Molecular Foundry
5-Year Strategic Plan

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1. Executive Summary

The Molecular Foundry is a knowledge-based User Facility for nanoscale science at Lawrence Berkeley National Laboratory (LBNL), supported by the Department of Energy (DOE). As an integral part of the LBNL research community, the Foundry contributes strongly to each of the Lab's strategic initiatives: Energy Innovation; Extreme Data Science; Microbes to Biomes; Brighter X-Rays, Sharper Focus; Service Technologies for Science; and Diversity and Inclusion. The Foundry's mission is to provide communities of users worldwide with access to expert staff and leading-edge instrumentation to enable the understanding and control of matter at the nanoscale in a multidisciplinary, collaborative environment. Users come from academic, industrial or national laboratories, both domestic and international, at no cost for non-proprietary research. They gain access to the Foundry on the basis of a competitive external peer-reviewed proposal process.

The Molecular Foundry is producing a body of world-class, high-impact fundamental user research that is advancing the forefront of nanoscale science. The Foundry's four multidisciplinary research themes focus the center's existing, leading-edge research in nanoscience and nanotechnology, its ambitious future, and strategic areas of opportunity for which the Foundry is best positioned to support and advance DOE's basic energy sciences mission.

This **Molecular Foundry Strategic Plan** focuses on the specific scientific drivers within these four themes that guide the Foundry's mission to share expertise with its expanding user communities in the next few years. The consolidation of the Molecular Foundry and the National Center for Electron Microscopy (NCEM) is an exciting new chapter that brings the Foundry to the forefront of electron microscopy, an added dimension that is vitally integrated throughout this plan, and provides an opportunity to develop and harness entirely new approaches to high-resolution, time-resolved, and *in situ* electron scattering of hybrid materials. Two new strategic future directions within each scientific theme, building on established strengths and leveraging our specific local environment at LBNL and throughout the Bay Area, are discussed in detail and summarized here:

- Combinatorial Nanoscience
    - From Nanocrystals to Mesoscale Assemblies
    - Molecular Folding Science
- Functional Nanointerfaces
    - Dynamic Nanointerfaces: Directing Energy Flow and Chemical Transformations
    - Functional 3D Hybrid Architectures from Designed Nanointerfaces
- Multimodal Nanoscale Imaging
    - Imaging Function and Interaction in Buried Environments
    - Mapping of Vector Fields in Space and Time
- Single-Digit Nanofabrication and Assembly
    - Precision Three-Dimensional Nanofabrication
    - Understanding and Controlling Heterogeneous Assembly far from Equilibrium

This strategic plan describes routes to realizing the potential of the opportunities listed above. While it is not meant to be comprehensive, nor does it mention every research area or approach that will be pursued in the coming years, it is a broad scientific and organizational outline that will serve to guide the Molecular Foundry while enabling us to adapt to the rapidly changing research landscape.

2. Introduction

Supported by the Department of Energy Office of Basic Energy Sciences (BES) through their Nanoscale Science Research Center (NSRC) program, the Molecular Foundry is a national User Facility for nanoscale science serving hundreds of academic, industrial and government scientists around the world each year. Users come to the Foundry to perform multidisciplinary research beyond the scope of an individual's own laboratory. By taking advantage of the Foundry's broad spectrum of core capabilities and expertise, users increase the scope, technical depth, and impact of their research. Moreover, while at the Foundry, users access LBNL's diverse scientific community that includes other user facilities, including the Advanced Light Source (ALS) and National Energy Research Scientific Computing Center (NERSC), as well as the Energy Innovation Hubs, such as the Joint Center for Artificial Photosynthesis (JCAP) and Joint Center for Energy Storage Research (JCESR), Joint BioEnergy Institute (JBEI), and a number of local Energy Frontier Research Centers (EFRCs).

The Molecular Foundry features world-class scientists with expertise across a broad range of disciplines and state-of-the-art, often one-of-a-kind, instrumentation. Staff spend at least half their time working with outside users, devoting the remainder of their time to internal research activities, which can be augmented with postdoctoral fellows hired using internal or external grant support. Internal research programs advance the frontiers of nanoscale science and, following our merger with NCEM, electron microscopy by developing new capabilities that are made available to users. In this novel feedback model, users are strongly engaged to advance Foundry research: many new Foundry capabilities arise out of synergistic projects with users.

Nanoscience can open new frontiers in energy, electronics, materials science, and biology. Research conducted with users at the Molecular Foundry defines these new frontiers and develops science and technology strategies to enable them. Organized into seven interdependent research facilities that support the four crosscutting scientific themes that were recently validated by a thorough strategic planning process, the Foundry provides access to state-of-the-art instrumentation, unique scientific expertise, and specialized techniques to help users address myriad challenges in nanoscience and nanotechnology.

At the Molecular Foundry, a vibrant, growing, and increasingly engaged community of users combines with a well-recognized, highly-productive staff. Following the merger with NCEM, the Foundry includes 28 independent researchers and 19 technical staff. In light of a recent leadership change, merger with NCEM, and turnover, the center is pursuing several opportunities to recruit new staff. At the same time, while the Foundry features in-house state-of-the-art instrumentation, several capabilities are nearing the end of their lifecycle. Motivated by the eight scientific future directions described below, this plan addresses these areas of need while also evolving the Foundry's scientific themes in step with the frontier of nanoscale science.

2.1 Foundry Research Facilities and Themes

The six-story, 94,000 square-foot Molecular Foundry building at LBNL overlooks the UC Berkeley campus and, from a distance, the San Francisco Bay. Directly adjacent to the Foundry is the NCEM complex that was established in 1983 to maintain a forefront research center for electron microscopy of materials with state-of-the-art instrumentation and expertise. Merged with the Molecular Foundry in 2014 to take advantage of growing scientific and organizational synergies, NCEM at the Foundry features 10 electron microscopes, many of which are world-leading.

Each of the six floors of the Foundry building, as well as NCEM, is managed as a technically distinct "facility" by world-class scientists equipped with state-of-the-art instrumentation, laboratories, and computational resources.

Summary of the Seven Technical Facilities

Imaging and Manipulation of Nanostructures

This facility develops and provides access to state-of-the-art characterization and manipulation of nanostructured materials – from "hard" to very "soft" matter – including electron, optical, and scanning probe microscopies.

Nanofabrication Facility

This facility focuses on understanding and applying advanced lithographies, thin film deposition, and characterization, emphasizing integration of inorganic, organic, and biological nanosystems with the potential for nanoelectronic, nanophotonic, and energy applications.

Theory of Nanostructured Materials Facility

This facility expands our understanding of materials and phenomena at the nanoscale through development and application of theories and methods for excited-state and charge transport at nanoscale interfaces, self-assembly of nanostructures, and X-ray spectroscopy in complex nanostructured systems.

Inorganic Nanostructures Facility

This facility is devoted to the science of semiconductor, carbon and hybrid nanostructures—including design, synthesis, and combinatorial discovery of nanocrystals, nanowires, and nanotubes and their self-assembly into 3D mesoscale functional materials for use-inspired energy applications.

Biological Nanostructures Facility

This facility designs and synthesizes new materials based on the self-assembly of biopolymers and bio-inspired polymers, creates new nanocrystal probes for bioimaging, and develops synthetic biology techniques to re-engineer organisms and create hybrid biomolecules to interface with a variety of applications.

Organic and Macromolecular Synthesis Facility

This facility studies "soft" materials, including the synthesis of organic molecules, macromolecules, polymers and their assemblies, with access to functional systems, photoactive materials, organic-inorganic hybrid structures, and porous materials.

National Center for Electron Microscopy (NCEM)

This world-renowned center for microscopy, recently integrated into the Molecular Foundry, features cutting-edge instrumentation, techniques and expertise required for exceptionally high-resolution imaging and analytical characterization of a broad array of materials.

Four research themes

Four research themes at the forefront of nanoscience integrate users, staff and techniques across all seven technical facilities, embodying the Foundry's core capabilities and synergistic activities in synthesis, characterization, fabrication, and theory. They were reinforced through the strategic planning process described in Section 2.4 and are regularly reviewed to evaluate their novelty,

relevance, productivity, and impact. New capabilities and expertise developed in the context of internal research activities significantly augment the Foundry User Program.

Combinatorial Nanoscience

This theme focuses on the rational design of targeted nanostructured materials. Robotic synthesizers are used to generate large libraries of biological, organic, and inorganic nanostructures, which, in combination with theory and characterization, are used for discovery of new materials with sought-after optical, electronic and thermal properties.

Functional Nanointerfaces

This theme centers on understanding and design of the physical and chemical properties of hybrid nanomaterials, defined as integrated materials composed of highly contrasting components, such as inorganic nanomaterials, organic supermolecular assemblies, and complex living organisms. This is accomplished through the synthesis of heterostructures and interfaces, the application of first-principles simulations, and the detailed characterization of form and function.

Multimodal Nanoscale Imaging

This theme develops and applies multiple spectroscopic and imaging technologies – including high-resolution flagship electron microscopies, scanned probe microscopies, and hyperspectral (nano)optical methods and imaging probes – to investigate structural and dynamic nanoscale phenomena in hard and soft nanostructured materials in solid-state, liquid, and vapor environments. This theme takes on the characterization challenges associated with the continued development of novel and increasingly complex hybrid materials.

Single-Digit Nanofabrication and Assembly

This theme aims to organize and structure material with critical features of dimensions at or below 10 nm, i.e., on the single-digit nanometer and atomic scales, to create nanoscale devices and architectures in inorganic, biological, or hybrid systems. Work in this theme is accomplished by developing protocols to both understand and implement methods of self-assembly and lithography in a variety of systems.

2.2 User Program

As emphasized throughout this document, the Molecular Foundry User Program is central to our mission to provide the research community with access to cutting edge tools and expertise and an intellectual hub for multidisciplinary, collaborative research in a safe environment. By continually leveraging the new capabilities made possible by the Foundry's user and internal research programs, and also neighboring facilities including the Advanced Light Source (ALS) and the National Energy Research Supercomputing Center (NERSC), the User Program remains at the cutting edge of nanoscale science. An MOU allows handling of proposals across facilities whereby users can jointly apply for time at the Foundry and ALS. Further synergies with the ALS, including plans for a joint beamline, are discussed in Section 3. At the same time, users of the Foundry also benefit from the annually allotted time provided by NERSC.

The Foundry's User Program is active and growing. In FY 2013, the Foundry and NCEM – merged in 2014 – served a combined 660 users and received a total of 481 proposals (~10% from industry) of which 79% were accepted. These programs facilitate productive, high-caliber science: 237 User publications in 2013, 72 of which were in high-impact journals as defined by the DOE. Since 2013,

37% of Foundry publications made use of one or more of the Foundry's co-located user facilities at LBNL, most notably NCEM (prior to the merge), ALS, and NERSC.

As of FY 2014, upon our merger with NCEM, a new review process was created, in which proposals are peer reviewed in onsite meetings by a newly formed Proposal Review Board (PRB). This new review process is not only more efficient (six weeks from proposal deadline to final decisions) but also fairer and more thorough.

2.3 Vision for the Future

The Molecular Foundry's vision is to provide multidisciplinary communities of users the opportunity to develop, probe, understand, and control matter and its behavior at nanometer length scales to address the most important technological challenges in energy and the environment.

To fulfill our mission, our broad institutional goals are to:

- Be a world-leading center of excellence for nanoscience, producing and enabling impactful user-inspired research in innovative materials synthesis, advanced electron and optical characterization, and predictive theory and modeling
- Attract and foster strong collaborations with outstanding users from academia, industry and government laboratories worldwide. Provide all users with world-class facilities and a one-of-a-kind expertise, both at the Foundry and within the LBNL environment, working together to identify and address the biggest challenges in nanoscale science
- Play a central leadership role at LBNL in materials science and serve as a conduit for high-resolution imaging; organic, inorganic, and biological synthesis; and computational efforts
- Influence, educate and train the next generation of interdisciplinary scientists who will carry forward Foundry expertise and safety culture throughout their careers at other institutions and in industry

2.4 Planning Process

The Molecular Foundry Strategic Plan describes an ambitious agenda to guide the facility over the next several years. It is a living document that has been created in response to scientific and organizational needs of our users and staff, with input provided by the Foundry's Scientific Advisory Board and a number of other outside stakeholders that represent the broad community of users.

As a DOE National User Facility, the Molecular Foundry's core mission is to provide world-class expertise and instrumentation that meet the needs of the greater scientific community. Accordingly, a series of listening sessions with outside thought leaders – many of which are users – were organized by each of the seven facilities to solicit input on those areas where the Foundry can have the greatest impact. These discussions were centered on the following questions:

- What are scientific areas of particular promise/excitement/opportunity?
- What challenges must be overcome to take advantage of these opportunities?
- What are the most pressing needs that would help overcome these challenges? How could the Lab environment be leveraged toward these goals?

Initial listening sessions involved members of the Foundry's seven external Proposal Review Boards that met with staff following their in-person proposal review meeting in May 2014. Later

that month, additional meetings were held with local researchers from academia and industry in groups that corresponded to our seven facilities. Both sets of events with outside researchers representing the user community, along with input from internal meetings among staff, were used to create a list of nearly 100 scientific drivers in the area of nanoscale science and electron microscopy. This list was discussed and sorted into groups by Foundry staff. Though the process encouraged the potential creation of entirely new themes for the Foundry, in the end, this exercise reinforced that the existing scientific themes remained central to the interests of nanoscientists outside the Foundry. It was also the genesis for the specific future directions within each theme.

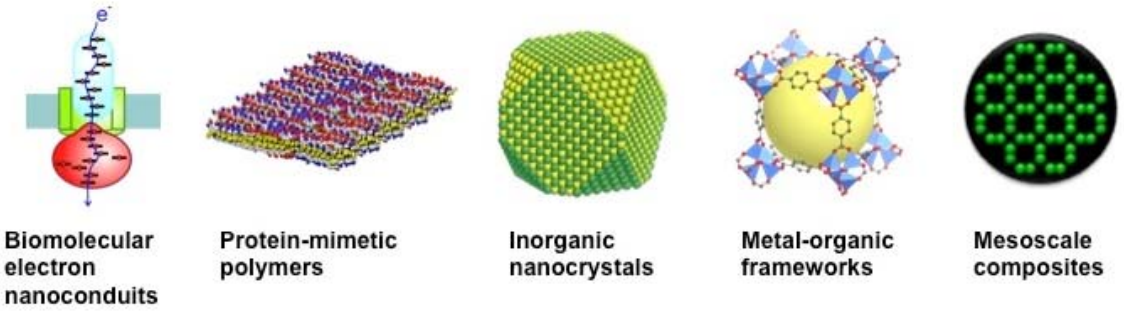
The contents of this strategic plan are the result of a deliberative process that included many diverse perspectives. In addition to the two sets of external listening sessions (who reviewed the final document following their initial input) and internal deliberations, the plan reflects the feedback of our Scientific Advisory Board (recently formed after the merger with NCEM), the input of the scientific leadership of the Advanced Light Source, and a number of other stakeholders, including the Foundry's User Executive Committee, who were also invited to contribute to the initial drafts. While these activities were initially motivated by the creation of this plan, an open channel of communication will be maintained with each of our constituents in order to continually meet the needs of our users.

3. Plans to Leverage Emerging Scientific Opportunities

The introduction provided an overview of the Foundry and its vision as a knowledge-based DOE User Facility and premier research institute in multidisciplinary nanoscale science. In what follows, we describe two specific scientific future directions within each of our four cross-disciplinary themes that best reflect the needs of the scientific user community and best capitalize on the Foundry's unique expertise and the scientific environment at LBNL. Each section also contains a number of planned capabilities – expertise and instrumentation – that are required to achieve the future directions of each theme, with essential participation from all seven scientific facilities.

3.1 Combinatorial Nanoscience

Combinatorial materials science involves the rapid exploration of a carefully chosen set of interrelated variables to achieve structural, catalytic, optical, electronic, or thermal properties of interest. At the Molecular Foundry, the approach involves the rational design, efficient synthesis, and thorough interrogation of large and diverse libraries of polymers, inorganic materials, and



A diversity of nanomaterial discovery platforms under study at the Foundry.

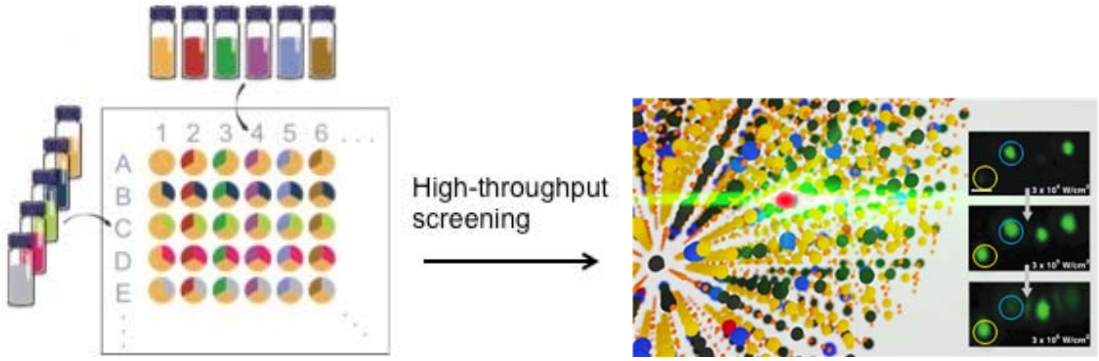
other nanoscale building blocks. This has required the development of a comprehensive suite of one-of-a-kind tools that are used in concert with theoretical predictions and scientific intuition. To date, these methods have been applied with substantial success to the discovery and optimization of new biomolecular assemblies, biomimetic polymers, inorganic nanocrystals, and metal-organic frameworks. The large datasets produced by these efforts are also guiding the development of new theoretical methods and tools (e.g., new force fields) to predict the properties of yet-uncharted nanomaterial compositions.

Although the morphologies of nanomaterials can be used to dictate some of their characteristics, an even richer set of properties can arguably be specified by controling the three-dimensional positions of heteroatoms, domains, and functional groups within them. As examples, the precise location of dopant atoms within a nanocrystal can lead to new photophysical properties, and specific combinations of organic functional groups can lead to highly selective catalysts. To access nanomaterials with this level of structural sophistication, multi-step chemical syntheses must be used to "program" the assembly of heterogeneous components in a particular order. By using our customized robotic tools to navigate sequences of synthetic parameters in systematically varied combinations, we have identified useful synthesis pathways that are often complex, highly interdependent, and non-intuitive. User demand for these specialized tools is rapidly growing and regularly exceeds capacity.

Future Directions

From Nanocrystals to Mesoscale Assemblies

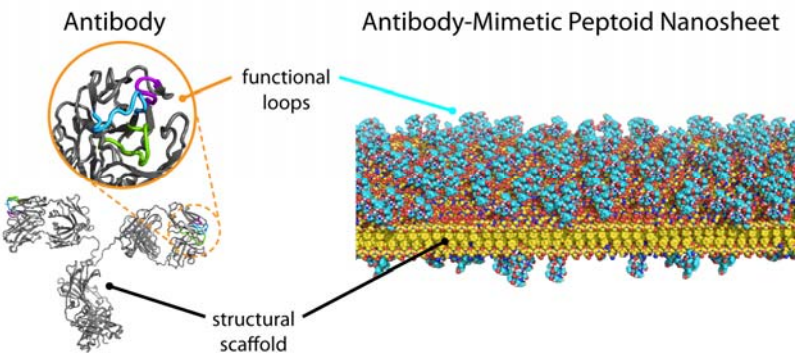
Across its facilities, the Foundry uses colloidal inorganic nanoparticles, small molecules and polymers, and in some cases living cells as modular building blocks to fabricate materials with mesoscale order that can store hydrogen, convert heat to electricity, sequester geologic CO_2 in minerals, and enhance efficiency of energy used in buildings. Precision control over the synthesis conditions enables the Foundry to provide the user community with reproducible nanoscale components, and it enables a fundamental understanding of their structure-function relationships. To create functional mesoscale materials with ever-increasing complexity, we must be able to predict the assembly pathways of the heterogeneous building blocks themselves, as well as the new properties that will emerge. We will achieve this by integrating deliberately synthesized and well-defined building blocks from combinatorial methods and harnessing the Foundry staff's considerable expertise in synthesis, assembly, characterization, and theory over multiple length scales, as well as those characterization capabilities of the ALS.



Upconverting lanthanide-doped nanocrystals, with near infrared excitation and visible light emission [Nat Nanotechnol. 9. 4. 300 (2014)]

Molecular Folding Science

We are rapidly extending the architectural paradigm found in biology–the folding of linear, information-rich polymer chains into defined 3D structures–into the world of synthetic materials. We aim to become the premier Facility for designing, synthesizing, and purifying sequence-specific polymers, characterizing and understanding their rules of folding and assembly, and creating nanostructured materials capable of complex, protein-like functions (e.g., molecular recognition and catalysis). Peptoid polymers are one family of materials whose synthesis by means of iterative covalent attachment is so efficient and controlled, that we can, for the first time, prepare high molecular weight polymer sequences from a vast chemical diversity of monomers. Predictive multi-scale simulations will allow us to design new polymers that fold and self-assemble into well-defined ion channels, specific binding pockets, and efficient catalytic sites. Testing these predictions will require high-resolution structural characterization using cryoTEM, *in situ* AFM, and X-ray scattering at the ALS. Crucial atomic detail will be possible with advances in electron microscopy that take advantage of spherical and chromatic aberration correctors, phase plate technologies, direct electron detectors for low-kV imaging, and the next generation of micro encased AFM probes for *in situ* imaging.



Architecture of a natural antibody (left) and an antibody-mimetic nanosheet (right) with a high density of loops on a peptoid nanosheet scaffold. [Nano, 7, 9276, (2013)]

Planned Capabilities

High Pressure, High Temperature, Multi-Step Robotic Synthesizer

Our capabilities in high-throughput colloidal nanocrystal synthesis will be significantly enhanced with our next-generation nanocrystal synthesis robot—the High-throughput Experimentation Robot for Multiplexed Automation of Nanochemistry (HERMAN) and the hiring of new staff in the Inorganic and Organic Facilities. Using machine-learning algorithms closely integrated with theoretical models, HERMAN will perform automated multi-step chemical synthesis at unprecedented temperatures and pressures. This will bring direct access to new classes of materials, such as complex nanocrystal heterostructures prepared through layer-by-layer growth and mesoscale architectures accessed through directed assembly. These new capabilities will complement those of WANDA, which is already a highly demanded tool.

Microfluidic Platforms for Parallel Synthesis and Characterization

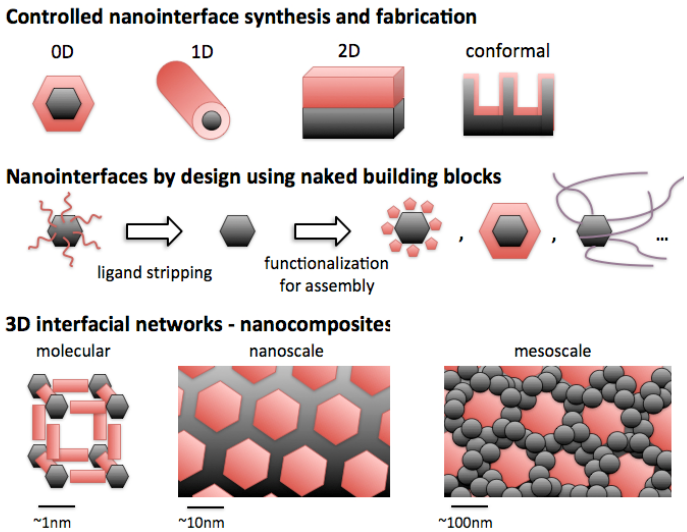
As characterization techniques are developed that use ever smaller amounts of material, we will miniaturize biopolymer and nanocrystal synthesis reactions using a suite of microfluidic equipment. This will accelerate nanomaterials discovery by enabling thousands of compounds to be prepared and screened in parallel. “Smart” synthesis chips will be developed that can evolve materials by *in situ* data analysis obtained by performing both synthesis and screening steps on the same chip. Nanomaterials discovered on these microscale devices will be validated by large-scale synthesis on the Foundry's robotic synthesizers.

High-Throughput Characterization

In order to evaluate the structure and/or function of materials produced by our combinatorial synthesis engines with rapidity and efficiency, we will establish increasingly insightful high-throughput screening and characterization methods. We aim to establish automated electron microscopy methods that leverages NCEM's expertise in electron microscopy, take advantage of X-ray scattering capabilities at the ALS, and pursue electrochemical and spectroscopic approaches capable of evaluating hundreds of samples with minimal human intervention post-synthesis. Furthermore, we will benefit from close connections with applied mathematicians at LBNL through the new Center for Applied Mathematics for Energy Research Applications (CAMERA) to help build screening methods and bring tools of computational geometry, optimization, and machine learning.

3.2 Functional Nanointerfaces

A frontier of materials science, and an area of increasing user interest, is the controlled integration of diverse nanoscale building blocks – e.g., inorganic, organic, biological – into functional mesoscale assemblies. As nanostructured building blocks intrinsically possess large surface-to-volume ratios, their assemblies feature a high-density network of nanoscale interfaces that present exciting new opportunities to control the propoagation of energy in hybrid materials. The goal of the Functional Nanointerfaces theme is to develop capabilities for the discovery, understanding, and design of novel functional nanostructured materials from the perspective of their component interfaces. This effort aims to harness their unique characteristics both individually and collectively, for emergent functionality, particularly for energy conversion, storage, and conservation.



The Molecular Foundry's synthesis and fabrication capabilities provide controlled approaches to create multidimensional interfaces spanning the nanoscale. Colloidal nanocrystals have insulating, inert coatings, which prevent easy coupling of nanocrystals for energy transfer. Naked nanocrystal building blocks can be assembled into molecular, nano- or mesoscale composites with nanoscale interfaces of controlled dimension and functionality

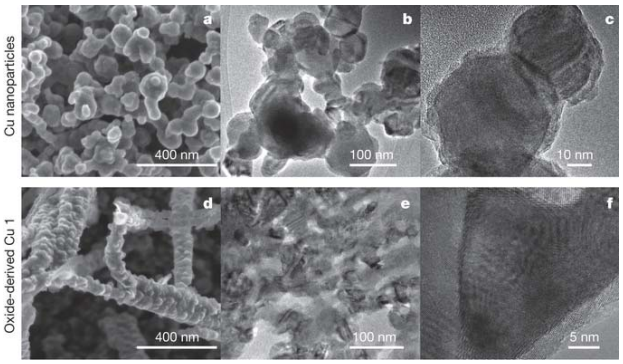
Interfaces can actively amplify or hinder the motion of charges, vibrational energy, light, or chemical information due to sharp contrasts in bonding modes, electronic energy levels and densities of states. There remains much to be learned about the exact nature of these emerging structural, electronic and dynamic properties and how they feed back across multiple length scales. However, a rich set of interdisciplinary scientific problems involve active transport processes at organic/inorganic, bio/inorganic, solid/electrolyte, and gas/solid interfaces. This theme involves cross-cutting activities spanning the creation of bottom-up 3D functional

mesoscale assemblies with precisely controlled interfaces; development of new theoretical frameworks and computational tools for understanding and predicting static and dynamic properties of these interfaces; mapping of chemical transformations and energy flow across scales using advanced electron microscopy and the ALS; and detailed imaging and transport studies at these complex, buried, and dynamic interfaces.

Future Directions

Dynamic Nanointerfaces: Directing Energy Flow and Chemical Transformations

Many renewable energy technologies depend critically on the efficient and reliable directional flow of charged (electrons, ions) or neutral (phonons, excitons, spin) excitations at interfaces. Additionally, chemical transformations across nanointerfaces are important for both the synthesis, nanopatterning, and function of many nanoscale materials with promising catalytic and energy storage applications. Over the next few years, we will advance our ability to chemically introduce orthogonal surface chemistries on arbitrary materials classes to enable new heteromaterial couplings. We will also advance *in situ* imaging capabilities for both hard and soft matter at various length scales and in relevant sample environments, while utilizing AFM and new approaches in advanced electron microscopy and scattering that capitalize on the recent merger with NCEM, as well as leveraging the ALS. Further, we will develop novel means to probe functional assemblies at the level of their nanoscale interfaces using microscopy, scattering, and spectroscopy to probe and validate interfacial structure under bias and illumination (described in Multimodal Nanoscale Imaging), as well as multi-scale theoretical models – from electronic structure to statistical mechanics – to guide and test hypotheses relating energy transport and chemical dynamics to changes in the size, composition, physical, or biological properties of constituent building blocks. We plan to tailor these capabilities for exploring novel functionality in environments that are out of equilibrium – e.g., conditions found in a battery, in a membrane, in a flow cell, or in a solar cell — and make them available to User communities both at the Foundry and the ALS.

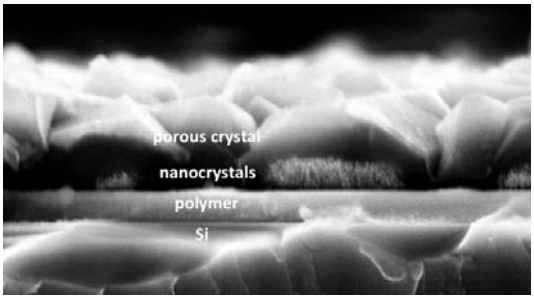


Copper-derived electrocatalysts that efficiently produce liquid ethanol fuel from carbon monoxide (CO) gas at room temperature and pressure with 10x improvement over conventional catalysts at low applied voltages [Nature, 508, 504-507 (2014)]

Functional 3D Hybrid Architectures from Designed Nanointerfaces

The Foundry commands a diverse library of building blocks (as elaborated in the Combinatorial Nanoscience theme) that includes organic small molecules and inorganic clusters, synthetic and biological polymers, porous crystals, colloidal nanocrystals, 2D atomic layers (graphene, transition metal dichalcogenides, etc.), and even living cells. We have also begun to realize complex material hierarchies from these simple building blocks. In the next 5 years, we will focus on elucidating the design rules by which desired functionality can be generated by exerting precise control over how individual components of arbitrary shape, size, and composition are assembled and ultimately interfaced. Given that assembly of matter emerges from a variety of driving forces during processing, understanding the energy landscapes and kinetics guiding both equilibrium and non-

equilibrium assembly will be vital, and allow for more reproducible, phase-pure materials to be generated. Success will require strategic investment in the development of both expertise and instrumentation to control and observe the evolution of structure across multiple length scales for a range of processing strategies on substrates with user-defined surface chemistry and topography, and as guided by the interfacial interactions between nanocomponents. We will develop capabilities that link, for the first time, computational simulations at the Foundry of mesostructured systems and their dynamics with time- and length scale-dependent X-ray scattering at the ALS and real-space evaluation of 2D and 3D structure and its evolution at NCEM using their *in situ* cells and tomography capabilities.



Controlling local chemical transformations at nanointerfaces yields complex heteromaterial architectures of porous crystals, colloidal nanocrystals, and functional polymers.

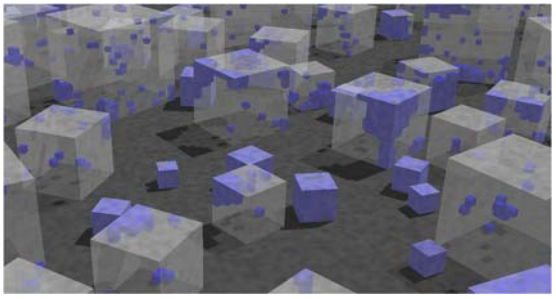
Planned Capabilities

Joint Molecular Foundry-ALS Small- and Wide-Angle Scattering Beamline

We will partner with the ALS to set up a dedicated beamline for Foundry users with advanced high-flux SAXS/WAXS capabilities for determination of nanoscale and mesoscale structure of soft and hybrid nano- and meso-structured materials. Operated by a joint Foundry-ALS scientist, the beamline would enable broad and rapid access to Foundry users in need of this essential characterization tool for complex hybrid materials.

in situ Combinatorial Electrochemical Interface Imaging and Analysis Endstation

We will develop a suite of coupled *in situ* tools capable of probing both structure and transport at individual solid/electrolyte interfaces, and across statistical ensembles of interfaces, in reactive environments. This endstation will provide a window into electrochemical dynamics impossible to probe by the standard tools of electrochemistry. Understanding how interfaces influence chemical confinement, concentration fluctuations, and transport across these complex interfaces will serve crucial needs demanded by our global network of users, and also other local synergistic DOE investments such as the Materials Genome Initiative, Joint Center for Artificial Photosynthesis (JCAP), and Joint Center for Energy Storage Research (JCESR).



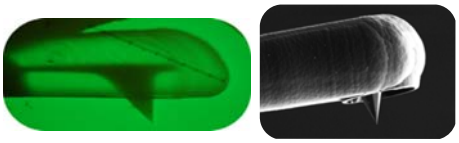
First-ever scaling laws for alloying transformations in nanocrystals developed for hydriding of Pd nanocubes. Experiments and simulations confirm that nanointerfaces create favored nucleation sites, accelerating phase transformation in nanocrystals due to dimensional confinement. [Nature Materials, 12, 905-912 (2013)]

Mesoscale Theory for Functional Nanointerfaces from Electrons to Assemblies

Our aim of understanding materials and phenomena from the scale of electrons to assemblies requires us to tackle head-on the mesoscale challenge that is the coupling of distinct physical mechanisms across a broad range of length and time scales. To do so we will bridge our current many-scale theoretical capabilities in electronic structure and

statistical mechanics – employing state-of-the-art mid-range cluster computing – towards an integrated predictive multi-scale simulation framework. We aim, for example, to discover new materials made by the self-assembly of molecules at surfaces, using coarse-grained dynamical simulations whose force-fields are systematically parameterized using quantum mechanical calculations.

3.3 Multimodal Nanoscale Imaging



Encased AFM cantilevers provide exquisite sensitivity and resolution for in-situ investigation of material interfaces [MEMS, v131, p128 (2014)]

Visualizing structure, and correlating it with properties and mechanisms at meso- and nanoscopic length, time, and energy scales under operating conditions is both an enabling tool and grand challenge for nanoscale science, as emphasized by the 2014 DOE report on the Future of Electron Scattering. Multimodal Nanoscale Imaging is therefore one of the four unifying scientific themes of the Molecular Foundry: multimodal, because we combine high-resolution electron scattering, local/scanning probes, multifunctional nanoscale reporters, and time-resolved optical methods for studying both device-like and biological systems; and nanoscale, because we must understand material properties and processes at their native length scales, most of which are intrinsically below 100 nm. This theme investigates nanoscale systems in complex cellular, solid-state, liquid, or gaseous environments, increasingly in relevant working conditions – for example, under bias, strain, or illumination – and thus has focus on development of new technologies for *in situ* techniques. Our goal is to explore the basic principles underlying functionality by correlating chemical composition, spectroscopic and mechanical properties, and nano- and mesoscale morphology, and to enable burgeoning areas of user research.

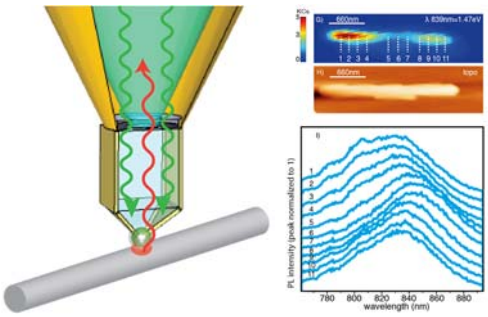
Unraveling the relationships between material composition, morphology, and function raises a number of fundamental scientific questions. For example, many of the synthesis efforts of Foundry users involve nonequilibrium systems that assemble dynamically and are responsive to changes in local environment. Understanding fundamental mechanisms of growth and evolution often require combined methods that can reveal the properties of materials in situ, explaining their growth or failure mechanisms, even when it necessitates an atomic scale understanding (provided by *in situ* electron microscopy) to couple to a macroscopic phenomenon. We aim to approach these challenges via (i) complementary multimodal characterization and (ii) development of instrumentation that can follow the dynamic evolution of parameters with the critical time resolution.

Future Directions

Imaging Function and Interactions in Buried Environments

In order to engineer revolutionary materials with new behaviors, we need first to understand the fundamental structure-property-function relationships in material and biological systems with abundant interfaces, and with interwoven heterogeneity and order on multiple length scales. For example, charge separation and migration in photovoltaic cells is dictated by the chemistry, structure, size, and electrostatics of individual semiconductor grains, and the connectivity

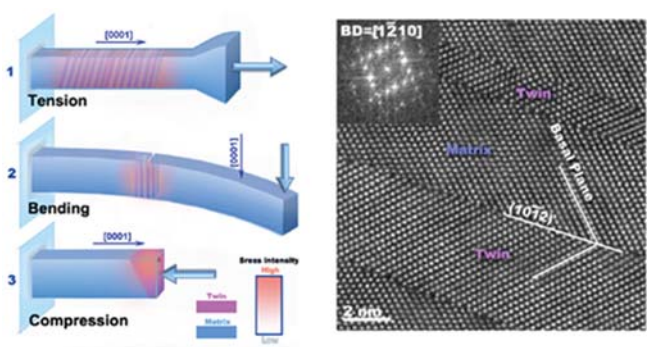
between them. Neurological function depends on real-time interactions of large sets of disparate cells in densely interconnected, widespread neural circuits. Systems engineered for catalysis, gas storage, and photoelectrochemistry also operate at complex heterogeneous interfaces between solids and gases or liquids. Currently there does not exist a complete set of imaging and localized spectroscopy techniques to enable probing of chemical reactivity at these interfaces. The goal of probing buried interfaces (e.g. well-beyond an extinction depth) also extends to the problem of nanoparticle nucleation or live cellular dynamics in liquid environments to enable imaging of individual components of nuclei or live cells with increasing speed and resolution.



Schematic of the so-called "campanile" microscopy tip (left) that reveals both shape and chemistry of a nanowire (right) [Science 338, 1317 (2012)]

Mapping of Vector Fields in Space and Time

How materials interact with applied and internal fields is critical to the design and control of functionality. For example, detailed in-situ analysis of the interactions of static and nanophotonic fields with materials and structures such as nanowires and core-shell nanoparticles could enable new technologies such as all-optical logic chips. Likewise, understanding the interaction of nanostructured defects in crystals or inhomogeneities in amorphous and heterogeneous materials relies critically on the ability to measure local strain in-situ during deformation. Electron holography is also capable of mapping electric and magnetic fields at the nanoscale of both amorphous and crystalline materials. State-of-the-art energy resolved electron microscopy permits imaging of plasmon modes in nanomaterials and integrated fiber-optics permits in-situ pulsed-laser processing experiments as well as photoluminescence experiments. The development of new multimodal and multidimensional imaging techniques involve collecting radically new quantities of data—N-dimensional spectra—and we will address head-on the management, searching, and indexing of this "big data". Experimental development efforts involving spectroscopy in the time-domain will require significant developments in theory and simulation of excited states to model realistic pumped and/or probed excited states in nanoscale systems and at interfaces.



Study of deformation twinning in pure Mg using in situ transmission electron microscope (TEM) at unprecedented spatial resolution [Nano Letters, 12, 887 (2012)]

Planned Capabilities

Nanoscale Spectroscopic Imaging of Subsurface Interfaces and Defects

We will develop minimally invasive technologies able to probe the structure, electronics, and bonding of complex buried interfaces and deep-tissue biological structures, revealing previously unobserved and emergent functionality; additionally coupling with ALS-based efforts to study the entire span of mesoscopic time and energy scales.

We will couple recent breakthroughs in photoacoustic microscopy – which combines deeply-penetrating NIR excitation and acoustic response, even within dense, highly scattering media – with cutting-edge Foundry NIR nanocrystal probes, allowing us to understand the physical properties of matter at deeply buried structures and interfaces with nanoscale or subcellular resolution.

State-of-the-art opto-acoustic methods – which combine the power of optical spectroscopies and acoustic penetration even within dense, highly scattering media – will complement current LBNL capabilities, allowing us to probe chemical, electronic and thermal properties of matter at deeply buried structures and interfaces with nanoscale/subcellular resolution.

Multimodal High-Resolution In situ Transmission Electron Microscopy

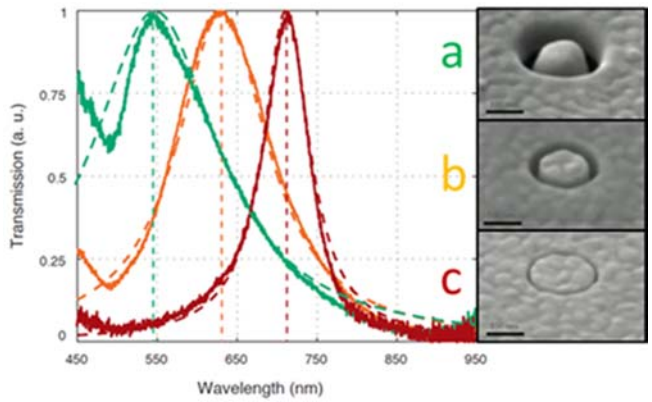
Building off of the success of the TEAM project, and current efforts in atomic resolution tomography and *in situ* microscopy, the development of a multimodal *in situ* TEM will combine imaging with optical, X-ray, and electronic spectroscopies at atomic resolution under chemical, electrical, optical, thermal, magnetic, and other stimuli. Multidimensional imaging of dynamic processes such as nucleation and transformation at the atomic scale will require dedicated electron microscopy instrumentation and technique development to increase image contrast, energy and time resolution, signal detection, sample environment, and probing capabilities. These developments will reinforce the strong position of the newly-merged NCEM facility at the forefront of electron microscopy, and strengthen the position of the Foundry for DOE goals outlined in its 2014 report on The Future of Electron Scattering.

Mapping Dynamics in Soft and Hybrid Materials

We plan to investigate exciton and photon transport using spatially independent excitation and probing with Localized Excitation Photo Current Microscopy (LEPCEM) and with combined cathodoluminesence excitation and near-field optical probing. Concomitantly, we will develop tools to watch biological, soft and hard material components as they dynamically combine and reorganize upon assembly with real-space *in situ* AFM/TEM and cryo-EM methods. Damage-free imaging is crucial here, so as not to affect assembly and dissolution pathways. We will build on our spin-polarized low-energy electron microscope (SPLEEM) expertise and instrumentation to image the distribution of charge and evolving transport pathways in soft and hybrid organic-inorganic semiconductor systems *in situ* and without damage. We will further develop near-real-time individual particle electron tomography with advanced electron detectors.

3.4 Single-Digit Nanofabrication and Assembly

In this theme, we develop a fundamental understanding of, and design principles for, the way components — atoms, molecules, nano and bulk materials — can be structured and assembled with "single-digit-nanometer" precision. Addressing this challenge requires an understanding of the mesoscale coupling of atomic-scale interactions with assembly-scale manipulation and driving protocols. This understanding is then used to create novel devices to promote breakthroughs in fundamental understanding and control in areas of technological interest such as solar energy conversion, energy storage, light based communications, data storage, and catalysis. Building on the Foundry's expertise in bottom-up (self-assembly) and top-down (lithography) nanofabrication – among the Foundry's most heavily demanded capabilities – we will advance the forefront of fabrication. Major goals include addressing the grand challenges of 3D nanofabrication and understanding and controlling far-from-equilibrium guided assembly of multi-component systems composed of biological, organic, inorganic, and hybrid materials.



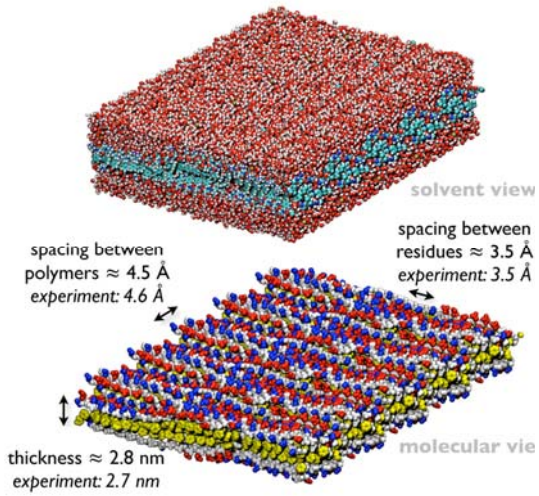
SEM images of coaxial apertures with 200 nm diameter in a 100 nm thick gold film. (a) Coax made with Ga-FIB with a nominal gap if 30 nm. (b) Coax made with a helium ion-microscope (HIM) with a nominal gap if 30 nm and (c) 8 nm. Corresponding transmission spectra, left panel. [Nano Lett., 13 (6), 2687, (2013)]

Future Directions

Precision Three-Dimensional Nanofabrication

Combining traditional tools of top-down nanofabrication with directed self-assembly, we aim to create complex functional structures that are uniquely patterned in all three spatial dimensions with single-digit nanometer control enabled by bottom-up approaches. Such 3D structures and assemblies will open up new applications for guiding the flow of energy, light, and chemical reactants and products. For instance, we will develop light-activated atomic layer deposition to build layered systems with engineered bandgaps that can direct electron flow. In addition, we will use sequential nanoimprint lithography with functionalized resist with precision alignment to create novel complex metamaterials and other light-guiding systems. We will create the highest quality scanning probes with new ion beam lithographies. Using novel scanning probes and two-photon lithography, we will explore new routes for writing 3D structures. The resultant fabricated 3D structures will, in some cases, act as both passive and active scaffolds to guide self-assembly in multiple dimensions, for instance to arrange di- and tri-block copolymers with other nano-objects.

Understanding and Controlling Heterogeneous Assembly far from Equilibrium



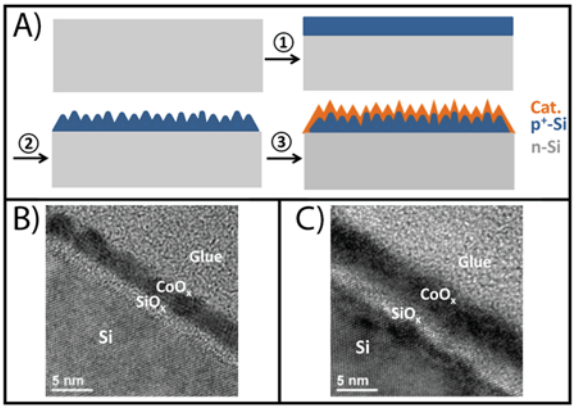
Atomistic simulations of peptoid nanosheets using the recently-developed MFToid forcefield [J. Comp. Chem., 35, 5, 360 (2014)] give nanosheet dimensions very close to those measured experimentally

While huge advances have been made in guided assembly of single component systems at or near equilibrium, forefront challenges are to understand and control the assembly of heterogeneous structures far from equilibrium. We will develop new theoretical approaches and fabrication strategies to understand how component shape, chemical functionality, chemical transformations, and the flow of energy influence the organization of materials into structures far from equilibrium. In parallel, we will structure heterogeneous devices with controlled surface chemistry, topology, and nm-scale feature sizes to replicate the virtual environments developed for simulation and theoretical modeling of assembly. Using multi-modal imaging techniques, we aim to observe assembly in real-time to validate and refine theoretical models. Fabricating assembly environments with more complexity, we can study how energy in the form of localized radiation, concentration and temperature gradients influence self-assembly. We already see potential applications of controlled far from equilibrium assembly. For instance, it is a route to overcoming roadblocks in areas such as semiconductor processing and data storage. We have an evolving relationship with industry to ensure adoption for rapid technological progress.

Planned Capabilities

Photon Initiated Atomic Layer Deposition (PI-ALD)

Atomic layer deposition (ALD) continues to attract new Foundry users because it allows for unprecedented control over material thickness and morphology. However, the complexity of its organometallic precursors, and inability to form materials beyond oxides and nitrides has limited its enormous potential application. We are investing in the development of a new layer-by-layer deposition method not constrained by wet synthetic development of new precursor chemistries, photon initiated ALD (PI-ALD). Using simple precursor materials, the desired chemistry will be initiated by gas phase light-matter interactions. Using advanced characterization techniques, it will be



User project with JCAP using the Foundry's thin film capabilities to modify and protect nanostructured silicon film devices with photocatalytically active cobalt oxide. Devices prepared at JCAP (A) with both planar (B) and nanostructured (C) interface show enhanced device performance. [J. Am. Chem. Soc. 136, 6191, (2014)]

possible to rapidly generate a library of precursor/light interactions allowing the deposition of more interesting binary materials, as well as materials with an arbitrary number of elements and arbitrary stoichiometry. We will be able to deposit a nearly endless number of materials, both known and unknown, with the sub-atomic thickness control found to be so valuable in conventional ALD.

High-Resolution 3D Lithography and Precision-Aligned Nanoimprinting

Spatial resolution in multi-source ion beam lithography and deposition go far beyond that provided by electron beam and allow the direct patterning of materials in three dimensions. In addition, the system offers secondary electron imaging capabilities with improved resolution. A two-photon lithography system, modified to incorporate Foundry-developed sub diffraction limited nanooptics, would push the resolution of the 3D features into the single-digit nanometer range. Nanoimprint capabilities provide a means to replicate over-and-over single digit nano templates created using other lithographic techniques. With alignment, nanoimprinting will be expanded to fabricate integrated devices and complex 3-D structures and probes with high volume. In combination, this suite of technologies will be used to build probes for multimodal imaging and tip-based lithography, while its advanced imaging capabilities can be used to study and screen nanomaterials as part of the Foundry's combinatorial efforts.

Simulation and Dynamic Imaging of Self-Assembly

Understanding the process of materials creation requires an ability to dynamically observe components as they combine and rearrange to produce a desired structure. To achieve these goals, real-space *in situ* AFM and TEM methods will be used, in tandem with far-from-equilibrium theories of self-assembly to guide the assembly of undriven systems that are prone to kinetic trapping (such as multicomponent mixtures), and of intrinsically nonequilibrium systems (such as those subjected to spinning and drying). Visualization tools include our multimodal imaging methods, particularly the 3D tomographic methods that build on the extraordinary performance of existing aberration-corrected electron microscopes and the gentle encased cantilevers for *in situ* high resolution imaging. We will further develop multiscale simulation tools to model and thereby infer structure across multiple length scales from time-dependent scattering measurements at the ALS. Such interpretation will allow new understanding of the dynamic "pathways" by which materials assemble.

4. Strengthening Scientific and User Resources

Above, several strategic scientific priorities were identified that will expand the productivity, efficiency, and utilization of the Molecular Foundry. In order to pursue these promising opportunities in nanoscience over the next five years, the center will seek to retain and recruit outstanding scientific, technical and administrative staff, and continue to develop a suite of state-of-the-art existing and new instrumentation.

The Foundry's four scientific themes are designed to connect current expertise and instrumentation with the needs of users. Each theme contains two distinct future directions that serve to guide the Foundry over the next five years and the capabilities required to achieve them. In the section that follows, two tables list resources – expertise and equipment – that will allow these capabilities to grow and enhance the effectiveness of Foundry research. Personnel and instrument capabilities that are of high demand by Foundry users, and are essential to existing and new research efforts, were identified for reinvestment. The tables map each resource to the

four themes, indicate if they are a new need or reinvestment, and assign a rough timeline for investment (short term=1-3 years; long term=3-5 years). Finally, organizational enhancements designed to maximize the User Program's exposure and operational efficiencies are described.

Given the resources, these lists are meant to guide our priorities, initiatives and investments in the future, but since they do not attempt to include every future capability, the lists maintain the flexibility required to evolve and react to changing needs of the larger scientific community.

4.1 Enhancement of Foundry Expertise

A major part of the Foundry's success has been the emergence of outstanding scientific staff that are seen by many in the general scientific community as the main draw to the Foundry. The maintenance of diverse, high-quality expertise among staff enables world-leading research and attracts top scientific talent as users. The enhancement of these areas of staff expertise could be addressed through new staff hires, training opportunities for existing staff, and the placement of postdocs and graduate students, and is contingent on the availability of resources in the coming years. The list below represents a combination of existing vacancies and anticipated priorities.

Expertise	Combinatorial	Interfaces	Multimodal	Single-Digit Nano	New, Short Term	New, Long Term
Staff scientist, Organic synthesis*	x	x			x	
Staff scientist, Theory*	x	x	x	x	x	
Staff scientist, Inorganic synthesis*		x	x		x	
Staff scientist, Inorganic synthesis			x			x
Technical staff, NCEM data analysis	x	x	x	x	x	
Technical staff, Multimodal Imaging			x			x
Technical staff, Nanofab/microfluidics	x			x		x
Joint project scientist, ALS SAX-WAXS	x	x		x	x	
20 postdoctoral fellows over 5 years	x	x	x	x	x	x

*Current vacancies

4.2 Enhancement of Equipment Resources

In addition to the expertise of Foundry staff and multidisciplinary training and collaboration opportunities, the Foundry offers users access to state-of-the-art instrumentation that leads to groundbreaking research. Keeping equipment current and anticipating trends in user demand is essential for the Foundry to maintain its position as a leading nanoscience center and to take advantage of the scientific opportunities within reach of Foundry scientists and users. This table identifies high-priority areas of need based on current user demand and the instruments required to achieve the goals outlined in this document.

Equipment	Combinatorial	Interfaces	Multimodal	Single-Digit Nano	Reinvestment	New, Short Term	New, Long Term
Multi-element platform Focused Ion Beam system[1]	x	x	x	x	x		x
Multi-source ion beam lithography system[2]			x	x	x		x
Mid-range high-performance compute cluster[3]	x	x	x	x	x		x
Multimodal *in situ* TEM: combine imaging with optical, X-ray, and electronic spectroscopies at atomic resolution under chemical, electrical, optical, thermal, magnetic, and other stimuli	x	x	x	x		x	x
Time-resolved nano-optical endstation		x	x			x	x
X-ray Powder Diffractometer	x	x	x			x	
Solid-state NMR	x	x	x			x	
High-throughput Experimentation Robot for Multiplexed Automation of Nanochemistry (HERMAN)	x	x		x		x	
Nanoimprinting with high-precision realignment		x	x	x		x	
ALD station for novel metal chemistries	x	x		x		x	
Scanning electrochemical microscopy endstation	x	x				x	
Joint Foundry-ALS SAXS/WAXS beamline	x	x				x	
MAD-LEEM: Dynamics of surface magnetism, damage-free imaging of soft matter, phonon-resolution spectroscopy		x	x				x
Microfluidic synthesis and characterization suite	x		x	x			x
Photo acoustic microscope for buried interfaces		x	x				x
Two-photon lithography		x	x	x			x

[1]Would replace the FEI Strata 235DB FIB that is currently used over 5000 hours every year and nearing the end of its lifecycle.
[2]Would replace the Zeiss Crossbeam 1540 EsB that is currently used over 3000 hours every year and nearing the end of its lifecycle.
[3]Would update the current clusters that run every hour of every day in support of our Theory Facility users and staff.

4.3 Enhancement of User Outreach, Engagement, and Services

In concert with enhancements to the expertise and equipment offered at the Foundry, efforts are made to continually seek to actively grow and strengthen the user community, while improving services to current and prospective users. Looking forward, the organization will focus on five priority areas of growth, detailed below.

Enhance User Community Engagement

In order to enhance their experience and meet the Foundry's user-centric mission, users should be invested stakeholders who, to a greater degree, actively participate in Foundry strategy. An important step toward this goal is to further empower the newly integrated Users Executive Committee (UEC) and ensure open communication between them, as representatives of the

larger user community, and Foundry leadership. To support the UEC, Foundry staff will be asked to amplify messages about UEC membership and elections, and encourage their users to participate. UEC messaging will also be shared during a newly established User Orientation event, a casual biweekly meeting open to all users and staff, where new users learn about the Foundry and the growing opportunities for interaction between users and staff of different facilities. Finally, efforts such as a monthly newsletter will be made to continue to engage users and other key stakeholders after they complete their work at the Foundry.

Increase the Geographic Diversity of Users

In the next five years, the Foundry will continue strive to expand access to more geographically-diverse User base. Historically, the most effective form of User outreach is peer-to-peer communication, such Foundry staff recruiting users at conferences, or existing users bringing their Foundry experience back to colleagues at their home institution. Our Proposal Review Board is a new group of strongly committed stakeholders who are now invested in and highly knowledgeable about the Foundry. As new Board members rotate onto the PRB, new members will be recruited from institutions and communities that do not yet have a strong presence at the Foundry to broaden the national exposure of the center.

A newly revamped weekly seminar series – started in May of 2014 – will also serve as a method of targeted outreach. Bringing outstanding scientists into the Foundry as seminar speakers simultaneously benefits our onsite users and provides the opportunity to introduce key researchers to Foundry capabilities and expertise. Future interactions with outside researchers will take into account user diversity to raise the awareness and engagement of non-local users.

More traditional forms of outreach will also be leveraged, most notably the pursuit of high-impact efforts such as special features within scientific journals and events. For example, a special issue of Advanced Materials that features the Molecular Foundry is being prepared for 2015.

Better Support for Industry Users

While the Molecular Foundry has a strong and growing engagement with industry (~10% of user projects, as of July 2014), it remains a priority to address evolving challenges that are unique to these users. The Foundry will also develop new means to work with industry (and other users) through Rapid Access and Partner User programs. Efforts are underway to improve outreach to industry on the Foundry website, expanding existing content to include “success stories” – case studies illustrating how other industry users have engaged with the Foundry’s many facilities – as well as best clarifying what our facilities have to offer to industry. In addition, the User Program Office will support prospective industry users by helping them build relationships with Foundry staff navigate the proposal process. Once an industry proposal is approved, the User Program Office will facilitate the user agreement process, to avoid delays in access due to unnecessary negotiations. Finally, data is being gathered to determine the outcomes of past industry user projects, with the aim of identifying performance metrics beyond publication numbers.

Enhance Leverage of the Local Environment

The Molecular Foundry will explore new ways to ensure that it capitalizes on its local scientific environment within LBNL and the Bay Area. We have recently revised and renewed our MOU with the ALS, improving coordination with the User Office to better facilitate Foundry user access to ALS beamtime through Foundry proposals; to increase the visibility of Foundry capabilities available to ALS users; and to cultivate cross-pollination of the ALS/Foundry/NERSC research communities through a joint seminar series. We are also revamping the Foundry’s Affiliate Labs program. New partnerships are being built through this program with groups such as the Zeiss-

UCSF Center for Microscopy and Correlative Imaging at the University of California, San Francisco, and the LBNL Advanced Microscopy Facility, a suite of microscopes established by the Life Sciences Division to support biosciences research.

Maximize the Impact of Research Data

We will develop shared databases and data mining strategies that best assist users in getting the most out of their Foundry-generated data. We will develop an online library of validated experimental recipes for inorganic nanoparticle synthesis through which to share the wealth of knowledge generated by our staff and users; making in-house analysis software for individual-particle electron tomography available over the internet to assist users in their data analysis; and a collaboration with LBNL's Energy Sciences Network to provide data transfer solutions for users who generate large data sets during their Foundry projects.