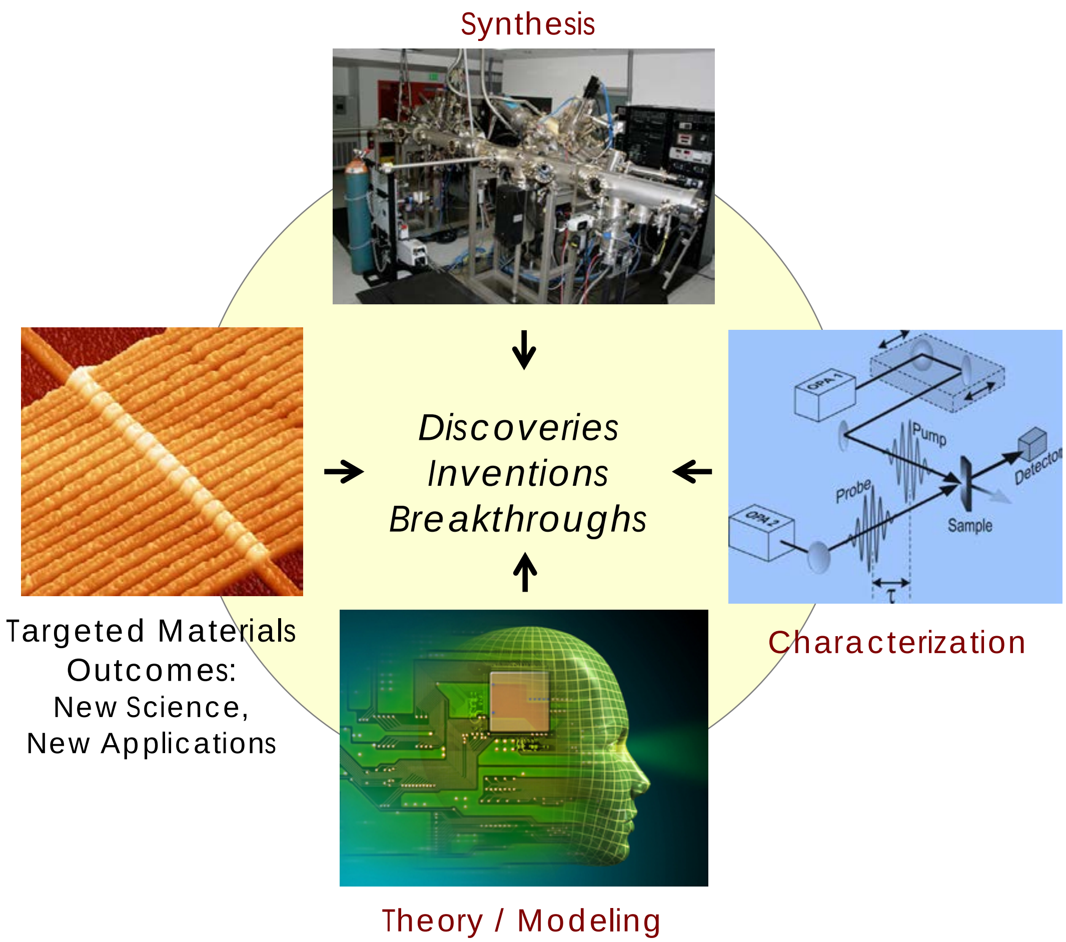
Closing the Loop



Report of the MPSAC Subcommittee on Materials Instrumentation

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National Science Foundation
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Charge Guidelines

Assuming a flat facilities budget, where should NSF invest for greatest impact on science advances (as opposed to paper production) across all materials categories, including biological materials, polymers, ceramics, metallurgy, solid state and materials chemistry, condensed matter physics and condensed matter and materials theory?

Consider existing major NSF multi-user facilities and other potential mid-scale investments, including electron microscopy, materials synthesis, crystal growth, and modeling in addition to characterization. Among these possible investments, which will produce the greatest impact on science advances?

Consider NSF investments in the context of other agency investments, such as DOE user facilities.

Executive Summary

Advances in scientific understanding of materials and phenomena are critical to society's progress, including intellectual progress to better understand the world around us, technological progress to create the next generation of innovative applications and economic progress to generate growth that raises quality of life. Scientific understanding of materials and phenomena advances by mobilizing three functional activities – synthesis, characterization, and theory/modeling of materials – toward outcomes that create new scientific knowledge or enable advances in manufacturing and new technology.

The US has fallen behind in its support of all aspects required for breakthroughs in materials science. Of the three functional activities leading to advances in materials science, synthesis has seen the least progress in the US in the last two decades. The National Academy report *Frontiers in Crystalline Matter: From Discovery to Technology* (National Research Council 2009) points out that US activities in discovery and growth of crystalline matter are significantly weaker now than they were 20 years ago. The growing areas of soft and bio-inspired materials are just beginning to explore rich new horizons of complexity and functionality that require their own set of innovative synthesis techniques. By comparison, characterization has seen remarkable growth with the advent of a host of scanning probe microscopies and spectroscopies with atomic or near-atomic resolution, ultrafast lasers and harmonic generation probing materials at femtosecond and shorter time scales, NMR at higher frequencies, higher fields and multiple colors, aberration corrected and time resolved electron microscopy, and x-ray and neutron sources and experiments with dramatically higher intensity and resolution in space, time and energy. Theory and modeling have likewise seen enormous progress, with density functional theory, quantum Monte Carlo, molecular dynamics, dynamic mean field theory, computational fluid dynamics and phase field modeling now routinely applied to molecules, clusters, and perfect and defected periodic solids; these advances are driven by scientific ingenuity and exponential increases in computational speed. This report identifies materials synthesis and discovery as the primary bottleneck in advancing the frontier of science and recommends that NSF emphasize its development.

Beyond materials synthesis and discovery, we find a second ripe opportunity to dramatically accelerate the pace of scientific discovery and innovation: tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes. The loop can be closed by greater, more frequent and more intimate communication among the scientific groups pursuing synthesis, characterization, theory/modeling and targeted materials outcomes, a basic requirement for acceleration of progress. Beyond communication, there are more profound, powerful and timely opportunities to close the loop. Characterization tools can be incorporated into the synthesis procedure so that, for example, a full phase diagram is measured as a new material is synthesized, or the intermediate steps and products in a complex synthesis process are characterized *in situ* as the process proceeds. Theory/modeling can connect with synthesis by predicting not only *what* materials to make but also *how* to make them, identifying sequences of thermodynamic, kinetic and chemical reaction steps that put atoms in the right places at the right times. There is a rich new horizon for connecting theory/modeling with characterization as well, with the simultaneous proliferation of computational speed and the rate and quantity of data production by multi-modal characterization protocols and at high intensity sources. These two exponential trends can be leveraged by combining high-speed data collection and analysis with simultaneous high-speed model calculation allowing real-time interaction of prediction and characterization. Instantaneous comparison allows immediate exposure and further investigation of the discrepancies between theory and experiment that often lead to breakthrough science. We recommend the NSF promote tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes as a high priority.

The space of worthy targeted materials outcomes is vast. Often outcomes that advance the frontiers of science and technology share similar or overlapping pathways, so that the same intellectual investment and research activities contribute to both kinds of outcomes. We emphasize three promising areas of materials research with the potential to drive new discoveries, reveal new phenomena and create new materials, without distinguishing science and technology outcomes. Each area is rich with opportunity, building on the discoveries and scientific advances of the last 15 years and ready for rapid advancement. These areas are mesoscale materials and phenomena, dynamic and far from equilibrium behavior, and interfacial phenomena. We recommend that NSF emphasize these areas of research as promising directions for high impact groundbreaking discoveries.

To implement a new emphasis on materials synthesis and discovery and on tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes in mesoscale materials and phenomena, dynamic and far from equilibrium behavior and interfacial phenomena, we recommend that NSF create a network of Materials Innovation Platforms as elaborated in the body of the report.

Major facilities play a special role in groundbreaking discoveries, offering the opportunity to use special facilities beyond the reach of ordinary research laboratories to explore new scientific horizons. We endorse the guiding principles in the Materials 2022 report (NSF Materials 2022 Subcommittee 2012) that NSF fund only major facilities that (a) have exceptional promise for groundbreaking discoveries that advance the frontier of science and (b) are not duplicated elsewhere in the scientific landscape.

We endorse the recommendation of the National Academy of Sciences report *High Magnetic Field Science and Its Application in the United States: Current Status and Future Directions* (National Research Council 2013) that NSF continue to fund the National High Magnetic Field Laboratory for its contributions to advancing the frontiers of science.

The Director of the Cornell High Energy Synchrotron Source (CHESS) presented to the subcommittee a four-stage upgrade plan bringing CHESS emittance to 2 nm and expanding the number of beamlines from six to twelve. The upgrade plan did not include detailed projections for costs and timelines to completion, nor an account of the unique science the upgrade will enable that is not duplicated by other sources now in the proposal, planning or implementation stages in the US or internationally.

The cost of upgrading existing sources and of building new sources has grown significantly since CHESS was commissioned, and is now in the range of \$0.5B – \$1 B or more. This cost is a significant fraction of the resources available for science in any country, requiring a significantly greater level of strategic planning and scientific justification for upgrades or new facilities than has been typical in the past.

We recommend that NSF ask CHESS to develop and submit a detailed plan for the cost and timeline to completion for each stage of the four-stage upgrade plan presented to the subcommittee. In addition, we recommend that NSF ask CHESS to develop and submit a detailed case for the unique science opportunities that the upgrade will enable. This unique science case should compare the upgrade to each of the other sources now in proposal, construction or implantation stages. The basic question to be answered is, "What unique science opportunities does the CHESS upgrade provide that no other source provides?" A compelling case for the uniqueness of the CHESS upgrade will be a critical factor in the ultimate decision on whether to proceed or not.

1.0 Materials Synthesis and Discovery

Synthesis and discovery of new materials are critical to scientific advances, innovative new technology and economic growth.[1] (Tomellini 2013) The pivotal impact of materials is evident even in the earliest civilizations, with the advent of pottery for storing grain and the replacement of stone tools with manufactured tools of bronze and then iron for hunting, agriculture and fighting. These materials innovations created enormous competitive advantages for the cultures that embraced them. The importance of new materials has continued unabated through history: cloth from fibers for clothing, glass for windows, papyrus and paper for writing and oil for energy are some of the landmark materials that changed society. In more recent times, Teflon and other plastics, liquid crystals, optical fibers, semiconductors, and carbon nanostructures are materials whose influence extends throughout science, technology and the economy. The pattern continues, with graphene, correlated electron materials, designer catalysts, topological insulators, meta-materials, multiferroics and many kinds of composites poised for potentially game-changing impact. Beyond discovery of new materials, the continuous improvement of materials is critical to technological and economic impact. The decades-long development of ground-breaking advances in semiconductor synthesis for ever greater purity, perfection, doping precision and miniaturization is a prime example, enabling the long reign and high impact of semiconductor electronics and Moore's Law on digital technology.

1.1 The US is currently well behind the global leaders in synthesis and discovery of hard materials. Of the Nobel Laureates honored by nine Nobel Prizes given for hard materials discovery since 1985, 13 laureates did their work outside the US and 10 did their work in large industrial laboratories in the US. There were only three US laureates from either academia or national labs and all of these were theorists. The US gap in synthesis and discovery of new materials has been recognized and documented, for example in the National Academy Report *Frontiers in Crystalline Matter: from Discovery to Technology,*[2] (National Research Council 2009) which points out that US activities in discovery and growth of crystalline matter are significantly weaker now than they were 20 years ago. The industrial labs that sponsored the great materials revolutions of the last century, such as Bell Labs and IBM Research are no longer supporting materials discovery and crystal growth, a significant loss to innovative synthesis of crystalline materials in the US. The dramatic rise of nanoscience and the synthesis of nanoscale structures with dimensions smaller than 100 nm further slowed advances in bulk crystalline materials synthesis. Other countries in Europe and Asia, however, have recognized the importance of new crystalline materials and are significantly building their crystalline synthesis capabilities, in sharp contrast to the decline in crystalline synthesis in the US.

1.2 Beyond hard materials, the growing areas of soft and bio-inspired materials offer rich opportunities for new discovery and innovation from basic science to applications. The dominant physical behavior of soft materials occurs on energy scales comparable to room temperature where quantum effects are typically unimportant. Soft matter often self assembles into structures intermediate between the atomic or molecular scale and the macroscopic material scale, such as turbulent vortices in a flowing fluid, the grains in a granular material or the bubbles in a foam; these emergent structures dramatically influence macroscopic behavior, often in surprising and unpredictable ways.[3,4] (Demortiere 2014, Liu 2010) Soft matter with intermediate scale architectures spanning liquids, colloids, polymers, foams, gels and granular materials offers many opportunities for emergent behavior and new functionalities arising from interacting mechanical, chemical, electronic and ionic degrees of freedom. In the area of synthetic polymers, the current worldwide annual production is about $400B. There is a huge area of opportunity in the development of sustainable materials, especially polymers, that are biodegradable and that do not damage the environment.

1.3 Bio-inspired materials exhibit remarkable behavior, such as the crack- and corrosion-resistant mesostructured materials in bone, teeth and sea shells[5,6,7] (Radha 2010, Olson 2012, Cheng 2014), self-healing of acute or gradual damage and degradation[8] (Blaiszik 2010), reconfigurability in response to environmental cues[9,10] (Balazs 2014, Studart 2014), and magnetic self-assembly of pneumatically controlled robots from soft and hard materials.[11] (Kwok 2014). Although nature has devised clever synthesis routes for these remarkable properties and functionalities, we are still in our infancy in understanding and exploiting them. Techniques for synthesizing these new classes of soft and bio-inspired materials with targeted functionality are a rich, active and still relatively unexplored horizon.

1.4 In contrast to synthesis, new techniques for characterization have advanced dramatically over the last two decades.[12] (Robertson 2011) Following the advent of scanning tunneling microscopy with atomic resolution, a host of scanning probes including atomic force microscopy, magnetic force microscopy and at least two dozen others have made atomic and molecular resolution commonplace in even the smallest research laboratories.[13] (Lucas 2012) Many of these scanning probes allow spectroscopies of excited states with nanoscale or atomic resolution, a revolutionary development for nanoscience. Ultrafast lasers allow probing materials at femtosecond and shorter time scales, and harmonic generation techniques continually push the time resolution boundaries.[14,15] (Ranitovic 2014, Sansone 2011) NMR has moved to higher frequencies, higher field and multiple colors, allowing unprecedented resolution and sensitivity for probing local atomic environments under *in situ* conditions.[16] (Blanc 2013) Aberration correction has extended the reach of transmission electron microscopy (TEM), and cryo-microscopy and tomography now bring nanometer resolution to life-relevant molecules. In addition, time resolved electron microscopy is probing ever-smaller timescales by several techniques.[17] (Flannigan 2012) Large user facilities for x-rays[18] (McNeil 2010) and neutrons[19] (Ehlers 2011) continuously push the boundaries of intensity and coherence, and of spatial, temporal and energy resolution for a host of innovative characterization techniques.

1.5 Like characterization, theory and modeling have seen dramatic advancements in the last two decades. Density functional theory is now routinely applied to small molecules, polymers, clusters and supramolecular assemblies to predict structures and equilibrium properties.[20,21] (van Mourik 2014, Walsh 2014) Techniques for predicting intermediate states and energy barriers for complex chemical reaction sequences are in place. Molecular dynamics reveals structure and dynamics for a wealth of materials by tracking millions of atoms, and continuum models such as computational fluid dynamics and phenomenological Ginzburg-Landau theory treat macroscopic behavior from micron to stellar and galactic dimensions.[22] (Kirchner 2012) These dramatic advances are driven not only by scientific creativity and inventiveness, but also by the exponential increase in computing power, which has been growing at approximately three orders of magnitude per decade. The enormous value of predicting the behavior of increasingly complex and functional materials before they are synthesized, and of interpreting the often unexpected behavior of complex materials systems once they are created are powerful driving forces for advancing theory and modeling. The emergence of genomic approaches, where the properties of thousands or tens of thousands of materials can be modeled, captured in searchable databases and analyzed for comparative trends promises not only to qualitatively advance our understanding of materials but also to accelerate the pace of discovery and innovation in selecting materials for targeted outcomes.[23] (Jain 2013)

1.6 Nanoscale Science and Technology

One area of materials science and engineering, nanoscale science and technology, has experienced dramatic focus and exerted remarkable impact in the last 15 years. The community has recognized the central role of nanoscience in controlling fundamental materials behavior at the most basic atomic and molecular levels; nanoscale properties ultimately combine at the meso and macroscale to produce the functional behavior we use daily in technologies from laser scanning to photovoltaic solar cells to liquid crystal displays to lithium-ion batteries. The intellectual resources, concerted effort and strategic coordination across US federal agencies and materials communities originally spearheaded by NSF into a National Nanotechnology Initiative encouraged many similar international efforts in nanoscale science and technology.[24] (National Research Council 2013)

2.0 Closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes

An opportunity for the US to dramatically enhance materials synthesis with potential for impact as large as that of the National Nanotechnology Initiative is now ripe for singular development and growth: this initiative would tightly close the loop among synthesis, characterization, theory/modeling and targeted scientific or technological outcomes (Figure 1). Traditional synthesis and discovery of new materials, carried out as a stand-alone activity, can be a slow and serendipitous process, guided by experience, intuition and guesswork. Following synthesis, a new material takes time to characterize, often by a second group of scientists with different skill sets, in order to reveal its properties and shortcomings for possible applications and to discover new phenomena it may harbor. The contribution of theory and modeling likewise is often remote from synthesis and characterization, carried out by a third group of experts who may not fully appreciate the opportunities and limitations of synthesis and characterization or grasp the vision of the targeted materials outcome for science or technology. The remarkable advances in characterization, theory/modeling and the sophistication of targeted outcomes in the last two decades require increasing specialization and often raise artificial boundaries separating these groups of experts. Integrating characterization, theory/modeling and targeted materials outcomes with synthesis and with each other will accelerate the pace of breakthroughs for science and technology. Indeed the successful discovery of materials in the great US industrial research labs of 20 years ago co-located those doing theory, synthesis and characterization in a problem-rich atmosphere of manufacturing needs. We have the opportunity to recreate such a rich, vibrant and innovative environment focused on today's forefront materials challenges and utilizing today's powerful tools.

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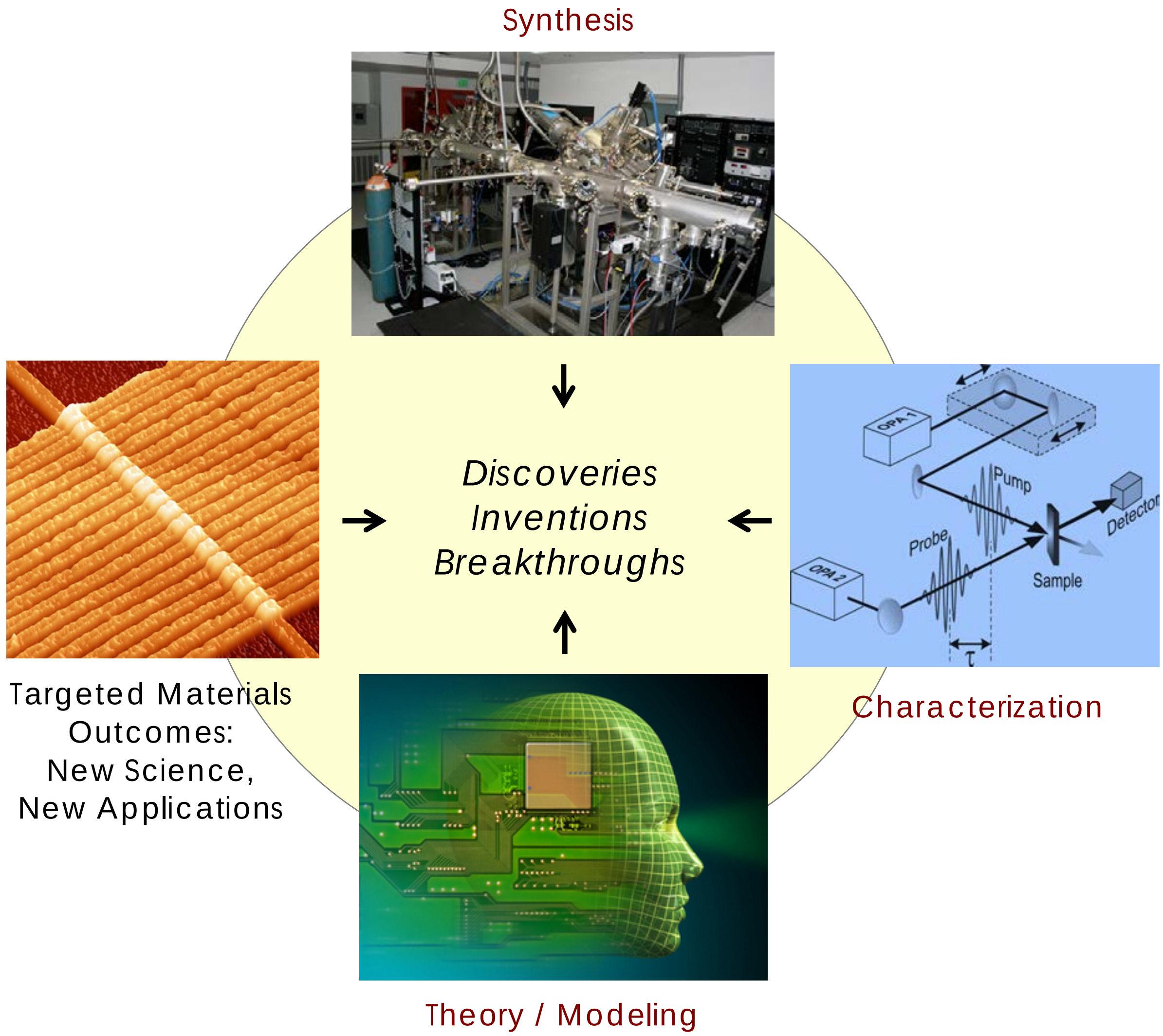

Figure 1. Tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes accelerates the pace of discovery and innovation in science and technology. *Source Charles Ahn, Yale University*

2.1 Closing the loop of synthesis, characterization, theory/modeling, and targeted materials outcomes changes the ways these four activities interact with each other. Synthesis typically involves many steps controlling temperature, composition and pressure in a given sequence, often as part of a serial deposition process, a directed self-assembly process or a chemical reaction sequence that takes precursors to final products. Characterization can be integrated with synthesis at each of these steps by monitoring structure, composition, phase equilibria and spectroscopic properties to reveal if the desired intermediate outcome has been achieved. This scale of multimodal characterization is not typically part of the synthesis process. It requires special skills and expertise not found in synthesis experts, as well as a tight linkage between synthesis and characterization teams to implement and operate multiple tools on the same apparatus. Linking synthesis and characterization in this way will significantly accelerate discovery and innovation of new materials.

2.2 Like characterization, theory and modeling can play new roles in synthesis. Theory and modeling traditionally guide synthesis by predicting what materials to synthesize, for example to produce a new high temperature superconductor, carbon nanostructure, liquid crystal, or soft material. But theory and modeling can guide not only *what* materials to make, but also *how* to make them. Synthesizing a targeted material requires putting atoms and molecules in specific positions relative to their neighbors, a task that often requires exploiting sequences of thermodynamic states or kinetic barriers or chemical synthesis steps that position atoms in the right places at the right times. Theory and modeling can discover and invent preparation protocols that accelerate the synthesis of targeted materials.

2.3 Theory and modeling can connect with characterization in new ways as well. As characterization becomes more sophisticated it produces data at rates and in quantities that are unprecedented. Multimodal experiments that track several properties simultaneously exacerbate the problem. The challenge is especially large at x-ray and neutron user facilities with exponentially increasing intensity capable of mapping diffraction, spectroscopy and imaging at ever increasing levels of detail. Theory and modeling are typically applied to these massive data sets post-characterization to interpret the features observed, understand the characterized phenomena and identify the remaining characterization needs. Computer hardware, however, is now fast enough to allow massive data sets to be analyzed as they are taken in real time. Models can be run using the data as they arrive, so that interpretation can appear to be instantaneous, fast enough to guide the strategic selection of the next set of experimental parameters to be explored such as energy, pressure, electromagnetic fields, or position in momentum space. This kind of real-time coupling of characterization and theory/modeling will dramatically enhance the efficiency of data taking, reduce the need for return trips to large facilities, and accelerate the pace of discovery and innovation.

2.4 The final element in the loop is a targeted materials outcome. Traditional synthesis can be done as its own discovery process – extending the boundaries of synthesis techniques and discovering new materials for pure scientific value, creating a library of knowledge that will serve future generations of innovators. This approach to synthesis has a long and distinguished record of outstanding accomplishments. The targeted materials outcome brings a new feature to synthesis: intentional design. The targeted outcome might be a scientific objective, such as finding a new class of correlated electron materials that displays high temperature superconductivity, multiferroic behavior, topological insulation or catalytic activity, a new soft material with reconfigurable morphology, or it could be a technological outcome such as finding a material to replace silicon in digital electronics, a self-healing polymer with specific electronic properties, or a higher performing and lower cost metal anode for next generation batteries. Such targeted outcomes serve science by focusing attention on specific, timely and promising materials challenges; they serve technology and the economy by creating materials that enable new functionality and thus new technologies, or that enhance performance or lower cost. Intentional design and synthesis of materials to a targeted outcome links synthesis to vibrant directions in science and technology, creates multidisciplinary teams that amplify value and accelerate progress, and exploits the advances in characterization and modeling with the potential to change the materials landscape.

3.0 Promising opportunities in synthesis

3.1 Synthesis of single layer hard materials has moved rapidly to the frontier, led by the stability, synthesis, and remarkable electronic and structural properties of graphene.[25,26] (Butler 2013, Zhuang 2014) In single layer form, graphene is extraordinary for its mechanical strength, electronic and thermal conductivity, and its unusual band structure with tunable linear dispersion at Dirac points. Graphene opens a new horizon of Fermi-Dirac electronic behavior including anomalous room temperature quantum Hall effects, and its single layer nature allows its properties to be extensively tuned by adjacent substrates and overlayers. We are now realizing that other single layer materials beyond graphene are ripe candidates for similar remarkable behavior, including layered metal dichalcogenides such as MoS_2[27], (Lin 2014) hexagonal BN, Zintl phases such as $CaGe_2$ and $CaSe_2$, metal carbides such as $Ti_3C_2\,(OH)_2$, and ReN_2. Single layer materials can be synthesized by a host of techniques beyond mechanical exfoliation ("Scotch tape") used for graphene, such as surface growth of conventionally non-layered materials, solution exfoliation of naturally layered van der Waals solids, and vapor deposition by a variety of techniques including chemical vapor deposition, molecular beam epitaxy and atomic layer deposition.[28,29] (Nepal 2013, Huang 2013) The realization that many materials classes and compositions are stable in single- or few-layered formats opens ripe unexplored directions for two-dimensional materials and their synthesis with the potential to advance the frontier of science and create novel applications such as field effect transistors, spintronics, "Diractronics," (exploiting linear electronic dispersion), thermoelectrics and topological insulators.

3.2 Complexity offers a second ripe direction for both soft and hard materials synthesis. The best understood materials are the simplest, where structure, composition and purity can be controlled reliably to produce targeted science or technology outcomes. Increased complexity, however, is a basic requirement for increased functionality, as amply demonstrated by biological materials capable of, for example, splitting water and carbon dioxide to synthesize fuel in the form of sugar, a feat still beyond the reach of human engineering. We have begun to explore the intimate connections between complexity and functionality, with techniques such as directed self-assembly of block copolymers and of colloidal anisotropic nanocrystals, producing a host of complex three-dimensional structures.[30,31,32] (Hu 2014, Zhang 2014, Miszta 2011) We are much less effective, however, in imparting functionality to these increasingly complex structures. Nature achieves functionality through complexity by a form of high throughput combinatorial synthesis: trying many complex atomic and molecular combinations through random mutation and filtering the outcomes for functionality by natural selection. The successful outcomes of this grand evolutionary synthesis experiment inform our materials synthesis efforts in two ways: as an existence proof for specific materials with unusual properties of interest to science or technology, such as sea shells with their high strength, corrosion and crack resistant architecture, and by demonstrating that specific functionalities can be realized such as photosynthesis using sunlight to reformulate water and carbon dioxide to fuel. The biological materials and functionalities we find in nature provide models for devising artificial bio-inspired counterparts. The methods of biological synthesis - bottom up assembly of simple components into functional hierarchical architectures - provide powerful alternatives to conventional human manufacturing, and nature's re-use of biological materials at the end of life expresses a key principle for sustainable technologies.[33] (Kushner 2011)

3.3 High throughput and combinatorial synthesis offer a solution to the complexity challenge, especially when coupled to high throughput simulation by materials genome approaches. Certain classes of complex materials can be explored by systematic variation of composition and structure, for example catalysts for targeted reactions, electrodes and electrolytes for beyond lithium-ion batteries, and multifunctional materials with contra-indicated properties such as transparent conductors. These opportunities are promising areas for high throughput synthesis.[34,35,36,37,38] (Xiang 2014, Goll 2014, Potyrailo 2011, Mulet 2013, Reinsch 2013) Inkjet printing and microfluidic approaches that allow rapid automated synthesis of thousands of small samples while systematically varying composition and processing conditions over wide ranges are attractive platforms for high throughput synthesis.[39,40,41] (Liu 2012, Katz 2009, Carbonell 2013) These approaches enable strategic exploration of libraries of materials of much greater number, complexity and functionality than traditional one-by-one analysis.

3.4 Over the last 15 years, we have seen tremendous advances in synthesizing, characterizing and understanding nanoscale materials where quantum mechanics, structural perfection and interactions among relatively few modular units dominate the science. Mesoscale materials take nanomaterials to the next level, where collective behavior, composites of nanoscale units, heterogeneity, interacting degrees of freedom, defects and statistical variation become dominant.[42,43,44] (Basic Energy Sciences Advisory Committee 2012, Crabtree 2012, Zhou 2012)

3.5 Synthesizing such mesoscale materials requires new synthesis techniques that control mesoscale structures. Mesoporous templating in bulk materials with random open structures such as zeolites and silica or in artificial periodic structures such as metal organic frameworks illustrates the possibilities.[45] (Shi 2011) Nanocrystal arrays made of nanoscale crystals with dimensions of order 1-20 nm and assembled into ordered superstructures of linear, planar or three-dimensional character offer rich new horizons for next-generation mesostructured materials.[46,47] (Choi 2012, Talapin 2010) The constituent nanocrystals in these arrays can be pure elements, binary or higher level compounds or core-shell particles, and the superstructures can have periodic or quasicrystalline order. In granular materials, where each grain is separated from its neighbors by a tunneling barrier, a grain boundary, a domain wall or a composition boundary, the mesoscale electronic structure can be controlled independently of the underlying nanoscale structure, allowing tuning of macroscale behavior over a wide range with often surprising results.[48] (Beloborodov 2007) Many soft and biological materials are textured, where the mesoscale orientation varies slowly rather than abruptly across boundaries; these slow variations in crystal orientation are critical for controlling macroscopic properties such as the mechanical strength of mollusk shells.[49] (Gilbert 2011) Additive manufacturing, where rapid and local laser heating of powders replaces traditional furnace heating protocols, opens new challenges and opportunities for synthesis of mesoscale mechanical and electronic textures.[50] (Gu 2012) Biomaterials, such as muscle fibers or hard skeletal structures, are generally built of many layers of similar hierarchies from cells or nano-sized particles forming self assembled structures that are themselves arrayed in mesostructures.[51] (Matson 2012) New synthesis routes to create these nanocrystal arrays, control textures and granular structures and allow designing mesostructures for targeted materials outcomes is a fascinating challenge and opportunity.

3.6 Many fascinating and potentially groundbreaking materials contain toxic components, such as arsenic in the iron-based superconductors (Ba-K)Fe_2As_2 or the semiconductor GaAs or

Cd in CdTe solar cells. These toxic components limit interest in widespread deployment of the final scientific or technological materials and require extra safety precautions in the laboratory for dealing with the nominally toxic elements. In many cases the final materials are much less harmful than the constituents because the toxic components are locked in stable chemical compounds. Safety concerns for final materials with potentially toxic components should be thoroughly researched and documented, and synthesis laboratories should be equipped to handle them so that the advances these materials offer to science and technology are not lost.

3.7 Materials synthesis and discovery is underappreciated by the funding agencies, the research community and the general public. NSF, the other funding agencies and the community can raise the prestige of the field by invigorating, celebrating, and awarding prizes to materials synthesis and discovery innovators and research teams. The Gordon and Betty Moore Foundation has recently recognized the need for building the community of quantum materials synthesis in the US.[52] (Gordon and Betty Moore Foundation 2014) This program can be a model and inspiration for other institutions and funding agencies to launch similar programs.

4.0 ***Promising Opportunities in Characterization***

Characterization has made enormous strides over the last two decades in determining the static structure of matter with ever increasing resolution. The next frontier is dynamics, which is ripe with opportunities to observe, understand and ultimately control the non-equilibrium interactions among atoms, molecules and functional units that drive chemical reactions, energy conversion, materials synthesis and innovative manufacturing. Time resolved, *in situ* characterization tools that capture the dynamics of physical, chemical and biological processes involving materials at length scales ranging from atomic and molecular dimensions to microns and at time scales from pico- and femtoseconds to seconds and days are now within reach and have enormous potential for innovation in next generation science and technology.

4.1 Atomic Resolution with Scanning Probes and Transmission Electron Microscopy

Scanning probe techniques and state-of-the-art aberration corrected electron microscopies are two fundamental characterization tools now answering some of the most challenging questions in materials science.[53] (Haight 2012) These probes operate at the atomic scale and provide key surface and bulk information on structural and elemental properties. Aberration corrected electron microscopies have achieved sub-Angstrom spatial resolution allowing for detailed imaging of atomic locations, point defects and grain boundaries.[54] (Batson 2002) Time-lapsed movies reveal new information on the motions of individual atoms under electron beam excitation and at elevated temperatures. Electron energy loss spectroscopy provides detailed maps of local electronic structure. Coupled with energy dispersive x-ray analysis, elemental mapping at this length scale provides information at an unprecedented level. Aberration correction has reached all levels of modern electron microscopy including transmission (TEM) and scanning transmission electron microscopy (STEM) and more recently low energy electron microscopy (LEEM) to map surface structure with nanometer spatial resolution. Electron cryo-tomography has enabled the structure determination of biologically relevant single molecules at angstrom resolution.[55] (Briegel 2014) Modern scanning probe microscopy (SPM) and its wide range of variants provide atomic scale spatial and electronic maps of surfaces, grain boundaries, step edges and more. Recent advances have added to the original scanning tunneling microscope; these include force, kelvin probe and cross-sectional microscopy providing a suite of capabilities.

These powerful techniques will be essential to any effort to study materials, both existing and yet to be discovered at an ever more detailed level.

4.2 Multimodal measurements

The increasing sophistication of hard, soft and bioinspired materials requires multimodal characterization to monitor the important length, time and energy scales that control complex behavior. Understanding catalysis requires monitoring linked chemical reactions at different active sites, characterizing reconfigurability and self-healing involves monitoring interacting mechanical, chemical, optical, electronic and ionic degrees of freedom, and directed assembly of a complex system requires monitoring the conditions of all the component parts. Designing and implementing multimodal characterization requires cooperation among specialty teams spanning, for example, mesoscale structure, transport of charge, spin and energy, and chemical transformation. Growing multimodal characterization capability will be necessary for understanding the complex materials of the future.

4.3 Dynamic imaging/tomography at micron and longer spatial scales and second and longer times scales

Understanding, predicting, and measuring the evolution of multiphase multicomponent materials is at the core of materials processing. Without an intimate understanding of the nonequilibrium processes controlling the evolution of multiphase structure, it is not possible to control the properties of standard materials or design the new materials that can address our most pressing problems. The evolution of multiphase materials, from nano to micron length scales, has typically been characterized using “quench and look” experiments, wherein an experiment is performed *ex situ*, often via two-dimensional sectioning to expose the interior of a bulk material sample. Laser and synchrotron sources promise to break this classical paradigm through the nondestructive *in-situ* characterization of the evolution of a material’s nano or microstructure on timescales from a fraction of a second to an hour.[56] (Alexandrov 2014) These experiments employ tomographic techniques to characterize the three-dimensional multiphase structure of material, and through the brightness of synchrotron radiation the reconstructions can be acquired on timescales that are short compared to the micro or nano-structure evolution process. Thus the temporal evolution of a multiphase material can be followed in real time in three dimensions. The materials that can be addressed are broad, from biomaterials to polycrystalline materials used in jet engine or wind turbine blades to the crystalline nanomaterials found in batteries. These “4D” experiments provide the long-sought insights into the manner in which the micro- and nano-structures of materials develop.

4.4 Characterization opportunities at high intensity light sources

A new linac-based, seeded, free electron laser, Linac Coherent Light Source–II (LCLS-II), will be built at SLAC over the next 5-6 years that will produce extremely bright ultra-short medium-energy x-ray pulses spanning the energy range of 0.2 keV to at least 5 keV using superconducting undulators with MHz repetition rates and transform-limited spatial and temporal coherence. This new light source will be ideal for studies of molecular-scale dynamics as well as novel “diffract before destroy” structural determination experiments important to a myriad of molecular systems. In addition, the Advanced Photon Source (APS) at Argonne will be upgraded to a diffraction-limited light source capable of producing extremely bright x-rays that will provide unprecedented spatial resolution in x-ray diffraction studies of extremely small crystals and thin films. The new LCLS-II and the upgraded APS, coupled with the new National Synchrotron Light Source II (NSLS-II) will enable a host of time resolved, *in situ* characterization techniques on time scales from sub-femtosecond to minutes or hours. Proposals for upgrades to the Cornell High Energy Synchrotron Source (CHESS) (see Appendix) would enable high brightness and low emittance in the hard x-ray regime above 30 KeV, an energy range of increasing importance in materials science. These advances promise to give users the ability to do imaging, diffraction and inelastic hard x-ray scattering, nuclear scattering and resonant soft x-ray scattering of materials.

4.5 These new or upgraded light sources will allow transformative new classes of materials science, chemistry, and solid-state physics experiments, including dynamical studies of phase transitions, the mechanistic pathways and kinetics of chemical reactions, the mesoscale behavior of aggregates of particles, the behavior of fluids in nanoscale pores, transformations of environmentally relevant inorganic and organic toxins into less harmful forms, and the controlled fracturing and enhanced fluid flow in subsurface rocks such as tight oil and gas shales stimulated by fracking, just to name a few applications.

4.6 Tabletop x-ray sources

Since the arrival of synchrotrons in the 1960s the peak brightness of light sources has increased by almost 13 orders of magnitude. Completion of several x-ray free electron lasers (FELs) will lead to further increases in the beam brightness. The underlying technology for these light sources is the radio frequency-based electron accelerator; the size and the cost of which grows dramatically as the 4th generation light sources head towards fully coherent x-rays. The needs of the user community meanwhile continue to diversify in terms of photon energy, pulse length and angular spread. While some users are satisfied with relatively long exposure times, others require a single shot exposure and short pulse duration. It is therefore worth scanning the R&D horizon for emerging x-ray technologies whose physics has been demonstrated and whose utility for practical or scientific applications has been shown. Of particular interest are those technologies that might lead to less expensive and compact mid-scale radiation sources with extended spectral range, reduced pulse width to the attosecond regime and peak brightness that is comparable to the existing 3rd generation light sources.

4.7 The new technologies that fall in the mid-scale category are: Laser-plasma WakeField Accelerator (LWFA)-based betatron and inverse Compton scattering (ICS) sources, RF linear accelerators coupled to a ring laser resonators that produce ICS photons, plasma-based extreme ultra violet (EUV) lasers, inverse free electron laser (IFEL) and or LWFA based x-FEL and finally a truly miniature optical accelerating structure coupled to an ultra short period undulator-all based on nanotechnology. Of these the LWFA-based betatron, ICS sources and plasma-based EUV lasers have been demonstrated while a LINAC-based ICS source is being commercially produced. The other technologies still await scientific demonstration.[57,58,59,60,61,62,63,64] (Basic Energy Sciences 2010, Assoufid 2013, Najmudin 2014, Krushelnick 2010, Duris 2012, Maier 2012, Yabashi 2013, Powers 2013)

4.8 The betatron radiation source gives sub-100 mrad divergence, broadband, spatially coherent but longitudinally incoherent photons with characteristic energies in the 10-80 kV range with peak brightness B_{peak} of 10^{21} photons/s/mm^2/mrad^2 (0.1% bandwidth). The current lasers in principle are capable of driving such a light source at up to 10 Hz but their commercial or scientific applicability will require the development of 30 TW class lasers operating at >1 kHz. The situation is similar for an LWFA-based ICS source. This source is capable of producing highly directional photons in the 100 KV to few MV range with B_{peak} of 10^{19} photons/s/mm^2/mrad^2 (0.1% bandwidth). Both LWFA-based betatron and ICS sources produce few fs duration x-ray pulses making them ideal as probes for ultra-fast physical and chemical processes. While single-shot, such a source may prove to be useful for diagnosing extremely high-energy density targets such as a compressed pellet in inertial confinement fusion. Their wider application in nuclear physics and homeland security will be contingent upon increasing the repetition rate of the sources.

4.9 The practical realization of these mid-scale and in some instances extremely compact novel radiation sources will require a concerted effort on the parts of both the scientific and engineering community and the funding agencies for a sustained period of about a decade. Some of these technologies are at the stage where a mid-scale instrumentation development grant from NSF would have a large impact. Many of these ideas require the development of high repetition rate high-peak power lasers as mentioned above. Following sufficient scientific development the technology can be transferred to industry to make one or more of these ideas a reality.

5.0 ***Promising Opportunities in Theory/modeling***

Theory/modeling is rapidly advancing along two frontiers: the “deep frontier” of innovative new computational approaches describing ever more subtle static and dynamic behavior dependent on the interaction of many degrees of freedom, and the “broad frontier” of surveys of simpler behavior such as structure, stability, mechanical and electronic properties across thousands or tens of thousands of materials using established computational approaches, often called materials genome methods. Advances of the “deep frontier” bring the predictive power of simulation to increasingly delicate and complex behavior, a prerequisite for designing greater functionality into materials for targeted scientific or technological outcomes. Genomic advances of the “broad frontier” dramatically extend the reach of simulation to large materials classes, organize the behavior of materials into rapidly searchable databases, and identify trends in materials properties that are central to designing to targeted outcomes. Aided by the continuing exponential advances of computational power, these two directions promise vibrant, exciting and groundbreaking advances in materials simulation.

In addition to the exciting advances of the “deep” and “broad” frontiers, theory and modeling have other opportunities to advance next generation materials development.

5.1 *Real-time Collaboration of Theory and Experiment*

Fresh paradigms are emerging that enrich the close interaction of theory and experiment, a critical driver of the scientific frontier. Exponential advances in computational speed and the intensity of x-ray, electron and neutron sources are dramatically shortening prediction and measurement times, enabling critical comparisons of theory and experiment to be made in minutes or seconds. Real-time discovery of unexpected behavior and immediate response to explore them further significantly accelerates the convergence of theory and experiment. For *in-situ* and *in-operando* experiments, real-time response is even more valuable, allowing theory and experiment to follow and adapt to unexpected dynamic outcomes, enabling new avenues of experimentation and theoretical interpretation to be pursued immediately. In addition, simulations can be used to model the raw data of the experiment, a so-called forward model. In this case, the simulations employ models of the beam characteristics and the detector, as well as a simulation of the processes under consideration. Thus, the comparison is made between the predicted and measured signals rather than inferring a process from the experimental data alone. Such approaches yield tests of simulations with unprecedented fidelity, since the conditions under which the data are acquired are included in the simulations.

5.2 Achieving the new paradigm of real-time comparison of theory and experiment requires installing high-speed data transmission from experimental facilities to computers capable of rapidly analyzing the data and performing theoretical simulations in seconds or minutes. The value and need for this capability is clear, but a strategic vision has not yet been developed. Early thinking emphasizes high performance data collection and analysis; the larger vision of real-time comparison of theory and experiment is a ripe and promising new opportunity that is now within reach.[65,66,67,68] (Hexemer 2014, Bauer 2012, Qin 2010, Sarje 2014)

5.3 Experimental genomic databases

The ability to design materials for a given application requires databases of materials properties including phase relations in multicomponent materials, structure and stability of compounds, and the transport properties as a function of composition. Creating these databases requires the ability to rapidly survey large swaths of composition, temperature, pressure, electric- or magnetic-field space. Rapid data acquisition combined with real time analysis by theory and modeling is ideally suited to provide the high throughput characterization needed to populate these databases. For example, by co-sputtering three elements and then heating to a temperature allowing interdiffusion, one experiment will produce the entire isothermal section of a ternary phase diagram. Techniques such as x-ray or electron diffraction and spectroscopy can then be used to determine the phases present, their crystal structures, and their compositions. Moreover, if these experiments are performed in-situ, such experiments can provide essential information on the temporal evolution of these multicomponent samples, thus providing information on, for example, the kinetics of compound formation. These results can then be used to populate the databases that are needed to design new materials.

5.4 Dedicated medium scale, ultrahigh performance computational system for materials development and discovery

Access to high performance computing facilities over high-speed data lines is often difficult due to limited computational time and cost. This restricted access to computing is often the limiting factor in tightly closing the loop of theory, synthesis, characterization and targeted outcomes. The ultimate solution may be high performance cloud computing with high bandwidth and massive data sets, an appealing vision that may not be widely available for a decade or more. A near term alternative is the development of smaller scale, ultrahigh performance computational systems that are optimized for and dedicated to materials development and discovery. Considerations that might be incorporated into the hardware of such an optimized computational system include raw speed, machine architectures tailored to the task at hand, ultrahigh speed data transfer rates required for parallel computation, high memory density and scalability. As an indication of the scale, calculations currently cost ~$1000/teraflop ($10^{12}$flops). Architectures involving multicore processors coupled with graphical processor units (GPUs), originally designed for high speed display graphics, provide a scalable, extremely high performance platform that can be optimized for materials calculations. For example, a 10 teraflop computer with several terabytes of connected memory and read+write rates of >200 Gigabytes/s can be imagined in the cost range <$50K allowing for future scale up as resources become available.[69] (Advanced Scientific Computing Advisory Committee 2010) Such a system, designed in parallel with and optimized for multiscale multiphysics codes would be capable of supporting high-speed calculations on multi-elemental, complex materials. These calculations, coupled with state of the art materials synthesis and characterization facilities would dramatically increase the rate of materials discovery with targeted functional capabilities.

6.0 ***Promising Targeted Materials Outcomes***

6.1 Targeted outcomes for science

Discovery science is the engine driving global competitiveness and societal progress, revealing new materials and phenomena that build our knowledge base, stimulate new ideas and open new horizons of thought. New materials and standard materials with improved properties are constantly needed to find the boundaries of known phenomena, to explore new phenomena and to confirm, refute and refine predictions from theory and modeling. Setting targeted materials outcomes for science challenges our scientific creativity; achieving the targeted outcomes advances and confirms our scientific capability.

6.2 Targeted outcomes for technology

The vibrant semiconductor industry, a pillar of our technological leadership for the last half-century, is presently entering an era of uncertainty and challenge based on the end of traditional silicon and silicon-oxide materials that enable Moore's law scaling. The search for new functional materials to augment or replace silicon and silicon oxide is critically important to the nation's technological leadership; inventing or discovering these materials may establish new paradigms for device physics and computation that define a host of digital applications. None of the candidates to replace silicon has produced a robust technology, including carbon electronics such as nanotubes and graphene, piezoresistive and phase change materials, and magnetic materials for spintronics, Beyond semiconductors, many key technologies with high potential economic impact are limited by lack of appropriately functional materials. The renewable energy industry is limited by a lack of electrode materials and membranes for advanced batteries, inexpensive and earth abundant polycrystalline materials for thin film photo-voltaics and solution based methods for synthesis and large area deposition. Soft functional flexible materials for use in harsh environments are needed in the medical and gas recovery industries and large area self-assembled materials for patterning from the nano to meter scale are urgently needed. In the pharmaceutical industry, the materials science of drug formulation and delivery presents enormous challenges. To address these issues a combination of rational computer-based design, coupled with intensive fundamental materials science investigation, invention and discovery is required to provide a pipeline of new soft and hard functional materials that can be utilized by the industries that provide high tech employment and generate hundreds of billions of dollars in economic activity.

6.3 The space of worthy targeted materials outcomes is vast. Although outcomes that advance the frontiers of science and of technology can be distinguished as noted above, often they share similar or overlapping pathways, so that the same intellectual investment and research activities contribute to both kinds of outcomes. Below we emphasize three promising areas of materials research with the potential to drive new discoveries, reveal new phenomena and create new materials, without distinguishing science and technology outcomes. Each area is rich with opportunity, building on the discoveries and scientific advances of the last 15 years and ready for rapid advancement.

6.4 Mesoscale materials and phenomena

Mesoscale materials offer new levels of complexity and functionality, building on the nanoscale knowledge base that we have created over the last 15 years. At the mesoscale interactions diversify and proliferate as the separation of quantized energy levels shrinks. In addition, statistical variation encompassing low energy defects and structural alternatives drives diversity at the mesoscale, collective behavior becomes fully developed, interactions among mechanical, electronic, ionic, structural, chemical and other degrees of freedom are common, and composite systems with component parts that cooperate to produce a single functional outcome become possible.[42,43] (Basic Energy Sciences Advisory Committee 2012, Crabtree 2012) The last half-century or more has witnessed a reductionist drive to understand macroscopic phenomena that we see with our eyes and feel with our hands in terms of often invisible meso- and nanoscale structures, using innovative tools of ever finer spatial, temporal and energy resolution. This reductionist drive continues to produce and advance our extensive knowledge of interactions among atoms and molecules at the nanoscale. Looking forward, the future holds a rich constructionist opportunity, reversing the reductionist drive of the last half-century and using the intimate knowledge of interactions at the atomic and molecular level to control, design and build new mesoscale architectures that display unique phenomena and functionalities that do not exist in the natural world. The mesoscale challenge of building materials from the bottom up, exploiting nanoscale interactions to produce functional mesoscale architectures and designing materials with targeted macroscale outcomes is now ripe for development and well within our reach.

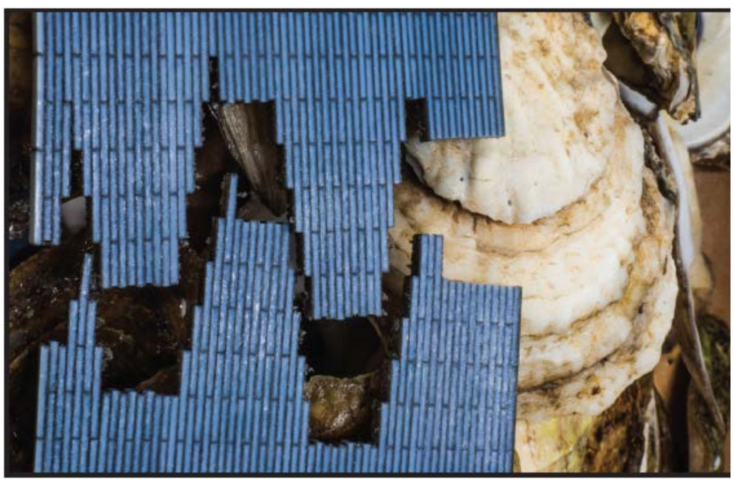

Figure 2. Bioinspired artificial mesoscale materials created by 3D ink-jet printing of two polymers, one soft and one stiff, based on the brick and mortar structure of nacre and bone. One of these materials demonstrates fracture resistance up to 22 times that of its strongest constituent. *Source: Leon S. Dimas, Graham H. Bratzel, Ido Eylon, and Markus J. Buehler, Tough Composites Inspired by Mineralized Natural Materials: Computation, 3D printing, and Testing, Adv. Funct. Mater. 23, 4629 (2013). Photo Credit: Graham H. Bratzel*

6.5 Mesoscale materials opportunities embrace all areas of science and technology. Biological materials are an excellent example, including structural proteins such as silk and collagen, and enzymes that control the synthesis of membrane-forming surfactants and complex macromolecules such as cellulose and lignin. Skeletal structures such as diatoms and other shells, exoskeletons, bones and teeth are built on the mesoscale from nanoscale building blocks. The specificity of biological interactions determines the three-dimensional shapes of proteins and nucleic acids, allows biological molecules to assemble into extended structures and to control the synthesis, structure and properties of biominerals. Our ability to determine, mine, and manipulate biological materials and phenomena is creating new opportunities to probe and program materials behavior in ways that were unimaginable a few years ago.[70] (Payne 2013)

6.6 Correlated electrons are rich with mesoscale behavior spanning Mott insulators, local moments, ordered and glassy magnetism, colossal magnetoresistance, high temperature superconductivity, charge and orbital ordering, topological insulators, quantum criticality, pseudogaps, non-Fermi liquids, normal metal behavior and interactions among spin, lattice and charge degrees of freedom. Fluid flow in mesoporous media is another rich example, spanning gas and oil flow in hydrofractured shales, membranes for chemical separation, reverse osmosis for water purification, and capture and storage of carbon dioxide in geologic formations. The degradation of materials comprising our built environment is an outstanding mesoscale challenge, extending from the initiation of cracks within a single unit cell due to fatigue or excessive stress, to mesoscale crack growth and propagation, to macroscopic failure as cracks reduce or destroy the strength of materials.

6.7 Dynamic and far from equilibrium materials and phenomena

Enormous progress in producing intense pulsed sources of light, neutrons and electrons and advances in sensitive detection of weak pulses scattered from matter opens a new horizon of time resolved measurements.[71,72,73] (Behrens 2014, Marques 2014, Krausz 2009) Such dynamic characterization allows observation of the time evolution of the chemical, electronic and structural character of materials.. The range of time resolution is now continuous spanning from tens of atto- to femtoseconds for electronic transitions, from femto- to picoseconds for nuclear motion, from nanoseconds to seconds for structural transitions and from minutes to days for glassy dynamics, crack propagation and defect aggregation. The use of pump-probe techniques allows the triggering of an event and monitoring the system evolution at specific time intervals after the event, a powerful and versatile approach for organizing time dependent phenomena for detailed observation.

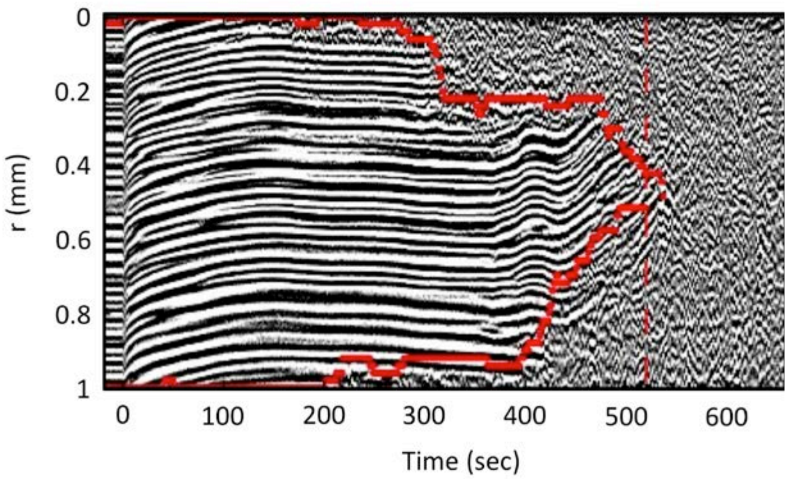

Figure 3. Time dependence of the solid-to-fluid transition in a gel of colloidal carbon black particles, showing that yielding proceeds in a spatially and temporally heterogeneous way and that the time needed for total fluidization decreases exponentially with the applied shear stress. *Source: T. Gibaud, D. Frelat, and S. Manneville, Heterogeneous yielding dynamics in a colloidal gel, Soft Matter 6, 3482-3488 (2010). Reproduced by permission of The Royal Society of Chemistry (http://dx.doi.org/10.1039/C000886A)*

.6.8 Only in the past few years have we been able to apply time resolved techniques to unravel complex dynamics on the atto- and femto- second timeframe relevant for atomic and molecular processes that underlie behavior at longer timescales. The grand challenge of making movies of chemical reactions revealing all the excited states and intermediate steps is now within reach for simple cases. Many chemical reactions involve both ultrafast electron transfer and slower reconfiguration of atomic positions, requiring multimodal measurements to follow and unravel their interactions. Understanding catalysis at the atomic and molecular level is especially interesting and challenging, a basic science frontier with broad and immediate impact on chemical technology and the economy. Observing and understanding the mechanism of mechanical motion in biological cells and applying this knowledge for bioinspired materials and technologies is a ripe research direction.[74] (Muretta 2013) Critical phenomena at phase transitions occurs over many time scales from nanoseconds to seconds or longer, and the mechanisms by which coupled structural and electronic phase transitions nucleate and grow presents fundamental challenges (Figure 3). Beyond simply observing dynamic behavior, controlling the outcome of a chemical reaction or physical process with external cues at intermediate steps is a grand vision coming closer to realization.[75,76,77] (Brinks 2014, Lepine 2014, Grinev 2013) The new field of soft active matter, where energy is continuously added by coupling inanimate objects to electromagnetic fields or by conversion of chemical food to motion in colonies of bacteria or viruses is revealing new fundamental principles of collective behavior.[78] (Marchetti 2013) Far from equilibrium dynamic behavior presents new challenges, where there is no nearby equilibrium state that serves as platform for a perturbation or fluctuation analysis.[79,80] (National Research Council 2007, Jaeger 2010) Time resolved studies of these and other dynamic phenomena are at the scientific frontier and rich with opportunities for breakthroughs.

6.8 Interfacial phenomena

Interfaces between different phases of matter (for example, gas-solid or liquid-solid) and between materials with fundamentally different properties (for example, structural or electronic) play a key role in determining both the evolution of novel material/device architectures and their resulting properties; arguably all structure and function originates from one or more interfaces somewhere in the system.[81,82,83,84] (Kaplan 2013, Yu 2012, Henderson 2011, Baxter 2010) The successful synthesis of materials that range from high quality crystals to colloids to glasses, from uniformly dense to highly porous, and that can reproducibly enhance properties over length scales from the atomic to the mesoscale and beyond, requires the ability to characterize and manipulate the kinetic processes that occur at interfaces. The recent advances in high spatial and temporal resolution *in-situ* and *in-operando* characterization techniques[85,86] (Gu 2013, de Jonge 2011) such as TEM (Figure 4), scanned probe, NMR, X-rays and Raman Scattering puts a full understanding of many forms of interfacial phenomena within sight: such as the molecular mechanisms behind the nucleation and growth of nano/meso structures; corrosion and the mechanical deformation of materials under extreme conditions; ionic diffusion at dislocations, grain boundaries and hetero-interfaces and the formation of secondary phases under temperature, pressure, and electrochemical driving forces; and the origins of activity and selectivity in heterogeneous catalysts. In addition, such methods also permit the interaction of inorganic nanostructures with biological systems to be quantified, leading to a full understanding of how nanoparticles interact with membrane proteins to positively enhance drug delivery and medical diagnostic imaging methods or lead to environmental health and safety concerns. On a global scale, *in-situ* studies of how solid nanoparticles interact with gases/liquids can provide a fundamental materials science basis to atmospheric chemistry that determines several of the major contributions to long-term climate change.

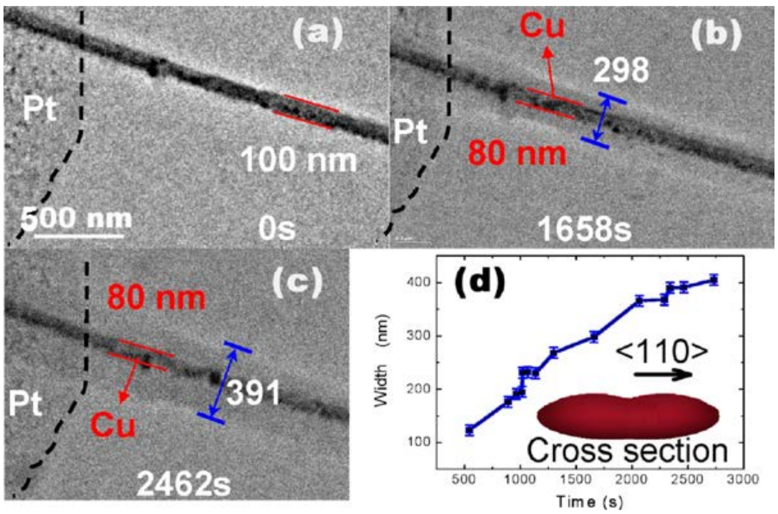

Figure 4: In situ liquid-cell TEM observation of the lithiation of the Cu-coated Si (Cu−Si) nanowire. (a) TEM image showing the pristine state of the Cu−Si nanowire at 0 s; (b) core−shell formation of the Cu−Si nanowire during lithiation at 1658 s; (c) TEM image of the Cu−Si NW at 2462 s; (d) plotted width changes of the nanowire as a function of time. *Source: Meng Gu, Lucas R. Parent, B. Layla Mehdi, Raymond R. Unocic, Matthew T. McDowell, Robert L. Sacci, Wu Xu, Justin Grant Connell, Pinghong Xu, Patricia Abellan, Xilin Chen, Yaohui Zhang, Daniel E. Perea, James E. Evans, Lincoln J. Lauhon, Ji-Guang Zhang, Jun Liu, Nigel D. Browning, Yi Cui, Ilke Arslan, and Chong-Min Wang,* Demonstration of an Electrochemical Liquid Cell for Operando Transmission Electron Microscopy Observation of the Lithiation/Delithiation Behavior of Si Nanowire Battery Anodes, *Nanoletters 13, 6106 (2013).Reprinted (adapted) with permission from Nano Letters. Copyright 2013 American Chemical Society.*

7.0 Features required for success

7.1 Sustained funding

The traditional NSF model of three-year grants does not provide sufficient sustained effort to develop the human and scientific interactions needed to effectively close the loop. Longer grant periods are needed for widely collaborative programs, as evidenced by new grants funded for collaborative research in the US and Europe. The Bioenergy Research Centers funded by the Office of Biological and Environmental Research in DOE's Office of Science specified a ten-year grant period conditional on a successful rigorous review after five years. The four DOE Energy Innovation Hubs have been given a five-year initial contract, with the possibility of renewal for another five years if they are making sufficient progress.[87] (Secretary of Energy Advisory Board 2014) An evaluation of funding schemes in Europe found that long-term commitment in a five-plus-five years scheme was instrumental for success enabling truly novel and scientifically daring projects.[88] (Danish Agency for Science, Technology and Innovation 2013). The significantly higher level of intimate coordination, frequent communication and innovative thinking required to tightly close the loop among synthesis, characterization, theory/modeling and targeted materials outcomes requires ten years to establish, refine and achieve transformative break-through outcomes. An annual review of progress followed by a rigorous mid-term review at five years are needed to evaluate the management and scientific quality of the procedures used to close the loop; a possible outcome of this midterm review should be cancellation of weak projects.

7.2 While sustained funding for ten years is required for groundbreaking outcomes, renewal of the same project after ten years with the same or similar targeted materials outcomes is not recommended. Ten years is long enough to achieve or make significant progress on a targeted outcome. At the end of ten years successful projects should build on their groundbreaking outcomes with other funding; unsuccessful projects should disband and allow the members to look for promising new directions

7.3 Competition and peer review

The responsibility for encouraging the kind of bold, potentially groundbreaking research advocated in this report rests not only with the proposers but also with the evaluators. Rigorous and thoughtful peer review of such proposals is critical to selecting the most meritorious research. Often panel reviews seek consensus and can only agree on the least radical research directions. Truly bold and potentially groundbreaking proposals often find one or more detractors whose opinions and scoring remove the proposal from serious consideration for the precious available funding.

There are several possible remedies for these reviewer dynamics. The deciding program officer can override the consensus opinion of the panel, the proposal can be sent to mail reviewers independently of the panel or without a panel, or evaluation criteria can be specified that specifically value novel, potentially ground-breaking proposals above low-risk incremental proposals. The deciding program officer should be required to document not only his/her decision but also its conformity to the principle of encouraging bold, potentially groundbreaking research for eventual examination by the Committee of Visitors.

8.0 ***Major Facilities***

The major facilities run by NSF offer unusual characterization opportunities that require specialized equipment and expertise not generally available to the research community.

8.1 National High Magnetic Field Laboratory

The National High Magnetic Field Laboratory (NHMFL) provides world leading steady and pulsed fields that enable groundbreaking science. NHMFL was recently reviewed by the National Academy of Sciences.[89] (National Research Council 2013) After considering the role of the NHMFL in condensed matter and materials physics, chemistry, biochemistry and biology, medical and life sciences, combining high magnetic fields with scattering and optical probes, magnet technology development and the international landscape, the Academy recommended that "the NSF should continue to provide support for the operations of the NHMFL and the development of the next generation of high-field magnets."

8.2 *Cornell High Energy Synchrotron Source (CHESS)*

8.3 CHESS has followed a distinctive trajectory as a synchrotron source, contributing an outstanding record and culture of innovation in accelerator science, synchrotron design, x-ray detectors and optics, and frontier scientific advances. These contributions are characterized by a rare combination of collaborative university research and large facility culture that encourages innovation in x-ray delivery and scientific use, promotes collaboration among users and CHESS staff scientists, and accelerates progress by providing frequent access to beamlines, endstations and experiments. Beyond its advances in x-ray science and technology, CHESS contributes a vital educational function, awarding 20% of US PhDs in accelerator physics. These graduates advance to become central players in next generation accelerator design, where innovation is central to US competitiveness in x-ray and neutron science, in new materials, and in the disruptive technologies that grow from them.

8.4 CHESS makes critical advances to beamline science through the CHESS Compact Undulator (CCU) using small inexpensive permanent magnets to extract high performance x-ray beams from the short straight sections between multi-bend achromats. In endstation science, CHESS contributes innovative new x-ray detectors and optics, a critical and currently underfunded area needing advances to exploit the full scientific potential of the new bright, coherent, time resolved sources. CHESS has pushed the frontier of science with its attosecond movies of electron motion and *in situ* strain/x-ray diffraction in cyclically loaded materials. These landmark innovations advancing beamlines, endstations and the frontiers of science illustrate the breadth, depth and impact of CHESS for international x-ray science.

8.5 The field of x-ray science has seen enormous advances in the last decade, with a profusion of new scientific directions exploiting the higher intensity, faster time resolution, greater coherence and improved spatial and energy resolution of 3^{rd} and 4^{th} generation x-ray sources. The cost of upgrading existing sources and of building new sources has grown commensurately with their new capabilities, and is now in the range of $0.5B – $1 B or more. This cost is a significant fraction of the resources available for science in any country, requiring a significantly greater level of strategic planning and scientific justification for upgrades or new facilities than has been typical in the past.

8.6 A primary element of strategic planning and scientific justification is the clear articulation of the unique capabilities of each proposed new source for advancing the science frontier. Duplication of the same capabilities by two or more sources drains precious resources from other areas of science with equally promising opportunities. Each new or upgraded source must clearly articulate the unique science it will carry out, beyond the science that can be done at other facilities that are now in the proposal, construction or implementation stages.

8.7 In the short term, CHESS can fill a national user need for hard x-rays during the expected 18-month or longer shutdown of the Advanced Photon Source (APS) for its upgrade to significantly higher brightness, coherence and time resolution. As stewards of the only two hard x-ray sources in the nation, CHESS and APS, NSF and DOE should work collaboratively with the management of these facilities and the scientific community to minimize the user gap created when APS goes dark for its upgrade.

8.8 In the long term, the demand for higher energy x-rays produced by undulators is growing. 50% of the beamlines at APS, ESRF, PETRA and Spring 8 provide x-rays at energies above 30 keV. This energy range cannot be accessed on the many 3 GeV lightsources now in operation or planned. Europe has two hard x-ray storage rings (ESRF and PETRA-3) and plans two hard x-ray free electron lasers (XFEL and SWISS FEL), Asia has one hard x-ray storage ring (Spring-8) and will have two hard x-ray free electron lasers (SACLA and PAL XFEL). The US has two hard x-ray storage rings (APS and CHESS), with no hard x-ray FELs in the planning stage. The US should consider the future user demand for hard x-ray science and the means to satisfy it.

8.9 The director of CHESS presented to the subcommittee an interesting four-stage upgrade plan bringing CHESS emittance to 2 nm and expanding the number of beamlines from six to twelve. The plan proposed
(i) adding Cornell Compact Undulators (CCU) to three of the six current beamlines (A, F and G), increasing flux by a factor of 20 and the spectral brightness by nearly a factor of 100 at 30 keV,
(ii) adding ten dipole magnets in the south section of Cornell Electron Storage Ring (CESR), reconfiguring them to optimize for x-ray production rather than particle physics, adding vertical focusing components to each one, reducing the emittance of CESR by a factor of two, doubling spectral brightness, and providing gaps for insertion devices for the remaining beamlines, further increasing brightness. In addition, the A, B and C beamlines will be reoriented to use beams circulating clockwise in the ring so that CESR can operate with a single beam, improving emittance by a further factor two. Following the beamline upgrades, the energy of CESR will be gradually increased from 5.3 GeV to 6.5 GeV,
(iii) converting the remaining dipole magnets throughout CESR to combined function magnets with dipole, quadrupoles and sextupole components, reducing emittance to 2 nm at 6.5 GeV, and dramatically increasing spectral brightness,
(iv) adding six new long, insertion device x-ray beamlines, doubling capacity. The new beamlines would be housed in an extension to Wilson Lab on the east side of the ring. The structural design and construction process of the extension has been examined in a Cornell graduate student civil engineering project that resulted in a working plan.

8.10 The CHESS upgrade plan presented to the subcommittee did not include detailed projections for costs and timelines to completion, nor the unique science it will carry out that is not duplicated by other sources now in the proposal, planning or implementation stages in the US or internationally. Both the detailed cost and timeline projections and the unique science case need to be thoroughly articulated, as they are critical features for deciding CHESS's future.

8.11 The high cost of building, upgrading and operating x-ray sources, beamlines and endstations and the rich opportunities for their use in advancing the frontier of science make cooperation among funding agencies both sensible and strategic. The Geo-Soil-Environmental Sciences (GSE) facility operated by the Consortium for Advanced Radiation Sources (CARS) at the University of Chicago at the APS is an example of successful cooperation between NSF and DOE, with operations funding provided by a combination of NSF Earth Sciences and DOE-BES-Chemical Sciences funding. The Center for High Resolution Neutron Scattering (CHRNS) is a successful example of cooperation between NSF and NIST. In a time of rising costs, broad opportunity and increasing international competitiveness, such examples of inter-agency cooperation for advancing the frontier of x-ray science should be encouraged.

9.0 **Recommendations**

9.1 *Individual Investigators:* The creativity and inventiveness of individual investigators in pursuing potentially groundbreaking materials science should not be jeopardized. This report does not challenge the commitment of NSF to individual investigator awards.

9.2 *NSF should create a network of Materials Innovation Platforms* with geographic and materials diversity to implement tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes. Each Platform should operate by the following guidelines.

- The primary requirement for Platforms should be tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes in support of groundbreaking advances of the frontier for new science and applications.
- Each Platform should be anchored by an appropriate unique suite of facilities, including materials synthesis, characterization, and theory/modeling capability and include multimodal characterization tools.
- Each Platform should have a strong on-site scientific faculty director who provides the guidance for the targeted outcomes, the scientific directions, and the interface to the user community as well as to a scientific and industrial advisory board.
- Funding should ramp up to the range of $3M - $8M/year with multiple faculty from multiple institutions directly involved. Representation of faculty and students from smaller institutions should be specifically encouraged. Platforms should be funded for ten years, with a rigorous five year evaluation of their effectiveness in tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes and in achieving ground-breaking advances of the scientific frontier and/or promise for applications. For those Platforms judged as not achieving this tight integration and materials advances, a possible outcome of the five-year evaluation should be early ramp-down and termination.
- Each Platform should integrate a mix of core faculty and students, external users and expert users.
  - A set of core faculty and students should develop and apply novel and innovative tools in synthesis, characterization and theory/modeling
  - A set of expert users from outside the core who are funded by the Platform to pursue exciting long-term problems and who need special tools should pursue promising groundbreaking advances. These experts benefit from strong intellectual and research ties to the Platform and participate in shaping its strategy and research directions.
  - External users who are not funded by the Platform should tap into the capabilities of the Platform; their research directions and needs should be considered in planning Platform directions.
- User proposals should be evaluated by the following principles
  - Only user proposals that tightly close the loop among synthesis, characterization, theory/modeling and targeted outcomes will be considered. Users who do not close

the loop but contribute to one or more of its elements may petition to join with others to create a proposal that closes the loop.
  - The Platform and its users should be intellectually and scientifically engaged in collaboratively pursuing potentially groundbreaking research. The Platform is not simply an isolated service provider.
  - Proposals should be evaluated on their potential for broad impact and groundbreaking advances of the science frontier, not on the production of scientific papers describing the applications of established techniques to standard materials.
  - Proposals should address potentially groundbreaking fundamental science informed by national materials needs.
  - A program committee or science advisory committee composed of distinguished external members including scientists from relevant industries when applicable should judge the user proposals using published evaluation criteria embracing the above principles
- Platforms should develop new paradigms for user support appropriate to tightly closing the loop among synthesis, characterization, theory/modeling and targeted materials outcomes. DOE and NIST have developed models for user support designed for large-scale x-ray and neutron user facilities; DOE has also developed models for the use of the DOE nanocenters. These models should be examined for their effectiveness at the facilities they serve and for their appropriateness for Materials Innovation Platforms. The “closing the loop” mission of Platforms requires deep and continuous engagement of users within the Platform over long time periods, unlike the more limited and often one-time interactions of users with a single element of the loop in existing DOE and NIST facilities. Platforms should consider this and other implications of the Materials Innovation Platform vision and clearly identify and create a unique user culture serving Platform and user needs.
- Each Platform as part of its operating budget should fund a superb technical staff to develop, implement and operate its suite of sophisticated tools supporting synthesis, characterization, theory/modeling and targeted materials outcomes. The technical staff should work closely with core faculty and students and users to achieve the targeted outcomes.
- Platforms may have strong connections with industry, especially those pursuing materials outcomes supporting applications. Materials outcomes supporting applications should not address specific products or companies, but rather a class of materials and serve an entire technology sector (e.g. microelectronics, photonics, pharmaceuticals) in pursuit of groundbreaking advances enabling a broadly based technology.
- Platforms should have industrial and scientific advisory boards, as appropriate, and user committees to evaluate and recommend best practices.
- Platforms should implement creative programs for training students and early career scientists. Such programs may include summer schools, hands on experience, industry internships and personal engagement with innovation and entrepreneurship.
- Materials Innovation Platforms differ from large MRSEC Interdisciplinary Research Groups (IRGs), in that they are larger than IRGs and their function is to tightly close the loop among synthesis, characterization, theory/modeling and targeted materials outcomes.
- Platforms should integrate with MRSEC networks, making use of facilities and expertise in synthesis, characterization, theory/modeling and materials outcomes where appropriate to create the required critical mass of equipment, people and ideas.

- Platforms may interact with other funding modalities, such as individual investigators, centers, national facilities, early career awardees, and other funding mechanisms as allowed by NSF policies. Platforms may enlist compelling intellectual and physical expertise from these and other funding mechanisms in fulfilling their mission to close the loop among synthesis, characterization, theory/modeling and targeted materials outcomes.

9.3 In addition to the Materials Innovation Platforms described above, NSF should address the need for small scale instrumentation in academia by providing a funding stream for single investigator and small group research and development of small scale materials instrumentation, such as lasers for attosecond characterization of materials dynamics, compact and table top light sources, new TEM techniques, x-ray detectors and optics and matching funds for electron microscopes. Small scale instrumentation grants of the order of $500K to $1M over three years would also pay for materials and supplies required for development of the new instrument as well as students, postdocs and technical staff as required.

9.4 Major Facilities

9.41 NSF should only fund the construction and operation of unique large facilities that are not otherwise available in the research landscape[90] (NSF Materials 2022 Subcommittee 2012), such as the National High Field Magnetic Lab, which provides world leading steady and pulsed fields that enable groundbreaking science.[89] (National Research Council 2013) These large facilities should be dedicated to discovery of break-through outcomes that advance the frontier of science for multiple users. Education should play a major role in NSF's user facilities, training the next generation of innovative scientists and engineers not only in applications of existing techniques but also in creation of novel, potentially ground-breaking techniques and research directions that advance the scientific frontier.

9.42 We endorse the recommendation of the National Academy report *High Magnetic Field Science and Its Application in the United States: Current Status and Future Directions* (National Research Council 2013) that "the NSF should continue to provide support for the operations of the NHMFL and the development of the next generation of high-field magnets."

9.43 NSF should expect CHESS to develop and submit a detailed plan for the cost and timeline to completion for each stage of the four-stage upgrade plan presented to the subcommittee.

9.44 NSF should require CHESS to develop and submit a detailed case for the unique science opportunities that the upgrade will enable. This unique science case should compare the upgrade to each of the other sources now in proposal, construction or implantation stages. The basic question to be answered is, "What unique science opportunities does the CHESS upgrade provide that no other source provides?" A compelling case for the uniqueness of the CHESS upgrade will be a critical factor in the ultimate decision on whether to proceed or not.

9.45 Beyond the source itself, CHESS provides other distinctive features that merit strong consideration, including a collaborative atmosphere that encourages strong interaction among scientists and staff, a convolution of academic science and large facility capabilities, training that advances x-ray technology worldwide and a platform of experience, innovation and engagement for developing next generation detectors and experimental stations. CHESS should incorporate these valuable and successful elements into its unique science case.

9.46 NSF should consider opportunities to cooperate with other science funding agencies in advancing the frontier of x-ray science. [91](National Research Council 1999) This cooperation could include, for example, strategic plan for the US capabilities to advance the scientific frontier, fund endstations at DOE facilities, fund next-generation multimodal *in situ* characterization capability at DOE facilities, fund development of innovative x-ray detectors and optics for use at synchrotron facilities, fund advances in novel undulators for extracting beamlines at synchrotron facilities, and fund education of the next generation of scientists and engineers who will both advance and use these facilities in the future. Such collaborations, for example with NIST at the Center for High Resolution Neutron Scattering and with DOE at the Center for Advanced Radiation Sources at APS have proven their mutual benefit to the funding agencies and to the collaborating scientists.

Report Development Process

The MPSAC Subcommittee on Materials Instrumentation held a Workshop by invitation only on January 11-12, 2014 to take testimony from a cross-section of the materials community including the facilities operated by NSF and DOE (see agenda below). The Subcommittee met several times by conference call and in-person to organize the workshop, discuss the information presented at the Workshop and evaluate the instrumentation needs of the materials community (see timeline below). The Subcommittee Report was iterated several times among the Subcommittee members for comment and revision.

Timeline of the Report Development Process

Spring 2013	Subcommittee established
May 22, 2013	Conference Call
June 14, 2013	Conference Call
July 9, 2013	Conference Call
August 20, 2013	Conference Call
Oct 8-9, 2013	Workshop cancelled due to government shutdown
Jan 11-12, 2014	Workshop rescheduled (agenda follows)
Feb 17, 2014	Conference Call
Mar 7, 2014	Conference Call
Mar 26, 2014	In-person meeting, Arlington VA
July 18, 2014	Report Complete

Agenda
NSF Synchrotron Subcommittee Workshop,
Marriott Residence Inn
650 North Quincy Street
Arlington, VA
January 11-12, 2014

January 11, Morning Session

8:45 - 10:45 am: Session A – Overview

1. Summary of NSF Mat 2022 report findings – Murray Gibson, NEU – *30 min*

2. Importance of materials research facilities for US research and economy, DOE role – Pat Dehmer, DOE - *30 min*

3. Biology/biomaterials talk – importance of materials research facilities – Pupa Gilbert , U. Wisconsin - *30 min*

4. Nanosci/tech talk – importance of materials research facilities – Stephen Campbell, U Minnesota – *30 min*

10:45-11:00 am: Coffee break

11:00 am - 12:00 pm: Session B – DMR facilities and materials research needs, funded major facilities past and present

5. NSF DMR funded materials facilities, past accomplishments and future potential*
    a. CHESS – Joel Brock, Cornell *20 min + 10 min Q&A*
    b. NHFML – Gregory Boebinger, Florida State U. *20 min + 10 min Q&A*

12:00 – 1:00 pm: Lunch

1:00 - 2:30 pm: Session C – Continued DMR funded major facilities past and present,

6. NSF DMR funded materials facilities, past accomplishments and future potential*

    a. NIST partnership – Rob Dimeo, NIST *20 min + 10 min Q&A*
    b. SRC - Tai Chiang, U. Wisconsin – *20 min + 10 min Q&A*
    c. General discussion – *open meeting 30 min*

2:30 – 3:00 pm – Coffee Break, closed meeting – committee discussion

January 11, Late Afternoon Session

3:00 - 4:30 pm: Session D – Novel materials facilities concepts and opportunities and how they are currently funded in the US

7. Future of higher harmonic light sources and their applications in materials science - Margaret Murnane, JILA *20 min + 10min Q&A*

8. Future U.S. X-ray light source facilities, and the international scene – John Hemminger, UCal, Irvine *20 min + 10 min Q&A*

9. Theory and Simulation of materials - what facilities or infrastructure is needed to advance the field faster – Peter Voorhees, NWU, *20 min + 10 min Q&A*

4:30 - 5:45 pm: Community input and general open discussion -

January 12, Morning Session

8:00 - 10:00 am: Session E – International materials facilities developments

10. International picture – new developments in light sources - Yves Petroff, LNLS *20 min + 10 min Q&A*

11. International picture - new developments in TEM facilities - Nigel Browning, PNNL *20 min + 10 min Q&A*

12. International picture – materials synthesis and characterization – Hard Materials – Charles Ahn, Yale *20 min + 10 min Q&A*

13. International picture – materials synthesis and characterization – Soft Materials – *Frank Bates, UMN 20 min + 10 min Q&A*

10:00-10:30: Coffee Break

10:30 – 12:00 am: Community input and general open discussion

** Guidelines for presenters on DMR past and currently funded facilities*

Facility being presented (e.g., compact light source, high magnetic fields, . . .)
Present status of facility and its impact on advances in science of materials
Five and ten year outlook for new facility capability and impact on advances in science of materials
Cost of new facility capability: $5M, $50M, $100M, $500M

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