** Three-dimensional X-ray imaging of acoustic phonons in an Au nanocrystal. The colors show the projected lattice displacement in orthogonal cut planes through the center of nanocrystal on the picosecond time scale after laser excitation.

The ongoing development of free-electron laser and diffraction limited synchrotron X-ray sources holds great promise for dramatic advancements of X-ray based techniques. Time-resolved imaging allows visualization of phonon modes in nanocrystals, an important step for measuring active states at specific points in time. Multimodal techniques are being implemented yielding simultaneous or even coincident electronic and structural information. Nonlinear techniques are within reach that will allow site-specific excitation and probing, and hold promise to follow the flow of energy in materials. The increasing brightness of future light sources, rapid advancements in data handling, and algorithm development will enable large field-of-view and sample-volume studies.

However, the investigation and characterization of heterogeneous materials poses challenges. X-ray probes are to some degree averaging. For highest spatial resolution a certain degree of translational symmetry is required and it is not yet possible to obtain atomic resolution over large length scales with chemical sensitivity.



**Figure 3.3.5.3:** The electron-transfer cofactors in photosystem I (PSI) reaction centers are arranged in two symmetric branches, A (red) and B (blue). HF (130 GHz) transient EPR spectroscopy of photo-induced spin-correlated radical pairs (SCRPs) ( $P^+A_{1A}^-$  and  $P^+A_{1B}^-$ ) in the A and B branch directly probes both the structure and kinetics of bidirectional electron transfer in PSI.

### STATE OF THE ART IN ELECTRON AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIES

Pulsed EPR and solid-state MAS NMR are complementary techniques that offer remarkable insight into the structure and dynamics of electron and nuclear spins in heterogeneous systems ranging from biological to synthetic materials. These methods have emerged as powerful tools in addressing spatio-temporal heterogeneity as they are not limited by the large size, low solubility, presence of paramagnetic cofactors or disorder of the samples under study. There are fundamental differences between

EPR and NMR spectroscopy that arise from the higher sensitivity (> factor of 10<sup>3</sup>), larger Zeeman splittings and extremely rapid spin-spin and spin-lattice relaxation of electrons in comparison with nuclei. Therefore, a combination of these methods accesses a wide range of spatial (0.1 – 100 Å) and temporal (picosecond to microsecond) scales.

Recent advances in pulsed microwave technology, fast data-acquisition capabilities and innovative pulse sequences have enabled the implementation of multi-frequency multidimensional EPR spectroscopy to elucidate the structure and dynamics of catalytic species in inorganic, biological and hybrid materials. Further, the synchronization of pulsed optical lasers with pulsed EPR spectrometers has allowed for characterization of transient photo-induced reactions. Recently, high-frequency (HF) (130 GHz) transient EPR spectroscopy has been used to study the distinct  $P^+A_{1-}$  spin-correlated radical pairs (SCRPs) during charge separation in photosystem I reaction centers in photosynthesis. The superior spectral, spatial and temporal resolution made it possible, for the first time, to correlate the kinetic and structural data of the distinct SCRPs (Figure 3.3.5.3).<sup>200</sup>

Similarly, high-field multidimensional MAS NMR spectroscopy has facilitated the study of a wide variety of complex heterogeneous materials. The lack of sensitivity in MAS NMR has been countered with the development of dynamic nuclear polarization (DNP) for signal enhancements. Recently DNP has been demonstrated to provide up to 300-fold (and typically 50-fold) gains in signal-to-noise of NMR spectra which has enabled definition of systems including dilute active sites of emerging materials for energy conversion and storage. For example, solid-state MAS NMR spectroscopy with DNP has demonstrated that the transfer of polarization from hyperpolarized protons of the solvent to rare carbon-13 nuclei at natural isotopic abundance makes it possible to detect surface species that are covalently incorporated into a silica framework.<sup>201</sup>

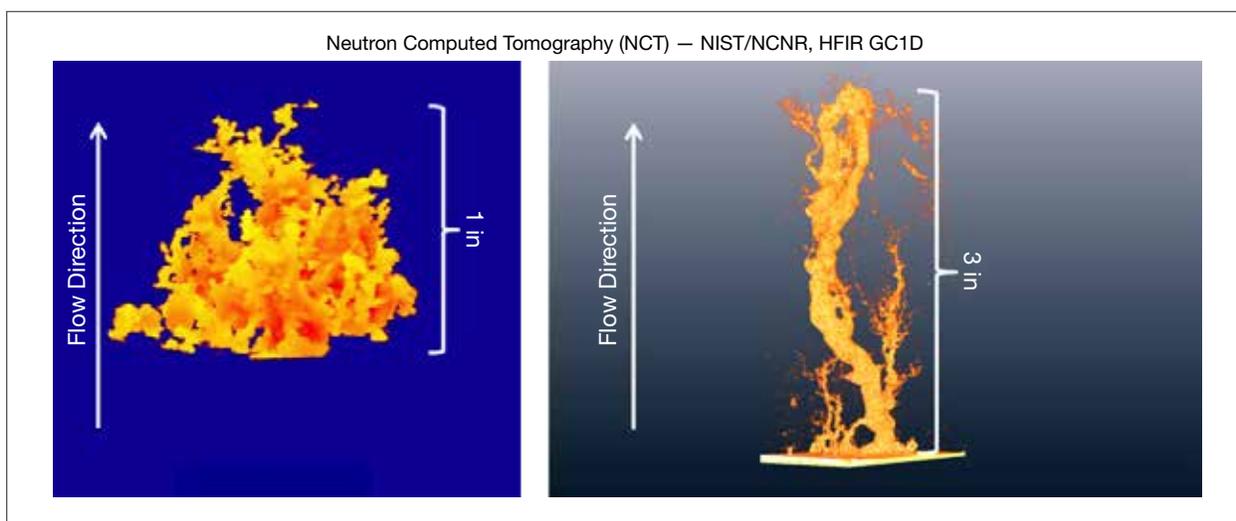
## X-RAY/NEUTRON RADIOGRAPHY AND TOMOGRAPHY — BACKGROUND AND NEW DEVELOPMENTS

Radiography and tomography are well known for their use in the characterization of both engineered and natural porous media, pharmaceuticals, and biological materials. In addition to interrogating pore features before and after the impact of a modification process (e.g., sintering, chemical reaction), and the distribution of mineral phases within a sample, they are also invaluable for assessing the nature of fluid flow. Indeed, predicting and controlling multiphase flow in porous media is key to industrial-related processes such as contaminant transport, geothermal energy production, enhanced oil recovery and CO<sub>2</sub> geologic storage, as well as understanding geological processes such as aquifer processes, diagenesis, and ore deposit formation. A key question that these techniques can address focuses on how the time-dependent pore regime in a given matrix controls the migration, wetting and reactivity of a fluid at variable state conditions at the pore scale.

Radiography and tomography are closely related because tomography is based on radiography, which is a two-dimensional (2D) attenuation coefficient distribution of a ray-path-integrated projection from a three-dimensional (3D) object. Tomography reconstructs the 3D object from the fact that the Fourier transform of any projection through a 3D object is a plane in the Fourier transform of that object (the projection-slice theorem). Multiple slices are then obtained by rotating the object.

High resolution nano- and micro-X-ray computed tomography characterization methods are now available at synchrotron X-ray facilities and some commercial instruments also exist. Most previous studies of multiphase flow phenomena are based on X-ray tomography. The high flux available in modern synchrotrons allows even dynamic imaging with high spatial resolution. However, in order to achieve sufficient X-ray contrast between the different phases, it is necessary to use modest concentrations of heavy-ion dopants, typically salts such CsCl, KBr, or ZnI<sub>2</sub> in the aqueous phase. In addition, while high resolutions can be obtained, the sizes of the samples decrease proportionately to the resolution. This can be limiting in cases where high resolution is needed over larger scales (e.g. mapping fine fracture or grain boundary networks, analysis of incipient dissolution along those networks). This is especially a limitation of laboratory-scale instrumentation, which tends to either handle large samples at low resolution or small or very small samples at higher resolution.

Neutron imaging has both significant advantages and limitations relative to X-ray imaging, which makes them nicely complementary. Due to the different contrast mechanism afforded by the large neutron scattering cross section of hydrogen compared to other elements neutron tomography/radiography can directly image water or hydrocarbons in porous or fractured matrices without the aid of an added contrast medium that could modify interfacial tensions,



**Figure 3.3.5.4:** Dissolution features revealed by neutron tomography in Indiana limestone with a permeability of 70 mD reacted with pH 2 HCl for two different flow rates (0.1 mL/min - left panel) and (10 mL/min - right panel).

wetting angles, fluid/fluid, and fluid/rock interactions. Because of this property, neutron radiography has been successfully employed to visualize single and multiphase flow in porous media. Neutron imaging has also been used to visualize the front shape of water moving into sandstones and to make tomography images of sandstones. Recent modifications to neutron radiography/tomography instruments at facilities such as HFIR and NIST have led to vastly improved spatial resolution approaching 10  $\mu\text{m}$  and below, and work is ongoing at both facilities to reduce this to 1  $\mu\text{m}$  using techniques such as multi-pinhole sources and Wolter optics. More advanced techniques include Bragg edge imaging of texture/phase, phase gradient imaging. Therefore it is now possible to use this approach to image and quantify in real time with time resolutions as short as 10 ms the capillary uptake of dilute brine in porous media like a carbonate rock core with different pore types typically encountered in the subsurface; degradation of fluid imbibition over time due to geochemical reactions with acidic brine; and possible sealing of flow channels due to carbonate precipitation (Figure 3.3.5.4).

## SCIENTIFIC CHALLENGES AND OPPORTUNITIES

The overarching scientific challenge of characterizing heterogeneous materials and chemical systems is the ability to explore functional properties, structure, chemistry and dynamics across a broad range of time and length scales, and under a broad range of environmental conditions that influence function. This will involve the use and development of a range of multimodal techniques, moving beyond the current status and limitations associated with these techniques (Section 3.3.5). For example, advances in techniques that shed light on spatial heterogeneity and temporal evolution of complex materials in their functioning environments will enable a truly predictive knowledge of energy-related systems and technologies. In addition, advances are needed in computation that can help us interpret and integrate the data collected across all length-scales, including for example correlating vibrational and electronic behavior, structure and dynamics of a chemical process.

In the following section we explore this issue more deeply, highlighting a number of specific questions, many of which share common themes, namely visualizing and understanding excited state dynamics and local charge transfer across interfaces, defects, and boundaries in the appropriate local environment.

Electrocatalysts are composed of metal oxides, metals, or metal alloys, and are inherently heterogeneous. Specific questions include determining the preferential binding sites on the substrate and the atomic-scale structural motif of the active site(s). Of course it is also critical to explore how these evolve as a function of time. Additionally, considering the multi-electron redox reactions of water oxidation or  $\text{CO}_2$  reduction, questions arise as to how the water or ionic layer at the solid/liquid interface changes the kinetics, reactivity and product selectivity, and how the reactions proceed under the presence of an applied potential in the electrolyte.

Biological systems are complex, heterogeneous organizations of matter that function at many different length-scales and their dissipative dynamics are inherently difficult to characterize. One question that arises, from which other scientific disciplines could learn, is how biology exploits the structural and spatiotemporal heterogeneity inherent to biomolecular materials to catalyze chemical transformations. Further, this must be done while synchronizing energy transfer between active (redox) centers in disordered environments.

In turbulent combustion systems it is critical to obtain direct full-dimensional characterization of the fundamental physical interactions between strong gradients (e.g., of composition and temperature) and chemical reactivity.

Heterogeneity and interfacial structure play an important role in charge separation in organic photovoltaics but are not well understood due to the lack of appropriate tools. Truly understanding the importance of spatial organization and heterogeneity in photosynthetic energy conversion requires the ability to study the whole process in a holistic manner, rather than exploring parts of the problem as is the case in most current experiments.

Current battery technology is in part limited by our detailed understanding of electrolyte activity. In addition to energy storage, a major challenge lies in energy conversion, namely how to overcome the irreversibility of the oxygen reduction

reaction in the electrolyte. In order to achieve this we need to directly observe an oxygen reduction process where protons are being supplied from a protic ionic liquid.

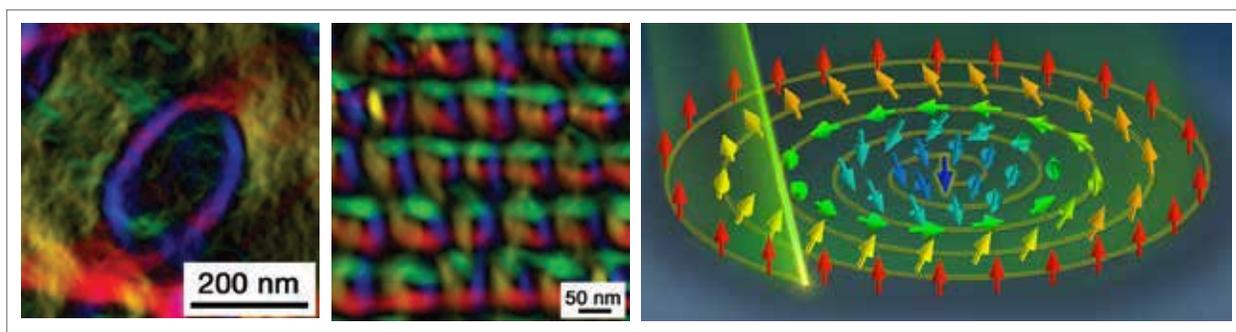
A scientific advancement that would benefit a broad set of areas is the direct imaging of the dynamics of magnetic and electric potentials and fields in 3D. This would have immediate impact in materials that contain more than one phase such as energy harvesting materials (layered or nanocomposite artificial multiferroics, thermoelectrics or magnetic materials), batteries during charge and discharge, and quantum materials.

In quantum materials we need to understand how atomic scale heterogeneity determines mesoscopic properties (e.g. of complex oxide interfaces, topological phases of matter and novel unconventional superconductors) in order to control and harness this heterogeneity and robustly realize desirable emergent phenomena and make them suitable for device applications. In strongly interacting systems, it will ultimately be crucial to probe the coupled quantum dynamics at the relevant length and time scales that define their functionality.

### MULTISCALE IMAGING FOR QUANTUM MATERIALS

In this “big data” era, the quest for next generation energy-efficient information technology has encouraged research in quantum materials at the nanoscale. One concrete example is the potential to exploit skyrmions as information carriers. A skyrmion is a topological spin texture whose spins point in all directions wrapping a sphere, with the spins at the skyrmion core and at the outer edge pointing out-of-plane in opposite directions. Technologically, it has been predicted that skyrmions can be efficiently controlled using spin transfer-torque effects, thus requiring very low electric current to drive their motion.

In spite of recent progress there are still severe limitations in our ability to harness the fundamental physics of skyrmions and emergent phenomena in quantum materials in general for device applications. There is a need for improving the sensitivity and resolution of existing characterization tools, for developing new non-invasive tools and for combining complementary tools. These tools need to operate over a wide range of spatial resolution to understand how local properties effect global characteristics, to understand the effect of disorder and heterogeneity on functionality, and to access and control order that emerges on different length scales. For example in thin film skyrmion devices we need to correlate atomic scale structure (interface roughness, structural defects) with the 3D spin structure at the nanometer scale and the desired transport behavior at the mesoscale, requiring the development of novel nanoscale magnetic probes integrated with the application of stimuli and appropriate time resolution (Figure 3.3.5.5).<sup>53-54</sup>



**Figure 3.3.5.5:** Specialized transmission electron microscopy of magnetism, in combination with simulations, allows observation of skyrmion formation, behavior, and stability. A skyrmion is a topological magnetic structure with spin directions (imagine tiny North-South magnetic poles) that are twisted in an axially symmetric vortex-like geometry such that the spin arrangement is not easily perturbed. Skyrmions have potential uses in transporting information because they are tiny, stable, and easily controlled with very low electric currents.

## 3.4 PANEL 4: TRANSFORMATIONAL EXPERIMENTAL TOOLS THROUGH INTEGRATION OF INSTRUMENTATION WITH THEORY AND COMPUTATION

Structural and chemical heterogeneity, interfaces, and disorder are central to the desired behavior and function of many natural and engineered chemical and materials systems. The ability to study these systems under realistic conditions and across relevant time and length scales is critical to gaining a complete picture that goes beyond model systems to functional energy systems. Developing rigorous approaches to measure, analyze, simulate, and interpret — let alone control — such complex systems presents a major challenge.

The recent advent of high brightness sources and the use of fast high-resolution detectors have led to unprecedented speed and resolution in a wide variety of characterization methods using electrons, neutrons and photons. For example, solid-state detectors, combined with aberration-corrected cryo-electron microscopy, have led to imaging of individual proteins and nanoparticles with about 3 Å resolution. Similar detectors have enabled ‘diffract before destroy’ single-particle imaging at free electron laser light sources, such as the LCLS.<sup>202-203</sup> Despite the great strides enabled by these advanced experimental techniques, the complexity and sheer quantity of data associated with each measurement remains a significant challenge. Future opportunities in imaging, scattering and spectroscopy of heterogeneous, functional materials out of equilibrium, combined with improvements in new sources and higher speed and higher resolution detectors, will lead to an avalanche of big data to be triaged, analyzed, and curated in such a manner to make it easily accessible to the broad science community.

Data management and sharing of time-dependent, multimodal, and/or multidimensional data associated with current and future instrumentation is a major challenge. But it also presents a significant, largely-untapped opportunity in basic energy sciences, particularly in the interplay between experimental tool, computational method, and theory development. Although multidisciplinary teams of experimentalists and theorists are increasingly brought together to address the grand challenge problems, these teams are usually formed in the context of existing experimental tools and theoretical methods. The increasing amount of data points to a new opportunity, namely one in which the instrument, data analytics, algorithms, and theory are co-designed and co-developed simultaneously and seamlessly integrated. This paradigm shift in experimental tool development would facilitate real-time, autonomous extraction of information from heterogeneous datasets via analytics, machine learning, and/or modeling, and provide direct feedback to experiments. Importantly, this approach would accelerate the development of predictive simulation of experimental observables via integration of new theories, algorithms, and information, with the ultimate goal of intimately coupling predictive theory and experiment, and reducing the number of trial-and-error measurements and expediting the pace of discovery and understanding significantly.

Below, we describe the state of the art in data collection, analysis, and theory tools, and identify scientific challenges in each area.

### 3.4.1 Management and Sharing of Time-Dependent, Multimodal, and/or Multidimensional Data

The ability to design materials and control chemical reactions provides significant opportunities for the development of technology and infrastructure. The ever-increasing spectrum of functionalities required for developing and optimizing materials fundamental to modern civilization requires efficient paradigms for materials discovery and design going beyond current serendipitous discoveries and classical synthesis-characterization-theory approaches. The rise of computational-data mining approaches have allowed computational screening of materials properties; however, neither experimental feedback to theory nor experimental preparation have been systematically addressed. Truly enabling a *Materials by Design* paradigm will require integrated and direct feedback from processing parameters and multi-scale measurements to obtained functionalities and thus must allow real-time and archival experimental data to be incorporated effectively. This includes integrating data efficiently from different characterization techniques to provide a more complete perspective on materials structure and function. Furthermore, reproducible and reliable pathways for materials synthesis need to be established. Presently, most synthesis protocols cannot be predicted by

theory and primarily evolve from the expertise of individual researchers. However, data analytics on existing synthesis pathways may be able to suggest general correlations between materials properties and synthetic routes, leading to entirely new materials and research directions.

National user facilities operated by DOE-BES — such as high-intensity synchrotron X-ray light sources and the free electron lasers at SLAC — currently allow scientists to probe matter and phenomena in unprecedented detail and with increasing time-resolution, enabling, for example, studies of mechanisms in photosynthesis and advanced battery materials. The computing and data requirements of beamlines at these X-ray sources are advancing at a rate that far outpace Moore's Law. In the coming decade, taking advantage of a wide range of computing resources will be required in some cases as users attempt to keep pace with capturing and analyzing the volume of the data at high frame rates, including on one end, fast machines directly coupled to detectors and on the other end, remote exascale computing devices. Increasingly, light sources are teaming up with supercomputing facilities, computational scientists, and applied mathematicians to tackle these challenges with new software and data analytics. This includes new methods to triage, accelerate, and scale up the analysis of data, to provide real-time feedback for researchers, and better compare observation to results from modeling and simulation. They also offer radically new experimental approaches driven by machine learning, where random sightings of a freely evolving system replace traditional tightly controlled experiments.

Recent breakthroughs in high-resolution imaging and spectroscopy have opened the floodgates of high-veracity information in the form of multidimensional data sets. These advances have, in turn, led to an increasing need for specialized data pipelines and nodes for high-speed communication with supercomputers, and customized data buffering and storage requirements. The resultant high-resolution images contain important, as-yet uncovered correlations between, e.g., atomic positions and local properties and function, as well as the evolution of these correlations with time, environmental conditions, and external fields. Understanding of these correlations will be game changing for understanding and design of functional materials and chemical systems.

Software for data acquisition, data management, workflow, and analysis is growing in importance as datasets increase in size and the analyses and related simulations become more complex. What was once a small side activity, with ad hoc hardware and software for each experiment, must now become an integrated development effort to guarantee success. Systematic design, reusable components, good software engineering practices, and formal verification and validation will all become essential. In many areas of science, most data is not stored, analyzed, or available for reuse. There is a need to store and analyze the most relevant data, and bring it to common data spaces. There is a concomitant need to structure research process in terms of networks of tools with similar outputs and integrated knowledge space, and workflows for specific problems, as opposed to the contemporary random social network/foraging strategy.

Today, most instrument data lack the metadata and provenance information that would make it feasible and possible to share the data. The (beamline) instrument may produce a series of spectroscopy, diffraction, tomography or combination datasets, but the vital information about the sample, experiment conditions, sample history, and instrument settings is not shared. This information is essential in any database that will be shared, or in analyses merging heterogeneous data.

Instrument developers should use self-describing common data formats for their instrument output (e.g., XML, NetCDF, HDF5). This facilitates the use of community tools to analyze and share data and create interactive visualizations, and the documentation of data formats to make it easier for others to use it for example when retrieved from databases or file repositories. Tools to move data and catalog data have to provide (a) fast, reliable file transport for large files and many small files, (b) capabilities to catalog and curate data with the ability to create data collections and control access, (c) tools to discover data across widely distributed collections from a common access point and (d) provide an interactive access point to apply analysis or learning tools to the data.

The scale of detectors (pixels) and the frame rates are continuously increasing. A doubling (and more) at regular intervals is not matched by improvements in computer networks. Network speed grows much more slowly. Therefore, data

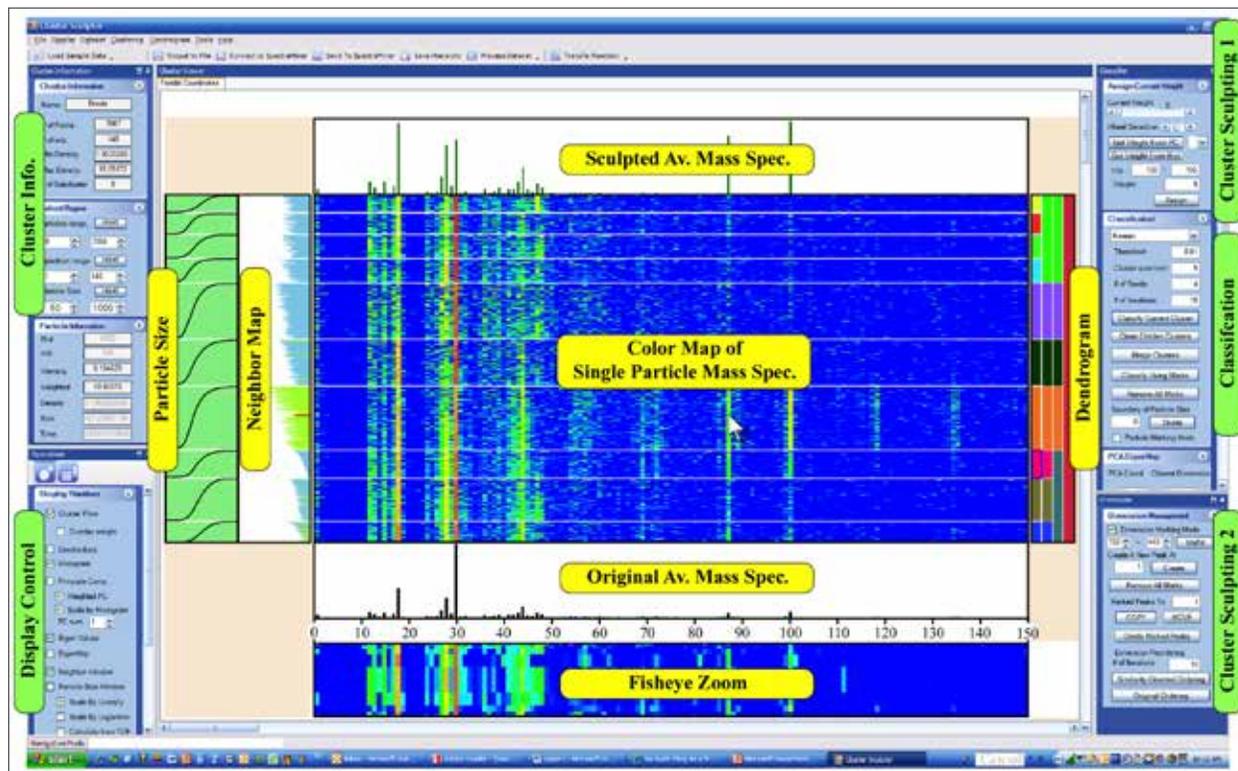


Figure 3.4.1.1: Screen capture of ClusterSculptor software that offers real-time visualization and expert-steered classification of multidimensional data.

must be reduced or analyzed where it is created. Data reduction can come from compression of data (with or without loss of fidelity), or by logic that rejects some data as not useful. Alternately *in situ* analysis can compute results at the data source or transform data into a more compact form.

Advances in coupling the multidimensional characterization and approaches for data visualization and analysis have recently been made in the field of multidimensional single particle characterization. Small particles are ubiquitous in natural and human-made environments and represent a form of matter of great import in nearly every field of science and technology, including nanotechnology, catalysis, mesoscience, atmospheric science, and combustion research. The properties, behavior, and impact of small particles depend on a multitude of their coupled properties, and on their environment. The size, composition, phase, density, shape, mass, morphology, fractal dimension, volatility, optical properties, interactions with gas-phase, and others — all play a role. Recent developments made it possible to measure simultaneously many of the relevant properties of *millions of individual particles in situ* and in real-time.<sup>204</sup>

By necessity, this *multidimensional* single particle characterization produces vast amounts of high dimensionality data, the visualization, mining, and analysis, of which calls for unconventional methods that must draw on statistical methods, while preserving the wealth and depth of information. Moreover, analysis should be based on all relevant data generated by different instruments, including their temporal evolution and the relationships between them.

These challenges, common to all fields that generate massive multidimensional, complex datasets, require matching advances in the science of data organization, visualization, and analysis. To that end, dedicated coupled data visualization, mining, and analysis approaches must be developed. One such example is SpectraMiner,<sup>55</sup> software that makes it possible to handle data on millions of particles, while avoiding loss of information, overcoming the boundaries set by traditional statistical approaches. Combined with a GPU-accelerated incremental correlation clustering,<sup>57</sup> it provides the user with a visually driven, intuitive interface to easily access and explore the data on millions of particles in real-time, and to detect and eliminate redundant data points, offering a viable means for data reduction, and for finding the outliers or a few “golden nuggets” in vast amounts of data.

This approach was extended by the development of an expert-steered real-time visual data classification, ClusterSculptor,<sup>205</sup> which offers the scientist the ability to insert their expert knowledge into the data analysis and interactive visual analytics framework that uses parallel coordinate interface and is designed to explore the relationships between different observables (Figure 3.4.1.1).<sup>204,206</sup>

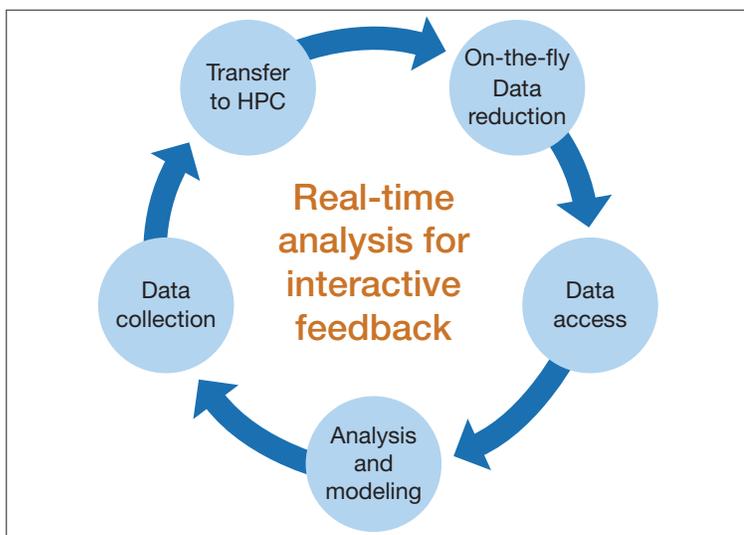
These approaches and tools represent a beginning. Present on-the-fly data acquisition display provides only limited controls and insight into the acquired data, which are analyzed at the end of experiments. New approaches need to include real time streaming data visualization that will be fully coupled to instrument controls to be used to fine-tune the experimental parameters and to direct processes to the desired outcomes. To accomplish this task may require significant changes that go beyond retooling and refining of existing approaches.

With appropriate *operando* experimentation and real time diagnostics of experimental parameters it becomes possible to guide the outcomes of experiments through a combination of machine learning and artificial intelligence methods. Such autonomous experimentation sees substantial application in the computer sciences, robotics<sup>203</sup> and unmanned vehicles.<sup>204</sup> These approaches have the ability to dramatically accelerate the time from materials discovery to deployment by rapidly converging on appropriate processing parameters for a given functional response. However, autonomous experimentation also has the ability to contribute significantly to understanding the links between structure/processing/property relationships and function. In the course of an autonomous experiment, the effects of multiple input parameters are correlated and are used to direct the experiment to a particular outcome. But — critically — they also identify the saddle points in parameter space where fundamental mechanisms both turn on and turn off. This can then be used to select specific sets of parameters to explore with advanced characterization approaches, allowing optimal usage of e.g. synchrotron beam time leading to direct insight into the specific fundamental mechanisms that yield desired functional outputs.

### 3.4.2 Extracting Information from Heterogeneous Datasets via Real Time Analytics, Algorithms, and/or Modeling; and Feedback to Experiment

Addressing many contemporary challenges in energy sciences requires a multidisciplinary approach and often necessitates the integration of data from multiple experiments that provide complementary information on materials structure, properties and functionality. Examples include scanning-probe and scattering experiments, transmission electron microscopy and atom probe, and other methods in combination. Often, the specific tools involved in the discovery process lead to measurement sequences with similar requirements for correlative data analysis and integration with theory. These multimodal experiments can benefit from development of universal workflows that allow seamless data and knowledge exchange, allow access to required computing facilities, and provide necessary data provenance and traceability across techniques.

To further advance instrumentation, new computational methods are needed to extract information from murky data, interpret experimental results, and provide on-demand analysis as information is being generated at high speed, as suggested by Figure 3.4.2.1. Advanced algorithms are required that can examine candidate materials that are too expensive and time-consuming to manufacture, rapidly find optimal solutions to energy-related challenges, and



**Figure 3.4.2.1:** A representation of how new computational methods might extract information from murky data, interpret experimental results, and provide on-demand analysis as information is being generated at high speed, including transfer to high-performance computing (HPC).

suggest new experiments for discovery science while sorting through existing data. New methods are needed that can build faster and more accurate mathematical algorithms to provide close to real-time analysis and feedback. Finally, we need new mathematics to analyze multimodal data that can extract information from time-resolved, high-resolution data, sometimes from multiple imaging sources.

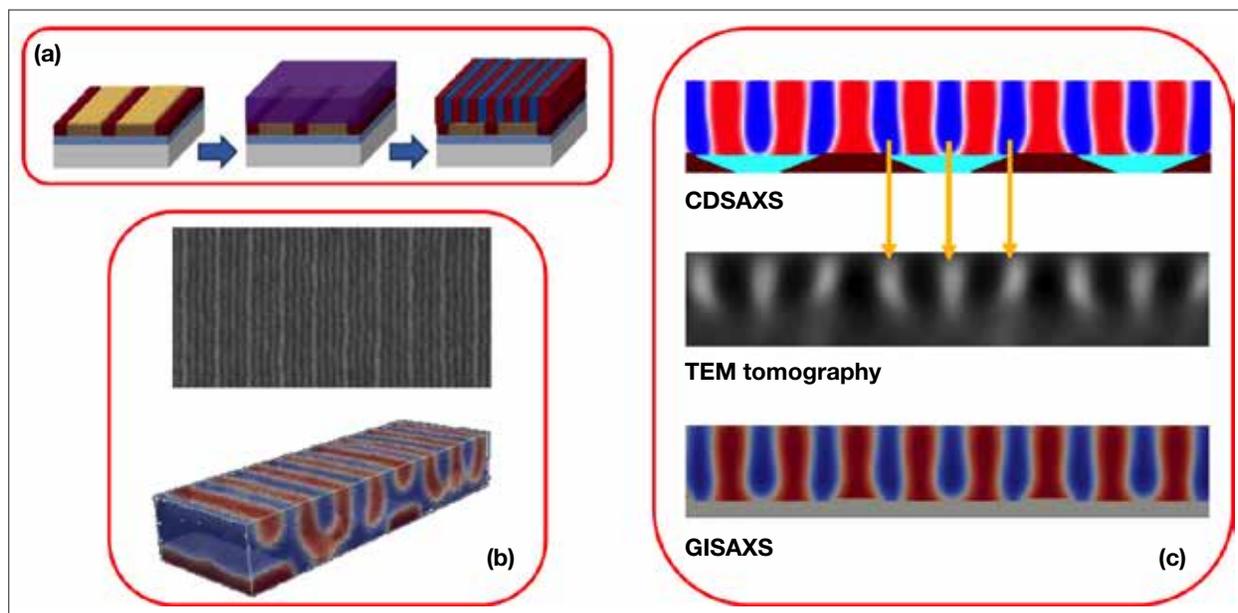
Together, these new data analytical techniques, applied mathematics, and theoretical and simulation methods will lead to tools that can, for example, reconstruct structure and properties from synchrotron light sources, predict behavior of new materials at the nanoscale, direct the hunt for new materials for batteries and gas separation, and optimize steps in the production of biofuels. This research cuts across traditional boundaries, and requires a close collaboration between applied mathematicians, computer and domain scientists. These teams can lay groundwork so that research is aimed at relevant scientific problems which can enhance current experiment. Models need to be formulated, equations need to be derived, and new algorithms need to be proposed.

One end of the spectrum aims at “on-demand” computational tools for analysis, data reduction, and feature extraction next to facilities, using embedded advanced algorithms and special-purpose hardware. Here, questions that arise include: What is the minimum/fastest computational model/algorithm that gives the required information in time? Can users assisted by algorithms determine whether data are useful, are not useful, or are in between? By taking advantage of powerful increases in core hybrid central processing units (CPUs) and general-purpose computing on graphics processing units (GPGPUs), can users quickly perform an analysis in order to steer ongoing experiments to more optimal configurations or output?

An example of existing efforts to this end is the Center for Advanced Mathematics for Energy Research Applications (CAMERA) at Lawrence Berkeley National Laboratory. CAMERA brings together a coordinated team of applied mathematicians, computer scientists, light-source scientists, materials scientists, and computational chemists to work on a vast array of new mathematical tools from graph theory, computational harmonic analysis, statistical sampling and data reduction. It also makes advances in hardware, new CPU architectures, GPU accelerators, and more, with the aim of quickly analyzing experimental data, steering, guiding and optimize experiments, and identifying promising materials and functionalities quickly.

Take, for example, organic photovoltaics (OPVs), which represent a potential cost-effective route toward renewable energy. To date, the power conversion efficiency (PCE) has been greater than 10%. However, translation to large-scale devices has been met with significant reductions in the PCE. This can be attributed in part to the differences in the methods of preparation. Spin coating is routinely used to prepare laboratory-scale devices, while industrial processes have used blade or slot-die coating processes in a roll-to-roll (R2R) setting. Understanding the morphology evolution by the industrial-coating process is critical in the next-phase OPV research.

To investigate the process of morphology evolution of optoelectronic organic thin films in real-time, a slot-die coater was mounted inside a scattering beamline at a synchrotron to measure the grazing incidence small-angle X-ray scattering (GISAXS) signal during printing. GISAXS is a unique method available at synchrotron light sources for characterizing the nanostructural features of materials, particularly at surfaces and interfaces, which would otherwise be impossible using traditional transmission-based scattering techniques. It is a surface-sensitive tool for simultaneously probing the electron density of the sample both in-plane and out-of-plane, and is being increasingly utilized to measure the size, shape, and spatial organization of nanoscale objects located on top of surfaces or embedded in mono- or multi-layered thin film materials. Individual GISAXS images serve as static snapshots of nanoscale structure, while successive images provide a means to monitor and probe dynamical processes, including self-assembly or other reorganization events, which occur at nanometer length scales. The success of GISAXS relies on the unique information that can be extracted from the data. Although microscopy techniques provide very valuable local information on the structure, GISAXS is the only one to provide statistical information on nanometer features averaged over centimeter sample sizes. Presently a major bottleneck preventing GISAXS from reaching its full potential is the availability of data analysis and modeling resources for interpreting the data. To gain insight into OPV thin film structure, *in situ* GISAXS data were collected at high frame rates to capture the detailed process of film formation, as solvent was evaporating. To fit a model in real time to the data, fast data movement and analysis was required, as well as a sophisticated



**Figure 3.4.2.2:** (a) Schematic representation of block copolymer directed self-assembly on stripe-patterned substrates. (b) Representative top-down SEM image for copolymers assembled on stripe-patterned substrate, and corresponding three-dimensional structure predicted by theoretically informed coarse grained (TICG) model. (c) Cross section of thin copolymer films assembled on stripe-patterned substrate inferred from CDSAXS, TEM, and GISAXS through the use of TICG simulations and evolutionary computation algorithms.

computational framework to automate the workflow. Scattering methods like GIWAXS (grazing incidence wide-angle X-ray scattering) generate reciprocal space data that cannot be directly inverted for the underlying material structure. Rather, fitting methods are employed to reverse engineer the sample morphology. To address the complex morphologies of OPVs, HipGISAXS (High Performance GISAXS) has been developed by CAMERA to run scattering simulations on massively parallel platforms such as Titan (Oak Ridge Leadership Computing Facility). For analysis, the collected data was moved immediately to NERSC, reduced, shipped to Oak Ridge to fit the data in real-time, and then the results were reported back to the scientist. The data management and workflow was performed using the SPOT Suite, the data handling and processing used CADES at ORNL, and the high-performance data transfer capability used Globus Online and ESNet. Over the span of 3 days many different organic photovoltaics were printed and the crystal structure evolution during drying was recorded using GIWAXS. Real-time GIWAXS fitting of the 36,000 frames collected during the experiments was attempted. While the analysis could not keep up with the experimental output, the results from online printing have since shaped and expanded our understanding of printed organic photovoltaics.

The other end of the spectrum aims at post-processing using reconstruction, inter-comparison, simulation, and visualization using data analytics, machine learning, high-performance and extreme-scale computing. Here, different questions arise, including: What is the maximum amount of information that can be measured, processed, organized, and displayed to help understand and shed light on further experiments? Can data be transformed to initialize computational models, with output framed to complement the experiment? New atomistic theories and simulation paradigms are needed, optimized with applied mathematics to address questions and to handshake with specific scientific data types from custom instruments.

For example, a grand challenge is to guide or direct the assembly of molecules and nanoscale objects into desirable target structures, which may or may not represent equilibrium states. Copolymer assembly can undergo microphase separation into ordered morphologies with characteristic dimensions in the range of 5 to 50 nanometers, guided by nanoscale patterns on a surface, as illustrated in Figure 3.4.2.2a. The resulting morphologies — perfectly aligned lamellae over large areas — are of considerable interest for applications, ranging from masks for advanced photolithography, to highly-conducting solid electrolytes for energy storage. In such applications, it is important that the resulting structure be defect free, and that the lamellae extend across the entire thickness of the polymer films. A majority of past work has relied on surface based techniques, such as SEM, to characterize film morphology. Such techniques are

insufficient, in that the three-dimensional structure of the films plays an essential role in their functional performance. In recent work, two-dimensional SEM images of ordered lamellae have been supplemented by three-dimensional predicted structures generated by theoretically informed coarse-grained (TICG) models. Figure 3.4.2.2b shows an example in which top-down SEM micrographs suggest that perfect lamellae are assembled on guiding stripes, but simulation predictions reveal that the lamellae do not cut across the entirety of the films. These images provide a compelling example of how theory and simulation can augment experimentation. In particular, critical dimension small-angle X-ray scattering (CDSAXS) and grazing incidence small angle X-ray scattering (GISAXS) have been used on the same aligned copolymer samples to provide a comprehensive view of the 3D structure of the films, including any defects that may arise as a result of the assembly process. These two techniques are complementary in that they probe the same morphology with different approaches; through their multimodal use, it is possible to arrive at a more reliable description of the morphology of the films.

In a departure from past work, where scattering spectra have been interpreted in terms of average, simple geometrical form factors, Figure 3.4.2.2c shows the results of the analysis in terms of a physics-based model that includes a small number of well-defined, material-specific constants. More specifically, the same theoretical formalism (TICG) used earlier to interpret SEM images, is now used in Figure 3.4.2.2c to describe simultaneously two independent data sets that were generated in different experiments (CDSAXS and GISAXS) performed on the same samples. Importantly, the model is fully three-dimensional, and it incorporates the effects of thermal fluctuations into the interpretation of the data. In this analysis, the simulations are used to calculate the scattering CDSAXS and GISAXS spectra. The predicted spectra are compared directly to those generated experimentally, and an evolutionary computation strategy<sup>209-210</sup> is then used to evolve the model parameters until satisfactory agreement between theory and experiment is achieved. In this example, the theory and the underlying computational algorithms serve as the link that serves to reconcile data from two very different experiments, thereby arriving at a more complete characterization of structure. Furthermore, the theoretical analysis enables extraction of important information pertaining to the geometry and chemistry of the underlying guiding stripes that is simply not accessible to traditional analysis approaches based on simple form factors. For completeness, for the particular samples considered in this example, it was also possible to perform TEM tomography<sup>211</sup> and, as illustrated in Figure 3.4.2.2c, verify that the 3D structure inferred from a theoretical interpretation of scattering profiles is indeed consistent with a third characterization method that is based in real-space measurements.

The examples presented here provide a proof-of-concept for what is possible when sophisticated analysis techniques based on state-of-the-art modeling are used to interpret multimodal experiments. It also serves to highlight some of the limitations that must be overcome in order for such techniques to become commonplace. First, the efficiency of the calculations and the underlying algorithms must be increased to the point where real-time analysis of data becomes possible. Second, it is of considerable interest to develop theories and computational methods that are capable of describing the time-dependent assembly process. Indeed, many of the block copolymer structures of interest for lithography or energy storage applications represent non-equilibrium, metastable states that arise as a result of carefully conceived, non-equilibrium assembly fabrication strategies. In order to provide an effective tool for analysis of scattering data throughout the process of assembly, the corresponding models should be able to provide a faithful description of the dynamics of assembly over time scales ranging from nanoseconds to minutes, or even hours. Such models and algorithms are in their infancy, and important efforts must be devoted to their development. More elaborate theories and models will necessarily be required to describe more complex materials and, in the case of polymers for energy storage, it will be essential that the effects of charges and long-range forces be taken into account. In order for such theoretical and computational efforts to augment ongoing experimental efforts, it will also be important that user-friendly software and interfaces be developed, thereby rendering sophisticated models accessible to non-experts.

In another example, imaging and understanding of functionality in individual nanostructures, proteins, and macromolecular assemblies has become possible with light sources and electron microscopy (Figure 3.4.2.3). In thermal equilibrium, such nanostructures assume an abundance of conformational states, with those at higher energies occurring less frequently. In fact, the number of times a conformational state is observed yields the free energy of the state via the Boltzmann factor.<sup>212</sup> Thus, a free-energy landscape can be constructed by associating an energy with each conformational state. A point in this landscape is defined by the (mutually orthogonal) “reaction coordinates” governing function, with a free-energy assigned to each point of the landscape. It is important to note that a sufficiently large number of

snapshots of machines *idling in equilibrium* reveals the entire energy landscape, with the highest accessed energy corresponding to the conformation sighted only once in the dataset.

Observing specific trajectories over the energy landscape can be directly correlated with functionality. Energy-efficient functions — work cycles — involve low-energy trajectories.<sup>212</sup> As any single trajectory is subject to strong stochastic effects, it is thus irreproducible. A thermodynamically meaningful description requires averaging over *homogeneous* ensembles large enough to suppress the influence of stochastic events.

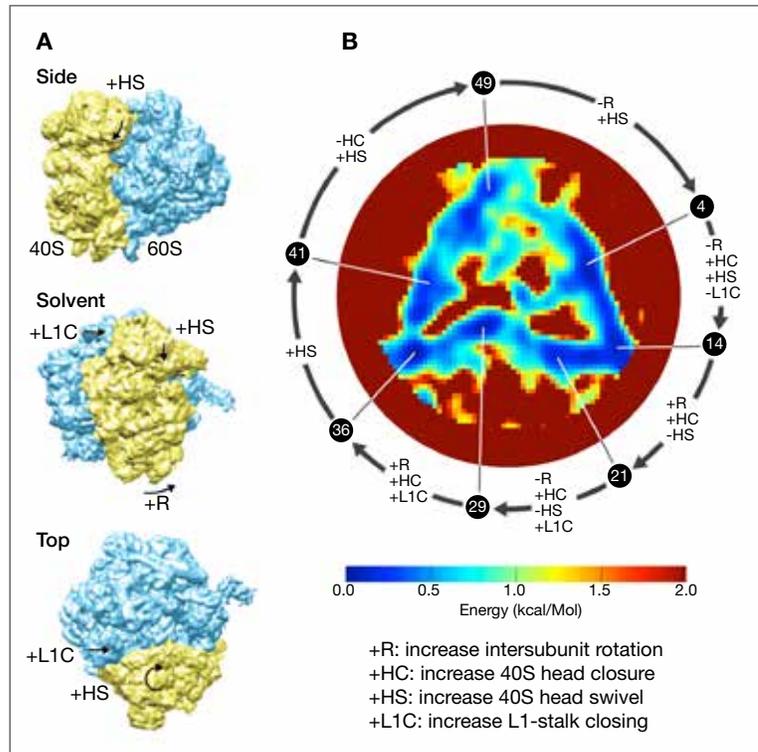
For example, the ribosome, a molecular machine responsible for protein synthesis, is buffeted by the random motions of surrounding molecules *in vivo*, exploiting these thermal motions for many of the required conformational changes in its work cycle. Using cryogenic electron microscopy in tandem with analytical approaches, the free-energy landscape of ribosomes can be imaged from the continuous trajectories from a large number of snapshots. Summarized in Fig. 3.4.2.3,<sup>213</sup>

this combined imaging and quantitative analytics approach can enable entirely new understanding of the ensemble behavior of nanomachines important for biological function.

Experimental datasets, in contrast, are often highly heterogeneous, comprising, for instance, snapshots of many individual machines, each in an unknown state and viewed in an unknown orientation. Statistically meaningful analysis must therefore begin with extracting homogeneous ensembles from heterogeneous data. Given the continuous nature of many types of heterogeneity, “clustering” approaches must be replaced with techniques capable of describing continuous changes in terms of orthogonal reaction coordinates. It is then possible to compile statistically meaningful averages over (nearly) homogeneous subsets, with each average pertaining to a particular state of the nanostructure or macromolecular assembly. Algorithms capable of dealing with continuous changes are in their infancy.

Modern experimental techniques routinely generate multi-terabyte datasets of snapshots. Each snapshot represents a projection, in the sense that only a subset of the governing parameters is measured. Following the prevalent precept that the best experiments are the most tightly controlled, much effort is devoted to constraining the number of degrees of freedom exercised by the system under observation. This can severely limit the amount of information gleaned from the experiment.

Modern data-driven analytical approaches, in contrast, extract rich information from snapshots of unconstrained systems in functions such as generating email or Facebook postings. Data-driven analysis “follows the data,” in the sense that the vocabulary and grammar best suited to describing a system are abstracted from the data, without preconceived notions or tight control of system variables. The vocabulary can consist of abstract memes, characteristic “empirical eigenfunctions,” or generalized principal components. The grammar can consist of rules for handling



**Figure 3.4.2.3:** (A) Three views of the structure of the 80S ribosome from yeast, with arrows indicating four key conformational changes associated with the elongation work cycle of the ribosome. (B) The energy landscape traversed by the ribosome. The color bar shows the energy scale. The energy range has been truncated at 2 kcal/mol to show details of the triangular trough. The error in energy determination along the closed triangle is 0.05 kcal/mol. The roughly triangular minimum free-energy trajectory is divided into 50 states. The arrows indicate the structural changes between 7 selected states, each identified by its place in the sequence of 50 states.

the extracted vocabulary, e.g., through analysis on curved surfaces defined by the data. General means for extracting interpretable information from such analytical approaches remain elusive, and are often heuristic. Recently, it was shown that the injection of physics-based constraints, such as the nature of possible operations on the system under observation, can, in particular instances, provide a route to extracting interpretable information from the analysis.<sup>214</sup> Such demonstrations must be generalized.

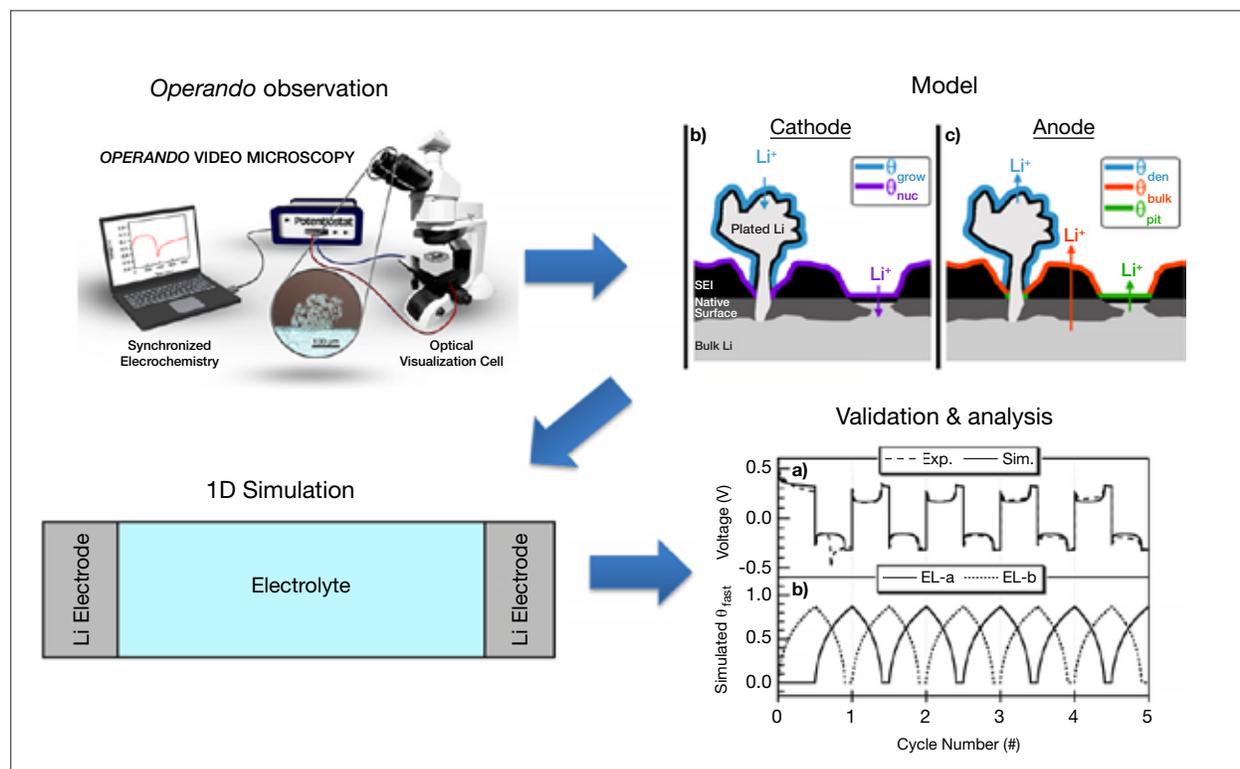
### 3.4.3 Predictive Simulation of Experimental Observables via Integration of Theories, Algorithms, and Information, Spanning Time and Length Scales

Experimental tool development and instrument design have always been done with the collection and analysis of datasets in mind. However, given the magnitude of the datasets discussed in Section 3.4.1, developing experimental tools needs to be, more than ever, intimately connected to the latest advances in data analytics, theory and computation to better incorporate information at various time and length scale phenomena into our observations. At the same time, for many observables of interest, new predictive theories and simulation paradigms are needed, particularly those spanning length and time scales. The development of such theories and methods will be accelerated by access to experimental data for validation. Therefore, there is a significant opportunity to advance both instruments and theory through co-development, leading to new kinds of experimental tools and approaches.

In the previous decade, atomistic simulations (including electronic structure calculations) have become central computational tools for materials science. They have provided prediction from first principles, ranging from quantum-level understanding of materials to data for hundreds of thousands of materials that could be mined. However, there is often a gap between the experimentally observable quantities and these predictions. Mesoscale modeling is a powerful approach that “maps” these data onto experimentally observable length and time scales. While capturing only the essence of the underlying electronic and atomic structures that are relevant to a specific problem, it enables predictions of nano- and micro-scale phenomena on the time scale associated with experiments, which can be seconds and even hours. These simulations, in turn, can inform continuum-scale models that would predict device scale phenomena. Such frameworks involve electronic/atomic-scale calculations via for example density functional theory (DFT), Monte Carlo/kinetic Monte Carlo models, and molecular dynamics (MD) simulations that can provide input to mesoscale models including phase-field models and dynamics at single-particle and multi-particle levels.

This multiscale simulation framework is of critical importance to advance energy science including catalysis, energy storage, and water filtration. The process inevitably involves “coarse-graining” not only to make feasible the analysis of the experiments but also to guide future experiments by providing information on parameters to be systematically sampled and to evaluate the effect of the experiment on the sample. That is, a back and forth feeding of experimental observation to theoretical and computational analysis is essential to determine mesoscale phenomena across a broad range of length and time scales. The success of systematic coarse graining is apparent in important examples.<sup>58</sup> However, regardless of the growth of computational resources, detailed, three-dimensional simulation tools and algorithms are not accessible today to make feasible *operando* studies in a vast number of systems. This lag currently hinders real-time coupling and feedback with experiments.

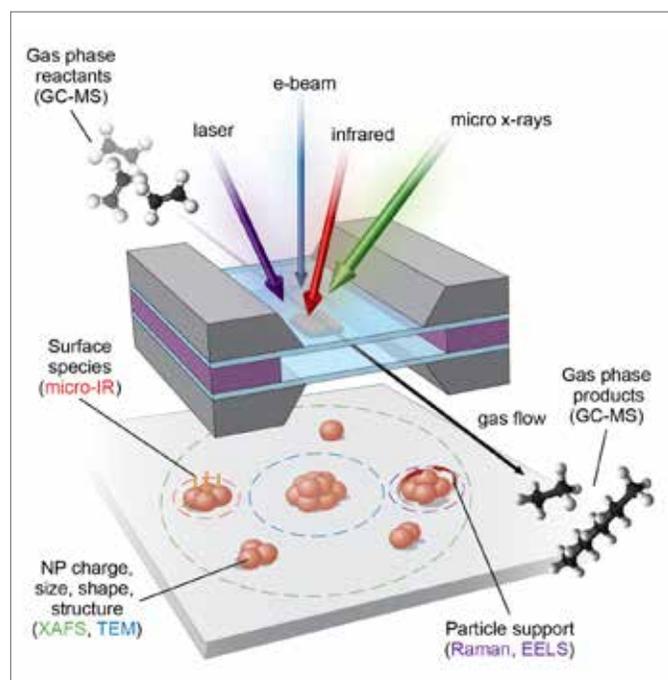
One of the real opportunities is to develop robust, reduced-order models that can be parameterized by mesoscale and atomistic simulations that can offer interactive, real-time prediction capability. It has recently been demonstrated based on *operando* microscopy of lithium electrodeposition/electrodissolution that one-dimensional simulations can predict the essential features of cyclic voltammetry (Figure 3.4.3.1).<sup>59</sup> Here, the complex morphology that develops during the deposition process is parameterized by assuming a simplified geometry. The predicted voltage as a function of time agreed well with the experimentally measured value. Furthermore, the simulations yielded understanding of the mechanisms that give rise to the features observed in the voltage stemming from the presence of heterogeneous surfaces upon which electrodeposition and electrodissolution occur. Such 1D simulations can be parameterized either by experiments or by more detailed simulations yielding macroscopic observable predictions. The computational time required in the simulations can be reduced from days on hundreds or thousands of CPUs to seconds on a single CPU by coarse graining, greatly reducing the computational time required and potentially enabling real-time feedback to experiments.<sup>60</sup>



**Figure 3.4.3.1:** Schematic of a catalytic microreactor that is capable of being probed by photons and electrons, allowing correlative experimentation through *operando* characterization. The various probes and the resulting information that can be gleaned from the data are indicated in the figure.

In another example, heterogeneous, photo- and electro-catalysis science exemplifies the grand challenges articulated in the recent BESAC report<sup>2</sup> directed to understanding the critical roles of heterogeneity, interfaces, and disorder in the functional characteristics of materials. A prototypical heterogeneous catalyst system might consist of nanostructured transition metal clusters adhering to an oxide support with a second, submonolayer oxide codeposited to act as a promoter for the target reaction. Optimization of the catalytic activity is controlled by several key factors including size and shape of the nanoclusters, interaction with the support and structural changes that emerge in the presence of reactive species in the environment. The details of structure and polydispersity in a given sample are the result of processes with limited opportunities to exert chemical control. The specific structural features that host the catalytically active sites in such complex systems often remain elusive. Yet the preservation of these motifs under what are typically harsh reaction conditions (elevated temperature and gas pressure) is paramount for a durable catalyst. The situation for photo- and electro-catalysis is further complicated by the role of the liquid at the catalytically active interface.

In the past decade, new tools have emerged which enable key characterization experiments, such as XPS, to be performed under *in situ* conditions that start to approximate more realistic catalyst operating environments. Each individual characterization tool reveals specific information, e.g., changes in local oxidation state probed by shifts in core level energies probed by XPS. Some tools effectively sample a broad area of the catalyst material while others (e.g. STEM imaging and the companion electron energy loss spectroscopy that yields chemical information) are inherently a local measurement. Overall, to build a physical picture of the operation of a specific catalyst material requires input from several probes. Ideally these probes could be controllably brought to bear on a sample that was not only under some approximation to operating conditions, but reproducibly and measurably under the same operating conditions. Recent innovations in microcell reactors show significant promise along this line<sup>22</sup> as highlighted in Figure 3.4.3.2. The state of the art instrumentation that is emerging clearly points to a future in catalysis science where fundamental advances can materialize from extensive, multimodal data sets measured under *in situ* or *operando* conditions. These can combine highly local probes (STEM and scanning tunneling microscopy), synchrotron X-ray techniques and other probes such as infrared spectroscopy, as well as the macroscopic characterization of reaction products downstream.



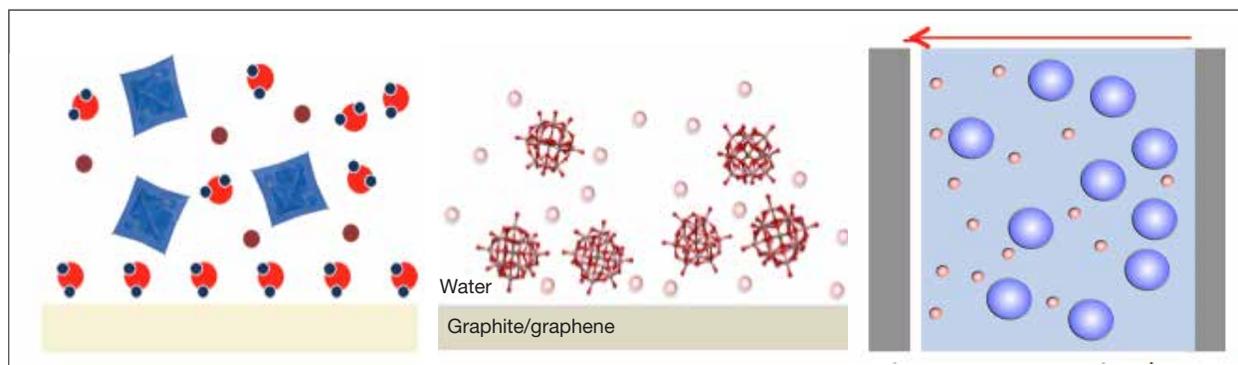
**Figure 3.4.3.2:** Illustration of a microcell reactor used for *operando* studies of catalyst samples using synchrotron extended X-ray absorption fine structure (EXAFS) and scanning transmission electron microscopy (STEM). The specific sample consists of SiO<sub>2</sub> supported Pt nanoparticles and the catalytic reaction is C<sub>2</sub>H<sub>4</sub> + H<sub>2</sub> → C<sub>2</sub>H<sub>6</sub>. The combined study reveals significant dynamical changes in the Pt nanoparticle size distribution under reaction conditions.

DFT-based calculations have had significant impact on catalysis science as recently reviewed by Norskov and co-workers.<sup>215</sup> The calculations provide quantitative information to understand fundamentals of the bonding molecular species at competing sites on the catalyst and are used to determine quantitatively the potential landscape for candidate reaction pathways. In this way, a cascade of possible reaction pathways can be mapped for a given set of reactants and products and key intermediates can be identified. This information can be used to build micro-kinetic or kinetic Monte Carlo models that allow analysis of macroscopic trends in reactivity and the distribution of products. This has been the basis for many studies of trends in catalytic activity (e.g. with choice transition metal). Generalizations of this idea are being used in a data-base driven approach to discover new catalysts. Very often the detailed DFT-based calculations of reaction pathways uniquely supply an atomic-scale picture of the catalyst mechanisms that complement the information gleaned from experimental probes.<sup>216-217</sup> The coarse-grained kinetic models naturally connect to macro scale measurements of catalytic activity.

Starting from DFT-based calculations, it is also possible to make direct connections to important experimental observables. For a specific structure, the set of harmonic vibrational frequencies can be calculated for comparison to infrared and Raman spectroscopy. The shifts in the energy of core levels between different sites in the structure can be computed for comparison to XPS spectra, including the impact of the screening of the core hole. The treatment of X-ray or high energy electron induced excitations, however, is subtle. Several different tools are available at different levels of approximation.<sup>218-219</sup> Depending on the level of accuracy, it is important to note that full spectral calculations typically require more computational resources than the ground state DFT calculations.

The development and validation of the model for the structure (e.g., nanoparticle size, shape and interface with the support) is a non-trivial problem. At the outset, there is simply the issue of size. Typical nanostructures under experimental study are on the scale of a few nanometers or a few thousand transition metal atoms. Model systems with about 200 atoms are routinely studied with DFT methods and at this scale, significant trends can be captured. Even so, to understand realistic motifs in systems such as bimetallic nanoparticles, simplified models play an important role together with DFT.<sup>216</sup> More broadly, a complete study of a catalyst system: identification of preferred binding sites for reactants, products and intermediates followed by establishing barriers for key reaction steps can require hundreds of individual calculations. As a practical matter, the modeler considers a much smaller nanostructure together with a periodic slab to model the support material. Model structure choice typically requires judgment to capture physically relevant motifs, consistent with what might be known about the structures from experimental characterization or the trends in chemical reactivity.

The pathway forward to extract maximal knowledge from the emerging instrumentation suite directed to characterize advanced catalyst systems (supported, multi-component, nanostructured materials with significant polydispersity) will require an integrated technical approach. Catalytically active sites are inherently relatively local, but likely can be functionally relevant with a range of local structure variation. Experimental probes include some that are highly local and others that inherently average over the ensemble of supported nanostructures. Understanding will be based on



**Figure 3.4.3.3:** The schematic organization of ions (e.g., polyoxometalate) along with counter ions at the electrode-electrolyte interface with implicit water (left), implicit water (center) and the mesoscale structure (right). Flat surface morphologies provide validation of methods. The goal is to systematically analyze ionic profiles structure and dynamics in non-homogeneous and evolving surfaces.

developing a set of physically relevant structural motifs, linking them to the available physical probes for validation and then understanding their role in the target chemical activity. There is a fundamental structure discovery challenge here, but it is not so neatly defined as traditional crystallography or molecular structure determination.

Traditional approaches to interpret spectroscopic signatures, e.g., by “finger printing” from known compounds, will need to be enhanced by advanced use of databases and machine learning approaches. Theory and simulation can play a significant role in developing those databases and substantiating the correlations that emerge, as indicated by recent progress.<sup>221</sup>

DFT-based calculations can also be enlisted directly in the search for relevant structure motifs. The idea is to generate candidate structures, including local energy optimization, but allowing for a scope of total energy that is plausible based on process conditions in experiments or other criteria, but certainly beyond equilibrium. Several existing approaches to structure discovery can likely be adapted. Examples include direct molecular dynamics simulations under accelerated conditions, Monte Carlo techniques, and genetic algorithms.

A key issue for DFT-based approaches will continue to be limitations to the size of the model structures employed based on computational capacity. There are many versions of local quantum treatment embedded in a larger empirically treated matrix (so called QM/MM methods). Recent experience with Green’s function methods, e.g. in transport or historically in point defect theory, may both allow more efficient treatment of the local structure and be sufficient for linking to the Green’s function based approaches to X-ray spectra.

The need for multiscale modeling is further evident in studies of the organization of ions at charged solid-water interfaces, which is central to understanding a broad range of energy-related systems, ranging from energy storage (e.g., adsorption) to energy conversion (e.g., photon absorption and charge transfer). Recent advances in high-resolution X-ray scattering to interrogate solid-liquid interfacial structures enable a direct probe of the molecular scale structures and processes that control phenomena at these interfaces. Such systems provide both a challenge and a benchmark for current computational approaches, due to their complexity and the range of length scales that must simultaneously be understood, both the molecular scale (e.g., ion hydration, adsorption) and the mesoscale (extended ion distributions).

Interfacial ion organization in electrolytes can be observed as a function of applied potentials, spanning the regimes of low to high charge densities using *in situ* X-ray reflectivity. For example, the solid-electrolyte interphase formed during the lithiation of a SiC anode coated with an epitaxial graphene layer was characterized in this manner.<sup>222</sup> The measured electrolyte organization can be compared to various computational and theoretical approaches. Benchmarks of relative accuracy and efficiency of various functionals versus empirical models and against experimental data is critical to advance our understanding of solid-liquid interfaces. These studies permit the systematic exploration of the role of cation/anion size and valence ratios on ionic profiles to evaluate the accuracy of the potentials for the various

components, which are obtained by quantum mechanical calculations. These potentials are then implemented in full atom classical simulations, from where coarse-grained interaction parameters are extracted to compute the structure at the mesoscale and compare the results to the experimental observations at the relevant length scale (Figure 3.4.3.3).

To date, experimental work has focused on ion-surface interactions through the idea of ion adsorption or as vertically diffuse ion profiles, but little has been done to understand the lateral modulations of the ion distribution extending away from the surface. The 3D ion distributions can be measured by making use of both specular and non-specular X-ray scattering and resonant scattering. Electrolyte systems have to be chosen with the goal of understanding the transition between the molecular-scale (i.e., ion adsorption) and longer-scale mesoscale interactions with the aid of theory and modeling.<sup>223</sup>

Implementing electrostatic interactions at a dielectrically heterogeneous solid-liquid or liquid-liquid interface, and accounting for van der Waals interactions, is of critical importance to cleaning of water and recovering rare earths methodologies besides energy storage and conversion. The ionic structure, which determines the surface reactivity, in surface with composition heterogeneities is accessible by anomalous grazing incident X-ray scattering (GIXS) with sensitivity to both the in-plane and out-of-plane components of the distribution. Modern algorithms to determine the dynamics of ions at fluctuating interfaces should be implemented to assist experimental observations.<sup>224</sup> These coarse-grained simulations offer a unique opportunity to validate theories and models that guide future experiments by providing the relevant parameters in the experimental design (such as the electrolyte characteristics, surface composition and length scale where cation and ion depletion and/or charge amplification are observed).

The above examples point to the need for “on-demand” information on components, interactions, and dynamics at different length scales; the development of new theoretical models to bridge time and length scales; and the design of experimental tools in tandem with theory and computational tools.

A key element to maximizing the benefit from theory and simulations is knowing their uncertainties. By having a quantitative understanding of the uncertainties, one can rule out experiments that would likely not be fruitful; on the contrary, not knowing uncertainties would lead to having to perform many more experiments in a much larger parameter space or, worse, rule out experiments that would result in successful material discovery. With the need-driven trends toward multiscale simulations and multimodal characterization, the linking between various methodologies will become ubiquitous. However, it must be recognized that each approach contains intrinsic uncertainties, and each level of coarse-graining introduces uncertainties, and propagates such uncertainties. In order to fully exploit the power of predictive modeling and simulations, a better grasp of the uncertainties associated with the predictions is needed. Predictions from well-established approaches should include a quantitative measure of uncertainties along with the predicted values. For less established approaches, efforts should include identifying and quantifying uncertainties by, for example, sensitivity studies, which will also reveal which parameters are more influential in determining the functionality.

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# APPENDIX B: FIGURE SOURCES

## Figure 2.1.1 (same as Figure 3.1.1.1)

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## Figure 2.1.2

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## Figure 2.2.1 (same as Figure 3.4.3.2)

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## Figure 2.2.2

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## Figure 2.3.1

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## Figure 2.3.2 (same as Figure 3.3.5.5)

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Skirmion diagram courtesy of Argonne National Laboratory

## Figure 2.4.1 (same as Figure 3.4.2.1)

Courtesy of Alex Hexemer, Lawrence Berkeley National Laboratory

## Figure 2.4.2

Courtesy of Colin Ophus, Lawrence Berkeley National Laboratory

## Figure 2.4.3

Figure courtesy of Katsuyo Thornton, University of Michigan

Battery: <http://www.azonano.com/article.aspx?ArticleID=3053>

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Particle: Courtesy of H. C. Yu and Thornton

Atomic: Y. S. Meng and M. E. Arroyo-de Dompablo, *Energy Environ. Sci.* **2009**, 2, 589–609.

## Figure 2.4.4 (same as Figure 3.4.3.1)

Courtesy of Katsuyo Thornton, University of Michigan. Adapted from Wood, K.N.; Kazyak, E.; Chadwick, A.F.; Chen, K.-H.; Zhang, J.-G.; Thornton, K.; Dasgupta, N.P. Dendrites and Pits: Untangling the Complex Behavior of Lithium Metal Anodes Through *Operando* Video Microscopy. *ACS Central Science*, **2016**, 2, 790–801.”

## Figure 3.1.1.1

See credit for Figure 2.1.1.

## Figure 3.1.1.2

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**Figure 3.1.2.1**

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**Figure 3.1.2.2**

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**Figure 3.1.3.1**

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**Figure 3.1.3.2**

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**Figure 3.1.3.3**

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**Figure 3.2.1.1**

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**Figure 3.2.1.2**

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**Figure 3.2.1.3**

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**Figure 3.2.1.4**

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**Figure 3.2.1.5**

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**Figure 3.2.1.6**

Courtesy of Oliver Gessner, Lawrence Berkeley National Laboratory

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**Figure 3.2.1.7**

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**Figure 3.2.1.8**

Courtesy of Xiaoxi Wu, Stanford University

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**Figure 3.2.2.1**

(A) Courtesy of Nigel Browning, PNNL

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**Figure 3.2.2.2**

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**Figure 3.3.1.1**

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**Figure 3.3.1.2**

Courtesy of Cemea Instruments, Inc.

**Figure 3.3.1.3**

Adapted from Fister, T. T.; Hu, X.; Esbenschade, J.; Chen, X.; Wu, J.; David, V.; Bedzyk, M.; Long, B.; Gewirth, A. A.; Shi, B.; Schlepütz, C. M.; Fenter, P., Dimensionally Controlled Lithiation of Chromium Oxide. *Chem. Mater.* **2016**, *28* (1), 47–54.

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**Figure 3.3.3.1**

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**Figure 3.3.4.1**

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**Figure 3.3.5.2**

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**Figure 3.3.5.3**

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**Figure 3.3.5.4**

From Anovitz *et al.* (unpub. ORNL)

**Figure 3.3.5.5**

See credit for Figure 2.3.2.

**Figure 3.4.1.1**

Zelenyuk, A.; Imre, D., Beyond Single Particle Mass Spectrometry: Multidimensional Characterisation of Individual Aerosol Particles. *Inter. Rev. Phys. Chem.* **2009**, 28, 309–358.

**Figure 3.4.2.1**

See credit for Figure 2.4.1.

**Figure 3.4.2.2**

Adapted from Segal-Peretz, T.; Winterstein, J.; Doxastakis, M.; Ramirez-Hernandez, A.; Biswas, M.; Ren, J. X.; Suh, H. S.; Darling, S. B.; Liddle, J. A.; Elam, J. W.; de Pablo, J. J.; Zaluzec, N. J.; Nealey, P. F., Characterizing the Three-Dimensional Structure of Block Copolymers via Sequential Infiltration Synthesis and Scanning Transmission Electron Tomography. *ACS Nano* **2015**, 9, 5333–5347.

**Figure 3.4.2.3**

Dashti, A.; Schwander, P.; Langlois, R.; Fung, R.; Li, W.; Hosseinizadeh, A.; Liao, H. Y.; Pallesen, J.; Sharma, G.; Stupina, V. A.; Simon, A. E.; Dinman, J. D.; Frank, J.; Ourmazd, A., Trajectories of the Ribosome as a Brownian Nanomachine. *Proc. Nat. Acad. Sci. US* **2014**, 111 (49), 17492–7.

**Figure 3.4.3.1**

See credit for Figure 2.4.4.

**Figure 3.4.3.2**

See credit for Figure 2.2.1.

**Figure 3.4.3.3**

Courtesy of Monica Olvera De La Cruz, adapted from Jing, Y.; Jadhao, V.; Zwanikken, J. W.; Olvera De La Cruz, M., Ionic Structure in Liquids Confined by Dielectric Interfaces. *J. Chem. Phys.* **2015**, 143, 194508.

# APPENDIX C: AGENDA

## BASIC RESEARCH NEEDS FOR

# Innovation and Discovery of Transformative Experimental Tools

HILTON WASHINGTON DC/ROCKVILLE HOTEL AND EXECUTIVE MEETING CENTER

JUNE 1–3, 2016

TUESDAY, MAY 31, 2016	
7:00 – 9:00 PM	Workshop preparation discussion (BRN chairs and Panels chairs)
WEDNESDAY, JUNE 1, 2016	
7:00 – 8:00 AM	Registration/Breakfast
OPENING PLENARY SESSION	
8:00 – 8:15 AM	<b>BES Welcome and Workshop Charge</b> Harriet Kung, Associate Director of Science for Basic Energy Sciences
8:15 – 8:30 AM	<b>Chair Welcome and Workshop Structure</b> Ali Belkacem, Lawrence Berkeley National Laboratory
8:30 – 9:05 AM	<b>Plenary 1: Dynamics of Heterogeneous Catalytic Reactions</b> Robert Schlögl, Fritz Haber Institute of the Max Planck Society
9:05 – 9:40 AM	<b>Plenary 2: <i>Operando</i> Characterization: Correlating Data from Multiple Probes to Understand the Function of Energy-Related Materials</b> Eric Stach, Brookhaven National Laboratory
9:40 – 10:10 AM	Break
10:10 – 10:45 AM	<b>Plenary 3: Exploring Nanostructured Magnetic and Electronic Materials</b> Amanda Petford-Long, Northwestern University/Argonne National Lab
10:45 – 11:20 AM	<b>Plenary 4: Theory, Simulation &amp; Deep Data as Drivers for New Experimental Tools</b> Sharon Glotzer, University of Michigan
11:20 – 11:55 AM	<b>Plenary 5 Title: Developing New Mathematics for Experimental Science: The Center for Advanced Mathematics for Energy Research Applications (CAMERA)</b> James Sethian, UC Berkeley/LBNL
12:00 – 1:30 PM	Working Lunch
AFTERNOON PANEL SESSION	
1:10 – 1:30 PM	<b>Panel Introductions — Workshop Co-Chairs</b>
1:30 – 5:30 PM	<b>Parallel Panel Sessions</b> <b>Panel 1: Chemical reactions and transformation in functional environments</b> Peter Crozier, Arizona State University Cynthia Jenks, Ames National Laboratory <b>Panel 2: Imaging materials far away from equilibrium</b> Paul Fenter, Argonne National Laboratory Wayne Hess, Pacific Northwest National Laboratory <b>Panel 3: Challenges of heterogeneity across multiple length scales &amp; multiple time scales</b> Ralph Nuzzo, University of Illinois Jennifer Ogilvie, University of Michigan <b>Panel 4: Transformational experimental tools through integration of instrumentation with theory and computation</b> Jeff Neaton, Lawrence Berkeley National Laboratory Monica Olvera de la Cruz, Northwestern University
5:30 – 9:00 PM	<b>Working Dinner — Parallel Panel Discussions (continued)</b>

**THURSDAY, JUNE 2, 2016**

7:00 – 8:00 AM	Breakfast
8:00 – 8:35 AM	<b>Plenary 6: Heterogeneity: The Bane of Catalyst Characterization</b> Simon Bare, SSRL, Stanford Linear Accelerator Laboratory
8:35 – 9:10 AM	<b>Plenary 7: Imaging in Liquids, Gases and Mixtures</b> Frances Ross, IBM
9:10 – 9:30 AM	Break and move to panel sessions
9:30 – 10:30 AM	<b>Parallel Panel Sessions for discussion/preparation of preliminary reports</b>
10:30 – 10:40 AM	Break and move to plenary room for panel reports
10:40 – 11:00 AM	<b>Report from Panel 1: Chemical reactions and transformation in functional environments</b>
11:00 – 11:20 AM	<b>Report from Panel 2: Imaging materials far away from equilibrium</b>
11:20 – 11:40 AM	<b>Report from Panel 3: Challenges of heterogeneity across multiple length scales and multiple time scales</b>
11:40 – 12:00 AM	<b>Report from Panel 4: Transformational experimental tools through integration of instrumentation with theory and computation</b>
12:00 – 1:30 PM	Working Lunch
1:30 – 5:30 PM	<b>Panel Discussions (continued)</b>
5:30 – 9:00 PM	Working Dinner <b>Panel Discussions (continued) &amp; Preparation for final panel reports</b>

**FRIDAY, JUNE 3, 2016**

7:00 – 8:00 AM	Breakfast
8:00 – 8:30 AM	<b>Report from Panel 1: Chemical reactions and transformation in functional environments</b>
8:30 – 9:00 AM	<b>Report from Panel 2: Imaging materials far away from equilibrium</b>
9:00 – 9:30 AM	<b>Report from Panel 3: Challenges of heterogeneity across multiple length scales and multiple time scales</b>
9:30 – 9:45 AM	Break
9:45 – 10:15 AM	<b>Report from Panel 4: Transformational experimental tools through integration of instrumentation with theory and computation</b>
10:15 – 11:00 AM	<b>Discussion</b>
11:00 – 11:30 AM	<b>Closing Remarks</b> Ali Belkacem, Lawrence Berkeley National Laboratory
11:30 AM	Workshop Adjourned

**CLOSED WRITING SESSION** Chairs, panel leads, and designated writers only

12:00 – 1:00 PM	Lunch
1:00 – 5:30 PM	Writing Session
5:30 PM	Adjourn

# APPENDIX D: ABSTRACTS FOR PLENARY TALKS

## ***Operando* Characterization: Correlating Data from Multiple Probes to Understand the Function of Energy-Related Materials**

**Eric A. Stach**

*Center for Functional Nanomaterials, Brookhaven National Laboratory*

The function of energy-related nanomaterials is deeply tied to how they interact with their environment. These interactions lead to the desired outcomes e.g.: energy storage, conversion of a gas, collection of an electron-hole pair. But most often, they also lead to changes in the physical and electronic structure of the materials themselves. These changes are often transient: they are present only when the materials function. Thus, *ex post facto* measurements nearly always yield either partial or even inaccurate information about the system. This means that one must characterize these materials ‘in a working condition’ (*operando*) to understand the structures that matter. In this presentation, I will provide an overview of recent progress in the area of *operando* characterization using electrons, photons and neutrons, and will describe how *operando* measurements allow explicit correlations to be made between the data obtained from different probes. Thereafter, I will present a vision for an integrated experimental and theoretical ecosystem that will enhance Data Driven Discovery of new materials.

## **Exploring Nanostructured Magnetic and Electronic Materials**

**Amanda Petford-Long**

*Northwestern University/Argonne National Laboratory*

As materials that display magnetic and electronic properties are patterned at the nanoscale, so novel emergent behavior can arise as a result of confinement and as a result of proximity of different materials at interfaces. It is critical to explore the local behavior of the materials and to correlate this behavior with structure and chemistry. *In situ* microscopy is being used to explore such materials since it is possible to image the spatial distribution of the magnetic and electric fields that contribute to the novel behavior, as a function of external stimuli such as applied fields and temperatures. Examples of recent materials of interest include topological insulators, chiral magnetic spin structures such as skyrmions, and resistive switching materials based on phase transitions or oxygen vacancy transport. In this presentation we will discuss the application of a range of *in situ* microscopy techniques based on X-rays, electrons and scanning probes to exploring the novel behavior of such materials.

## **Imaging in Liquids, Gases and Mixtures**

**Frances M. Ross**

*IBM T. J. Watson Research Center*

Quantitative imaging and analysis of liquids, gases and mixtures of phases is a central challenge associated with materials for energy sciences. Transmission electron microscopy has shown its applicability to liquid-based samples, but the exciting results obtained over the past few years also highlight experimental limitations. We discuss the current state of the art through examples that illustrate requirements for future experiments. Developing TEM of liquids into a transformative experimental tool will involve gradual progress in resolution, calibrations, and the use of correlative techniques. It will also require new functionality such as combined pressure and temperature control, the movement of well-defined fluid volumes, and the control of mixing patterns and liquid/gas or liquid/solid geometry.

## **Developing New Mathematics for Experimental Science: The Center for Advanced Mathematics for Energy Research Applications (CAMERA)**

**James Sethian**

*University of California-Berkeley/Lawrence Berkeley National Laboratory*

Fundamental computational methods are needed to extract information from murky data, interpret experimental results, and provide on-demand analysis as information is being generated. Advanced algorithms can examine candidate materials that are too expensive and time-consuming to manufacture, rapidly find optimal solutions to energy-related challenges, and suggest new experiments for discovery science. New and clever mathematics will provide tools that can, for example, reconstruct structure and properties from synchrotron light sources, predict behavior of new materials at the nanoscale, direct the hunt for new materials for batteries and gas separation, and optimize steps in the production of biofuels. The necessary research cuts across traditional boundaries. Building this new mathematics requires a close collaboration between applied mathematicians and scientists. These teams can lay groundwork so that research is aimed at relevant scientific problems which can enhance current experiment. Models need to be formulated, equations need to be derived, and new algorithms need to be proposed.

In this talk, we will describe some of the work of the ASCR-BES jointly funded Center for Applied Mathematics for Energy Research Applications (CAMERA), whose focus is to build applied mathematics for DOE facilities. We will describe on-going work in multiple areas, drawing from examples in ptychography, image processing, analysis of multimodal experiments, fast methods for density functional theory and new methods for reconstructions from fluctuation scattering and single particle imaging.

## **Heterogeneity: The Bane of Catalyst Characterization**

**Simon R Bare**

*SSRL, SLAC National Accelerator Laboratory*

The dream of every catalytic scientist is to develop a uniform single site catalyst where each active site is identical to the others and thus exhibits uniform activity. Unfortunately, most catalysts are heterogeneous in nature and it is instructive to begin by asking on what length scale and time scale is the material heterogeneous, as that will determine the appropriate course of action to study the material. It is also important to remember that catalysts are dynamic and their physical and chemical structure inevitably change under operating conditions and so any study of the heterogeneity of the catalyst must factor this into account. Moreover, it is not sufficient to characterize the structure of the catalyst without also characterizing its function — to ensure that it is the structure of the active site that is being probed. This talk will explore these topics using examples from the literature. More importantly I will address several areas of opportunity for furthering our understanding of the heterogeneity of catalysts and other energy materials.

# APPENDIX E: WORKSHOP PARTICIPANTS

**Chair:** Ali Belkacem, *Lawrence Berkeley National Laboratory*

**Co-chairs:** Cynthia Friend, *Harvard University*

Yimei Zhu, *Brookhaven National Laboratory*

## **Basic Energy Sciences Team:**

Tom Settersten, Bruce Garrett, Linda Horton, Helen Kerch, Jeff Krause, Peter Lee, George Maracas, Gail McLean, Raul Miranda, Joshua Haines (administrative), and Katie Runkles (administrative)

## **Plenary Speakers:**

Simon R. Bare, *SLAC National Accelerator Laboratory*

Sharon Glotzer, *University of Michigan*

Amanda Petford-Long, *Argonne National Laboratory, Northwestern University*

Frances M. Ross, *IBM T. J. Watson Research Center*

Robert Schlögl, *Fritz Haber Institute, Berlin*

James Sethian, *Lawrence Berkeley National Laboratory, University of California, Berkeley*

Eric A. Stach, *Brookhaven National Laboratory*

## **Panel 1: Chemical reactions and transformations in functional environments – Beyond model systems**

**Leads:** Peter Crozier, *Arizona State University*

Cynthia Jenks, *Ames Laboratory*

Hendrik Bluhm, *Lawrence Berkeley National Laboratory*

Peng Chen, *Cornell University*

Peter Chupas, *Argonne National Laboratory*

Tom Jaramillo, *Stanford University*

Gil Nathanson, *University of Wisconsin*

Robert Schlögl, *Fritz Haber Institute (Berlin)*

Dario Stacchiola, *Brookhaven National Laboratory*

Eric Stach, *Center for Functional Nanomaterials-Brookhaven National Laboratory*

Peter Stair, *Northwestern University/Argonne National Laboratory*

Esther Takeuchi, *Stony Brook University/Brookhaven National Laboratory*

Harry Tuller, *Massachusetts Institute of Technology*

## **Panel 2: Imaging materials far away from equilibrium**

**Leads:** Paul Fenter, *Argonne National Laboratory*

Wayne Hess, *Pacific Northwest National Laboratory*

Ara Apkarian, *University of California-Irvine*

Jordi Cabana, *University of Illinois at Chicago*

Jianming Cao, *Florida State University*

David Cole, *Ohio State University*

Paul Fuoss, *Argonne National Laboratory*

Oliver Gessner, *Lawrence Berkeley National Laboratory*

Laura Kaufman, *Columbia University*

Frances Ross, *IBM*

Mark Sutton, *McGill University*

Xijie Wang, *SLAC National Accelerator Laboratory*

Judy Yang, *University of Pittsburgh*

**Panel 3: Challenges of heterogeneity across multiple length scales and multiple time scales**

**Leads:** Ralph Nuzzo, *University of Illinois*  
Jennifer Ogilvie, *University of Michigan*

Simon Bare, *SLAC National Accelerator Laboratory*  
Austen Angell, *Arizona State University*  
Christoph Bostedt, *Argonne National Laboratory*  
Moh El-Naggar, *University of Southern California*  
Kollarn Lakshmi, *Rensselaer Polytechnic Institute*  
Suljo Linic, *University of Michigan*  
Katja Nowack, *Cornell University*  
Amanda Petford-Long, *Northwestern University/Argonne National Laboratory*  
Markus Raschke, *University of Colorado*  
Alex Sushkov, *Boston University*  
Craig Taatjes, *Sandia National Laboratory*  
David Wesolowski, *Oak Ridge National Laboratory*  
Junko Yano, *Lawrence Berkeley National Laboratory*

**Panel 4: Transformational experimental tools through integration of instrumentation with theory and computation**

**Leads:** Jeff Neaton, *Lawrence Berkeley National Laboratory/University of California-Berkeley*  
Monica Olvera de la Cruz, *Northwestern University*

Ray Bair, *Argonne National Laboratory*  
Jasna Brujic, *New York University*  
Hui Cao, *Yale University*  
Juan de Pablo, *University of Chicago*  
Sharon Glotzer, *University of Michigan*  
Alex Hexemer, *Lawrence Berkeley National Laboratory*  
Mark Hybertsen, *Center for Functional Nanomaterials-Brookhaven National Laboratory*  
Sergei Kalinin, *Center for Nanophase Materials Science-Oak Ridge National Laboratory*  
Abbas Ourmazd, *University of Wisconsin*  
James Sethian, *Lawrence Berkeley National Laboratory/University of California-Berkeley*  
Katsuyo Thornton, *University of Michigan*  
Tom Weinacht, *Stony Brook University*  
Alla Zelenyuk, *Pacific Northwest National Laboratory*

## INVITED PARTICIPANTS

C. Austen Angell, *Arizona State University*  
V. Ara Apkarian, *University of California, Irvine*  
Ray Bair, *Argonne National Laboratory*  
Simon Bare, *SLAC National Accelerator Laboratory*  
Ali Belkacem, *Lawrence Berkeley National Laboratory*  
Hendrik Bluhm, *Lawrence Berkeley National Laboratory*  
Christoph Bostedt, *Argonne National Laboratory*  
Nigel Browning, *Pacific Northwest National Laboratory*  
Jasna Brujic, *New York University*  
Jordi Cabana, *University of Illinois, Chicago*  
Jianming Cao, *Florida State University*  
Hui Cao, *Yale University*  
Peng Chen, *Cornell University*  
Peter Chupas, *Argonne National Laboratory*  
David Cole, *Ohio State University*  
Peter Crozier, *Arizona State University*  
Juan de Pablo, *University of Chicago*  
Moh El-Naggar, *University of Southern California*  
Paul Fenter, *Argonne National Laboratory*  
Cynthia Friend, *Harvard University*  
Paul Fuoss, *Argonne National Laboratory*  
Oliver Gessner, *Lawrence Berkeley National Laboratory*  
Sharon Glotzer, *University of Michigan*  
Zahid Hasan, *Princeton University*  
Wayne Hess, *Pacific Northwest National Laboratory*  
Alex Hexemer, *Lawrence Berkeley National Laboratory*  
Mark Hybertsen, *Brookhaven National Laboratory*  
Tom Jaramillo, *Stanford University*  
Cynthia Jenks, *Ames Laboratory*  
Sergei Kalinin, *Oak Ridge National Laboratory*  
Laura Kaufman, *Columbia University*  
Kollarn Lakshmi, *Rensselaer Polytechnic Institute*  
Suljo Linic, *University of Michigan*  
Gil Nathanson, *University of Wisconsin*  
Jeff Neaton, *Lawrence Berkeley National Laboratory/University of California, Berkeley*  
Katja Nowack, *Cornell University*  
Ralph Nuzzo, *University of Illinois*  
Jennifer Ogilvie, *University of Michigan*  
Monica Olvera de la Cruz, *Northwestern University*  
Abbas Ourmazd, *University of Wisconsin*  
Amanda Petford-Long, *Argonne National Laboratory/Northwestern University*  
Markus Raschke, *University of Colorado*  
Frances Ross, *IBM*  
Robert Schlögl, *Fritz Haber Institute, Berlin*  
James Sethian, *University of California, Berkeley/Lawrence Berkeley National Laboratory*  
Dario Stacchiola, *Brookhaven National Laboratory*  
Eric Stach, *Brookhaven National Laboratory*  
Peter Stair, *Northwestern University/Argonne National Laboratory*  
Alex Sushkov, *Boston University*  
Mark Sutton, *McGill University*  
Esther Takeuchi, *Stony Brook University/Brookhaven National Laboratory*

Craig Taatjes, *Sandia National Laboratories*  
Katsuyo Thornton, *University of Michigan*  
Harry Tuller, *Massachusetts Institute of Technology*  
Xijie Wang, *SLAC National Accelerator Laboratory*  
Tom Weinacht, *Stony Brook University*  
David Wesolowski, *Oak Ridge National Laboratory*  
Judy Yang, *University of Pittsburgh*  
Junko Yano, *Lawrence Berkeley National Laboratory*  
Alla Zelenyuk, *Pacific Northwest National Laboratory*  
Yimei Zhu, *Brookhaven National Laboratory*

## INVITED OBSERVERS

Paul Bayer, *DOE Office of Science, Office of Biological and Environmental Research*  
Steve Binkley, *DOE Office of Science, Advanced Scientific Computing Research*  
Geoff Campbell, *Lawrence Livermore National Laboratory*  
Hans Christen, *Oak Ridge National Laboratory*  
Adam Cohen, *Department of Energy*  
Chris Fecko, *DOE Office of Science, Basic Energy Sciences*  
Peter Fischer, *Lawrence Berkeley National Laboratory*  
Bonnie Gersten, *DOE Office of Science, Basic Energy Sciences*  
Nancy Haegel, *National Renewable Energy Laboratory*  
Joshua Haines, *DOE Office of Science, Basic Energy Sciences*  
Craig Henderson, *DOE Office of Science, Basic Energy Sciences*  
Linda Horton, *DOE Office of Science, Basic Energy Sciences*  
Jim Horwitz, *DOE Office of Science, Basic Energy Sciences*  
David Hurley, *Idaho National Laboratory*  
Helen Kerch, *DOE Office of Science, Basic Energy Sciences*  
Jeff Krause, *DOE Office of Science, Basic Energy Sciences*  
Harriet Kung, *DOE Office of Science, Basic Energy Sciences*  
Eliane Lessner, *DOE Office of Science, Basic Energy Sciences*  
George Maracas, *DOE Office of Science, Basic Energy Sciences*  
Gail McLean, *DOE Office of Science, Basic Energy Sciences*  
Talia Melcer, *DOE Office of Science, Basic Energy Sciences*  
Raul Miranda, *DOE Office of Science, Basic Energy Sciences*  
Chuck Peden, *DOE Office of Science, Basic Energy Sciences*  
Kelly Perry, *DOE Office of Science, Basic Energy Sciences*  
Eric Rohlifing, *DOE ARPA-E*  
Tom Russell, *DOE Office of Science, Basic Energy Sciences*  
Bob Schoenlein, *SLAC National Accelerator Laboratory*  
Andy Schwartz, *DOE Office of Science, Basic Energy Sciences*  
Tom Settersten, *DOE Office of Science, Basic Energy Sciences*  
Emily Smith, *AMES National Laboratory*  
Peter Sushko, *Pacific Northwest National Laboratory*  
Amy Swain, *DOE Office of Science, Office of Biological and Environmental Research*  
Thiyaga Thiyagarajan, *DOE Office of Science, Basic Energy Sciences*  
Robert Tranter, *Argonne National Laboratory*  
John Vetrano, *DOE Office of Science, Basic Energy Sciences*  
Aaron Washington, *Savannah River National Laboratory*  
Lane Wilson, *DOE Office of Science, Basic Energy Sciences*  
Dzmitry Yarotski, *Los Alamos National Laboratory*  
Jane Zhu, *DOE Office of Science, Basic Energy Sciences*

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