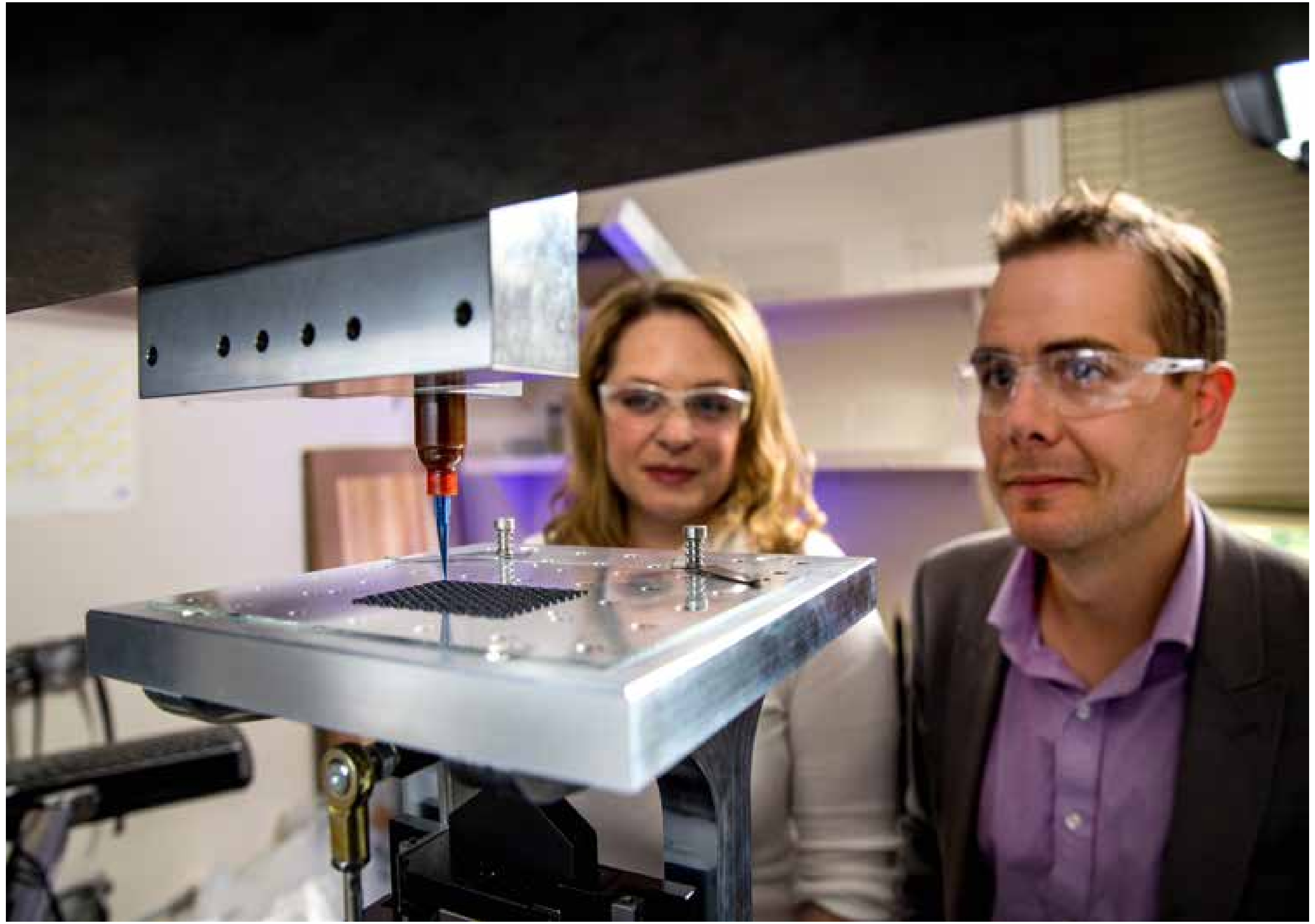
Materials Science on a Mission

Advancing the Science and Technology of Materials

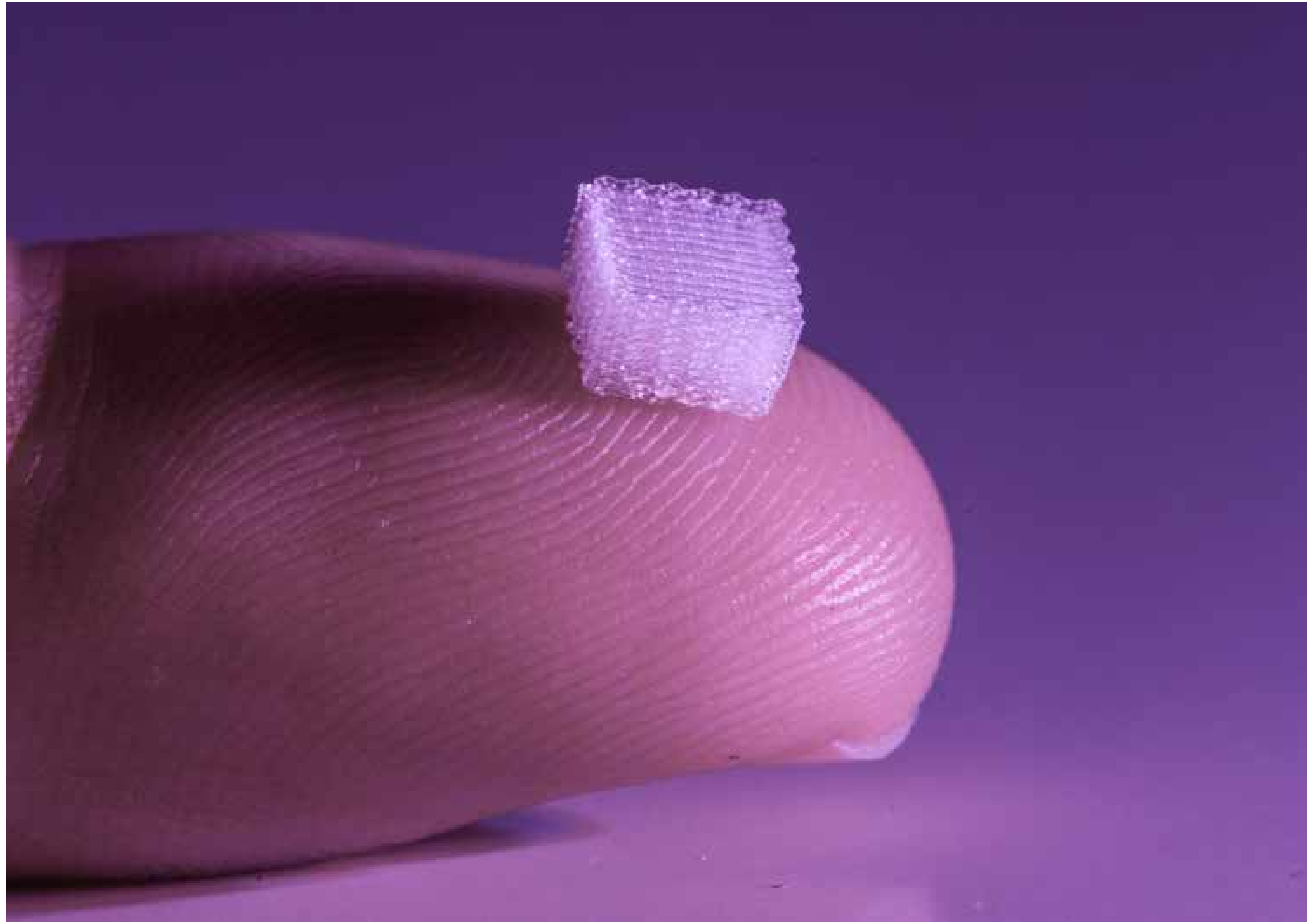
MSD



Materials Science on a Mission

Advancing the Science and Technology of Materials

MSD



contents

WELCOME TO MATERIALS SCIENCE AT LLNL

Robert S. Maxwell
Materials Science Division Leader

The Materials Science Division (MSD) at Lawrence Livermore National Laboratory (LLNL) plays a critical role in strengthening the nation's security through pioneering science and technology. Our organization is dedicated to understanding the properties and performance of legacy materials and integrating new materials and processes into programmatic activities at LLNL. We use state-of-the-art experimental and computational tools to accelerate the discovery, qualification, and deployment of uniquely functional materials and advanced manufacturing methods. With these capabilities, MSD supports a broad range of existing and emerging LLNL programs.

Presented here are seven focus areas that showcase the depth and breadth of our research: composites and soft matter, nanomaterial synthesis, computational materials science, energetic materials, optical materials, target materials, and actinides and lanthanides. Understanding how materials behave in various conditions drives MSD scientists to develop new materials for diverse applications, such as feedstocks for additive manufacturing and target development for the world's most powerful laser system at LLNL's National Ignition Facility. Other efforts include innovations in materials assembly and processing to capture emergent properties at the nano-, meso-, and macroscale, as well as exploiting our characterization and synthesis expertise to optimize and scale the production of functional materials.

> “ **Materials science is essential to the Laboratory's missions.**

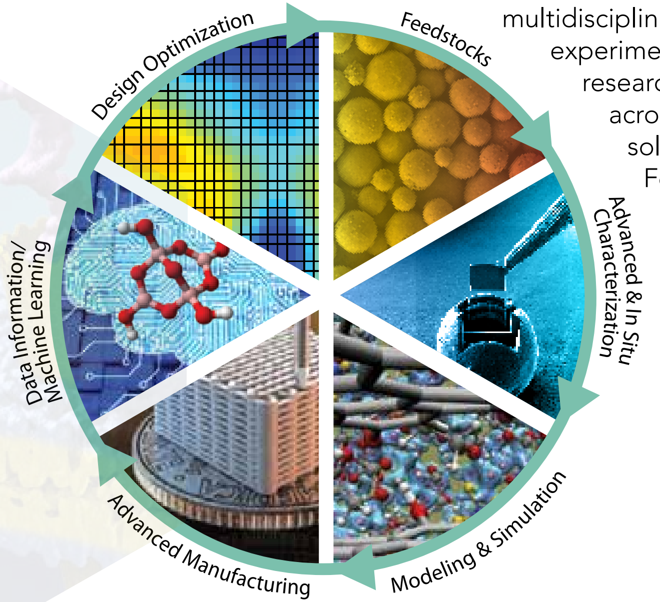
As a recognized and trusted leader for innovative, timely, and effective materials science solutions, MSD works closely with collaborators both inside and outside LLNL on a number of key national security and energy-focused initiatives. We also mentor the next generation of materials scientists through internship and postdoctoral fellowship programs. For decades, MSD has made major contributions to LLNL's key science and technology milestones.

This exciting work would not be possible without dedicated staff—more than 300—who advance materials science every day. At MSD, we are proud to conduct research that matters. We are honored to pursue materials science on a mission.

STRATEGIC LEADERSHIP IN MATERIALS SCIENCE

MSD's pursuit of mission-oriented research and development relies on strategic alignment of our core competencies to LLNL's national security goals—from defense and counterterrorism objectives to biosecurity and energy technology. These competencies include composition and microstructure design optimization, feedstock development, *in situ* characterization methods, high-performance computer modeling and simulation, advanced manufacturing techniques, and advanced data informatics methodologies.

At all phases of the materials development lifecycle, we work closely with other areas of LLNL, production sites, and end users. Bringing together multidisciplinary teams, leading experimental facilities, and research tools available across LLNL enables us to solve tough challenges. For example, our extensive collaboration with LLNL's Engineering Directorate and other internal and external partners ensures both the science and technology aspects of a project are covered.



In addition, our staff play critical support and leadership roles in LLNL capability centers and institutes to provide advanced capabilities for a broad range of scientific disciplines. The Nanoscale Synthesis and Characterization Laboratory unites physics, materials science, engineering, and chemistry to fabricate advanced nanoscale structures with novel properties for use in targets for the National Ignition Facility and now more broadly to support the nation's energy security. The Energetic Materials Center brings multidisciplinary experimental and computational capabilities to advance the science of energetic materials, including high explosives. The Forensic Science Center is home to nationally recognized scientists and advanced analytical characterization capabilities that support chemical, biological, radiological, nuclear, and explosive counterterrorism. Within the Jupiter Laser Facility, our work focuses on matter under extreme conditions with the help of nano- and femtosecond-pulse laser systems. Leveraging a range of expertise—from actinide materials and ultrafast experiments to electron microscopy, polymer science, and beyond—MSD delivers tailored materials solutions to address the nation's critical scientific challenges.

Focused ion beam technology enables micromachining, x-ray microanalysis, and electron microscopy sample preparation.

MSD by the Numbers

MSD staff are recognized internally and externally for the excellence and impact of their work. Our researchers actively engage in scientific enterprise by leading or participating in national and international review panels, user facility boards, workshops, and conferences. MSD scientists contribute to numerous professional associations including memberships and fellowships in the American Chemical Society, the American Physical Society, the International Society for Optics and Photonics, the Optical Society, the Institute of Electrical and Electronics Engineers, the Materials Research Society, and the National Academy of Engineering.

>200
peer-reviewed scientific papers published in the open literature each year

>30
LLNL Director's Science & Technology Awards since 2016

15
Defense Program Awards of Excellence since 2012

15
R&D 100 Awards since 2011

8
LLNL Early and Mid-Career Awards since 2012

6
Presidential Early Career Award for Scientists and Engineers

4
Lawrence Fellows since 2012

3
Secretary of Energy Awards since 2012

COMPOSITES AND SOFT MATTER

With access to world-class facilities and instrumentation, MSD scientists specialize in the synthesis, characterization, integration, and application of composites and soft matter. Our broad expertise includes research and development of solgels, polymers, ceramics, organic compounds, and low-density cellular materials such as aerogels. We approach innovation from both *process* (sol-gel chemistry for the fabrication of porous composites; advanced ceramic synthesis of hard materials for cutting, grinding, and polishing) and *product* (materials with gradient densities, specialty plastics, energetic materials, ceramic–metal composites, sensors for neutron and gamma radiation detection, modular reactor components) perspectives.

At the forefront of materials fabrication and assembly, MSD explores a range of technologies and materials for creating novel composites. For example, combining LLNL advances in three-dimensional (3D) printing with new conductive, smart feedstock materials to build complex structures is one way MSD scientists and collaborators explore the potential of merging additive manufacturing with advanced composite inks. These multidisciplinary teams are the first to fabricate micro-architected structures (boxes, spirals, and spheres) from inks containing shape-memory polymers. Made from environmentally friendly components, soybean oil, copolymers, and carbon nanofibers, the ink is used to “program” a temporary shape at a specific temperature. We then induce shape-morphing with ambient heat or an electrical current, which reverts the part from its temporary shape back to its original shape.

Energy Applications

MSD’s composite portfolio supports the Department of Energy through solutions focused on energy and natural resources. As carbon dioxide accumulates in Earth’s atmosphere from human-made emissions and disrupts the planet’s climate, MSD staff seek efficient ways to capture and convert greenhouse gasses from industrial processes and energy production. Innovative materials for capturing carbon dioxide, such as silicone microcapsules containing carbon-trapping chemicals and 3D-printed composites containing only silicone and baking soda, have been developed with an eye toward increasing efficiency while reducing environmental risks.

We also produce carbon-based materials for energy storage, converting different carbon allotropes into functional, high-surface-area materials. For example, MSD has pioneered the use of single-walled carbon nanotubes in an aerogel, harnessing the stiff, yet flexible nature of individual nanotubes for better structural integrity. The resulting material is mechanically robust, highly compressible, and more electrically and thermally conductive than carbon nanotube structures created through other methods. In addition, we assemble 3D foam structures using graphene building blocks and cost-effective, scalable synthesis techniques.

Because of their high surface area, electrical conductivity, and compressibility, new members of the porous carbon family—carbon nanotube and graphene structures—show great promise for energy storage applications such as batteries and capacitors. Shown is an artist’s rendering of lithium ion storage on graphene sheets.

Using carbon aerogels, MSD researchers have developed novel approaches for removing contaminants such as uranium and arsenic from groundwater and salt from seawater (see *Spotlight on Capacitive Desalination*). Our expertise includes materials such as hierarchically ordered high-surface-area structures (catalysis, energy generation, and energy storage, including catalytic aerogels for electrosynthesis), high-surface-area carbon electrodes (batteries and supercapacitors), thin films (high-efficiency solid-oxide fuel cells), and carbon-based composites (onboard vehicle hydrogen storage).

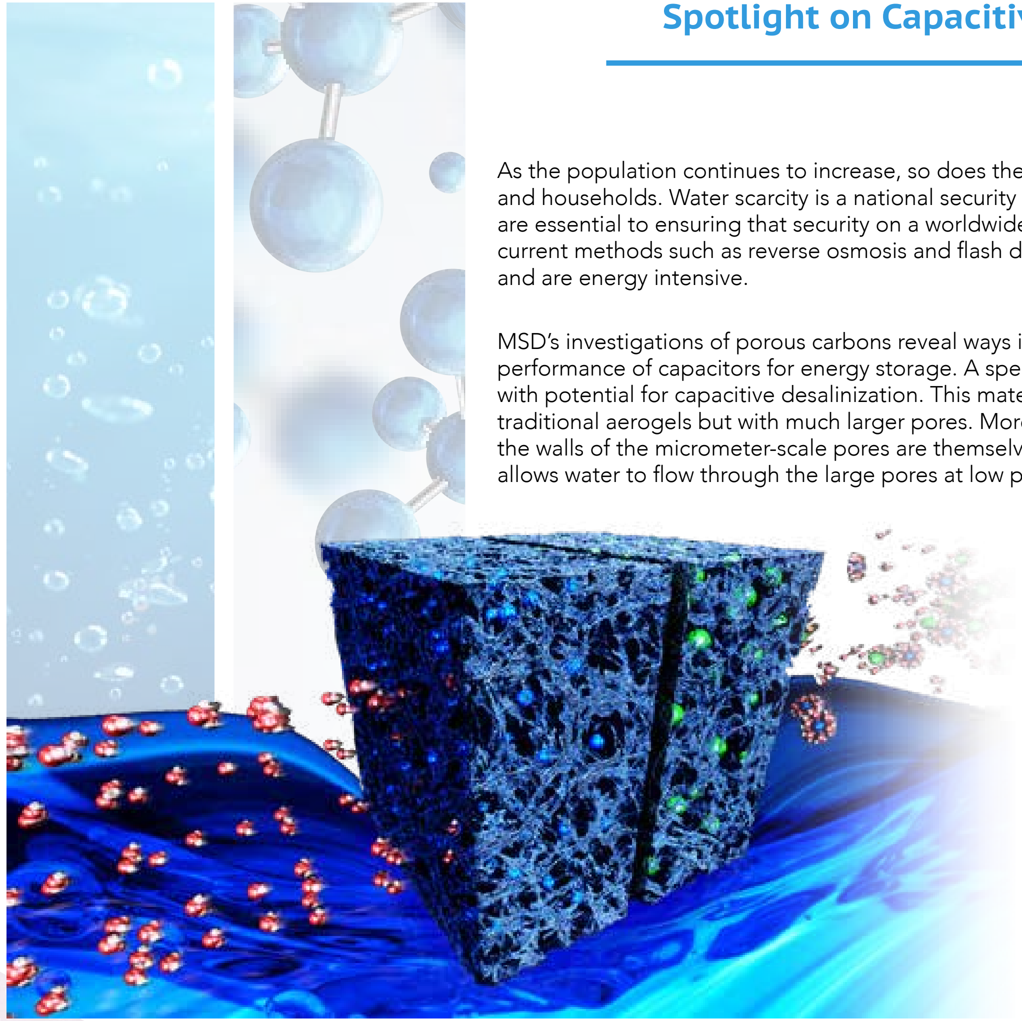
Next-Generation Feedstocks

MSD works with internal partners to optimize additive manufacturing (3D printing) techniques, such as direct-ink writing, through focused investments in feedstock development. By engineering high-performance inks, we have improved the efficacy of ink curing and enabled on-demand printing of cellular foams that meet the chemical, structural, and mechanical standards established for weapon components. Other advancements in ink technology for energy applications include incorporation of nanomaterials and biocatalysts, photosensitive feedstocks, and those with built-in porosity and length-scale control.

We design custom feedstock formulations for a variety of advanced manufacturing needs. For example, MSD scientists are developing the capability to produce high-explosive feedstocks and plastic-bonded explosives components with tailored functionality, providing more flexibility for a number of industrial and defense applications. In addition, we explore tailored mass transport properties for high-energy-density physics target fabrication, such as for the National Ignition Facility, with a goal of transforming large-scale energy storage solutions. Our fiber-reinforced composite materials advance carbon fiber additive manufacturing, particularly for applications requiring high strength or stiffness and low weight. The technique aligns fiber direction during extrusion, resulting in high-performance microstructures made from less material. Using computer programs to simulate particle size and scale, we develop new feedstock materials from combinations of polymers, composites, and ceramics.

MSD relies on multiple techniques for precision fabrication of three-dimensional materials. Electrophoretic deposition uses an electric field to drive suspended colloids from a solution onto a conductive substrate. The process allows a wide range of materials such as ceramics, metals, and polymers to be deposited in a controlled manner.

Spotlight on Capacitive Desalination



As the population continues to increase, so does the demand for freshwater for use in industry and households. Water scarcity is a national security issue, and new sources of freshwater are essential to ensuring that security on a worldwide scale. One solution is desalination, but current methods such as reverse osmosis and flash distillation require extensive infrastructure and are energy intensive.

MSD's investigations of porous carbons reveal ways in which pore structure affects the performance of capacitors for energy storage. A specific type of carbon aerogel has emerged with potential for capacitive desalination. This material has the electrical properties of traditional aerogels but with much larger pores. Moreover, its hierarchical porosity—that is, the walls of the micrometer-scale pores are themselves porous with nanometer-scale pores—allows water to flow through the large pores at low pressure, while the small pores increase the material's surface area. This aerogel can also be fabricated into various sizes and shapes. After establishing feasibility via computer modeling, MSD researchers built an energy-efficient flow-through electrode capacitive desalination module using this specialized aerogel.

Potential applications:

- Industries that use partially desalinated water for their processes
- Industries that require substantial amounts of water and seek alternatives to freshwater
- Desalination units for military packs and transport vehicles
- Water filters for use in disaster areas or to soften household water supplies

NANOMATERIAL SYNTHESIS

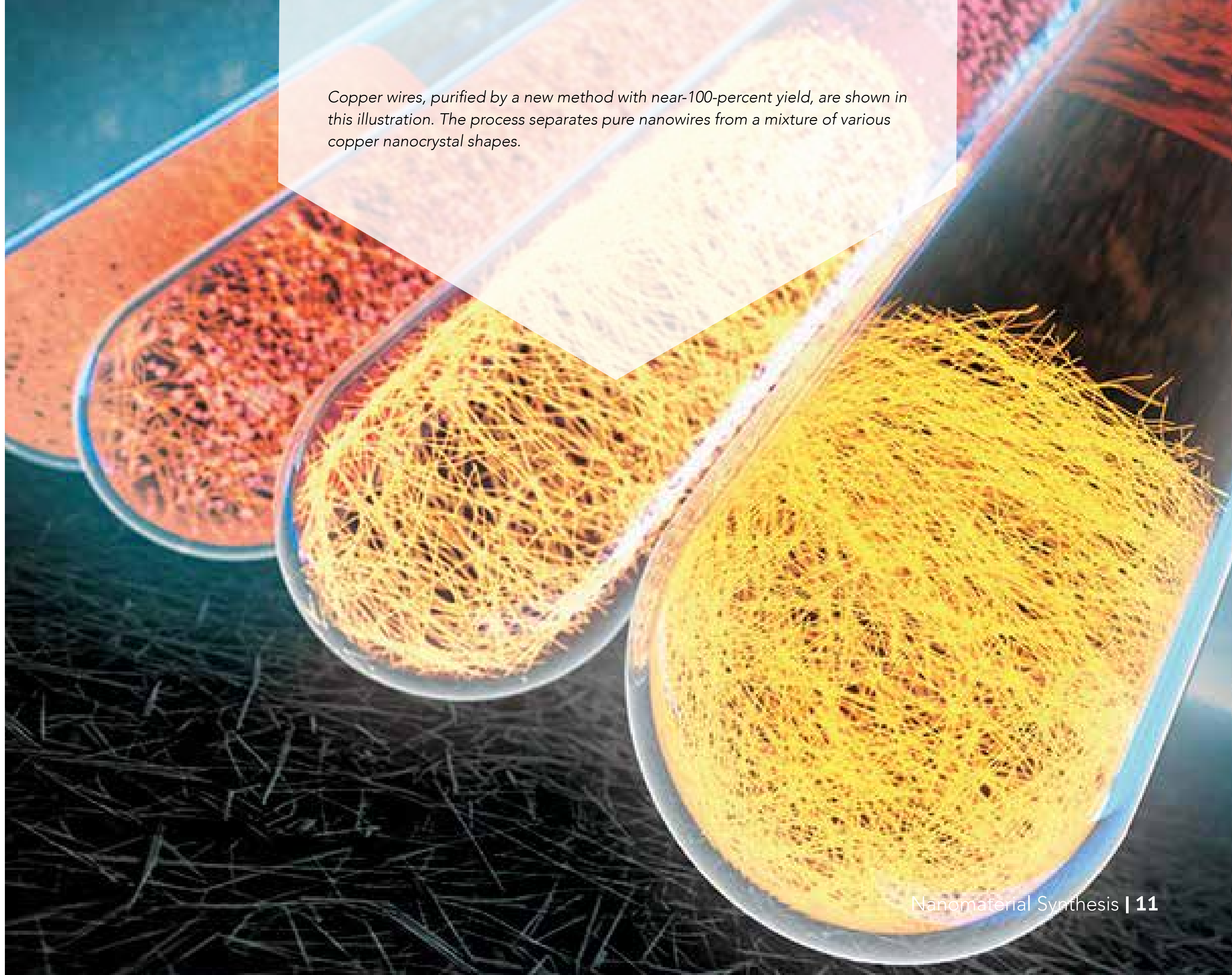
Nanoscale materials possess unique properties that are highly sensitive to structure, shape, and composition. MSD's research and development investments focus on the design, development, optimization, and characterization of nanoscale architectures for a wide array of applications. Our research in accelerated development of advanced nanomaterials allows efficient and scalable syntheses; assembly of metal, metal oxide, polymer, and ceramic micro- and nanoparticles; and control of surface properties such as exposed facets. We have also designed novel plastic scintillators for radiation detection and imaging based on light-emitting plastics and nanoceramic materials and developed carbon nanotube–based biomimetic systems that can mimic the transport properties of membrane proteins in cell walls (see *Spotlight on Biomimetic Materials*).

MSD explores methods for assembling nanomaterials into functional materials while retaining the unique properties of the nanomaterial building blocks. Our scientists optimize optical, electromagnetic, and catalytic activities for specific applications in sensing, light manipulation, and energy conversion and storage. For example, controlled (or directed) assembly of nano- and microparticles provides a route for fine-tuning of material properties and device fabrication.

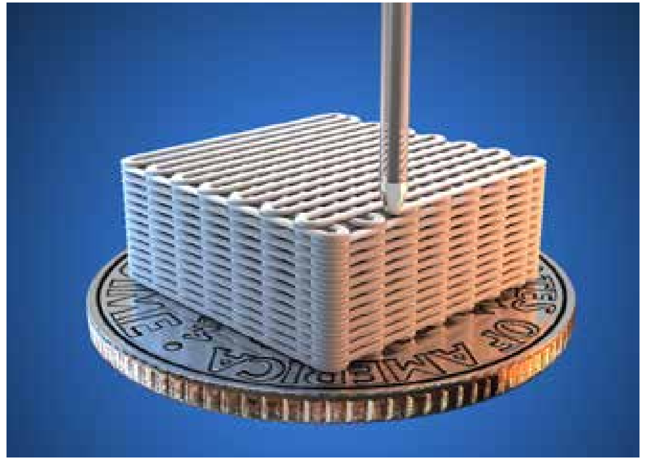
Patterned electrodes and electrophoretic deposition enable us to control particle assemblies with single-particle precision as well as control structural color via assembly of amorphous photonic materials. Controlled assembly opens the door to many potential applications including photonic bandgap crystals, nanoelectronics devices, display technologies, optical switches and filters, and smart window technologies.

Additive Manufacturing on the Rise

LLNL has emerged as a leader in additive manufacturing (AM) technology among Department of Energy laboratories. In this laboratory-wide effort, MSD staff advance the design and fabrication of new nanomaterials for feedstock materials and provide deep insights to the physics of laser-based powder bed fusion AM. We provide leadership in this field to meet the needs of LLNL programs, particularly stockpile stewardship, high-energy-density science, and renewable energy technologies. High-fidelity models are being applied to understand how defects behave in metal AM parts and how thermal histories can be tuned to control materials' phase and microstructure. Ultra-high-speed imaging of fluid flow and powder dynamics have revealed new physics governing powder-based metal AM approaches, leading to improved modeling and prediction. In addition, our scientists explore nanometer-thick, low-density foam coatings for three-dimensional objects, using a combination of electrophoretic and atomic layer deposition to control density and composition. These coatings can be applied to the inside



Copper wires, purified by a new method with near-100-percent yield, are shown in this illustration. The process separates pure nanowires from a mixture of various copper nanocrystal shapes.



Three-dimensional (3D) printing technology can be used to create graphene aerogels with a highly ordered pore structure and more predictable properties. An artist's rendering shows a 3D-printed aerogel microlattice.

of hollow cylinders, such as those used as target capsules in the National Ignition Facility's inertial confinement experiments.

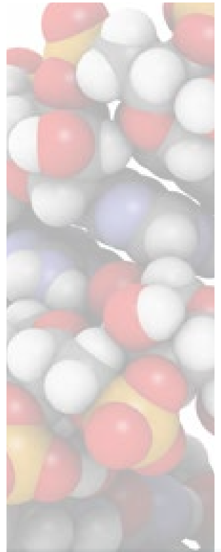
Complementing AM, dynamic transmission electron microscopy (DTEM) offers ultrafast nanoscale observation of unique material properties. With this award–winning technology, we investigate dynamic materials processes including phase transformations of metals. DTEM allows MSD scientists to probe laser–material interactions including previously inaccessible solidification dynamics of metal alloys—a key process in powder-bed AM technologies.

Scalable Results

Transitioning a nanomaterial synthesis protocol from a small to larger scale is challenging because material quality often degrades as the scale increases. MSD staff seek to develop synthesis processes resulting in high-quality materials in high quantity. This research relies on a combination of *in situ* diagnostics, machine learning and computational modeling, and rapid data analysis for efficient scaling and production of advanced nanomaterials.

Copper, a key area of focus, offers a low-cost solution for advanced nanoelectronics with electrical conductivity and thermal conductivity comparable to that of silver and gold. To meet the demands for this application, copper nanowires of high quality and purity must be produced at an industrial scale. MSD researchers developed an inexpensive multiphase method to separate small, undesirable nanoparticles from long, uniform nanowires for large-scale production.

Other nanoscale copper production efforts include multilayer alloys for protective coatings, mirrors, and sensors. Multilayers are atomic-scale sandwiches, composites made from dozens of alternating layers of materials, with each layer just 1 to 200 atoms thick. In one project, copper–copper-zirconium multilayers possess significantly higher tensile strength than nanocrystalline copper.



Spotlight on Biomimetic Materials

LLNL's biomimetic materials research focuses on designing and synthesizing materials with properties that mimic biological functionality found in nature, such as self-repair and adaptability to changing environments. Possible applications of biologically inspired synthetic materials include sensors, membranes for pharmaceutical filtration, drug delivery, platforms for nanofluidic studies, bioelectronic interfaces, and artificial cells.

One innovative project is developing synthetic biomimetic pores called carbon nanotube porins (often down to sub-nanometer in diameter), which mimic the characteristics of membrane proteins—in particular, their transport functions and ability to self-assemble into a range of membrane systems. Using an array of transport studies to understand pore permeability, along with small-angle x-ray scattering and scanning transmission x-ray microscopy, MSD scientists and colleagues from LLNL's Biosciences and Biotechnology Division probe the porins' atomic-level structures to understand the fundamental characteristics of the assembly of biomolecules in a fully synthetic scaffold.

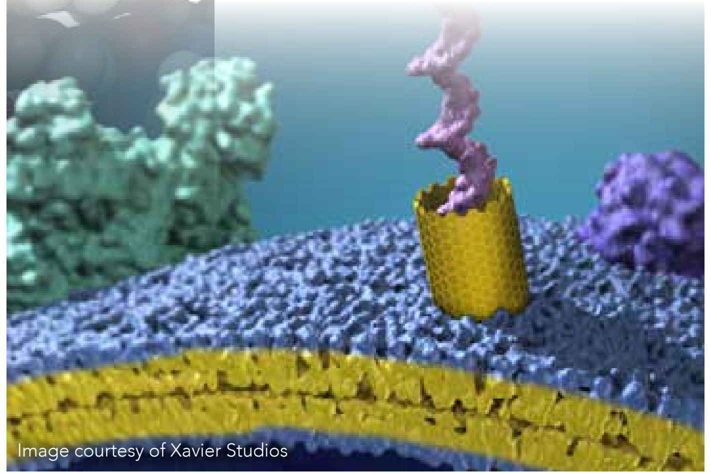


Image courtesy of Xavier Studios

Key innovations:

- *In situ* diagnostics to understand the structure of biomimetic materials
- Superior selective membrane transport properties for water purification
- Synthetic ion channels as components of more complicated systems, such as carbon nanotube porins that act as synthetic analogues of a biological channel

COMPUTATIONAL MATERIALS SCIENCE

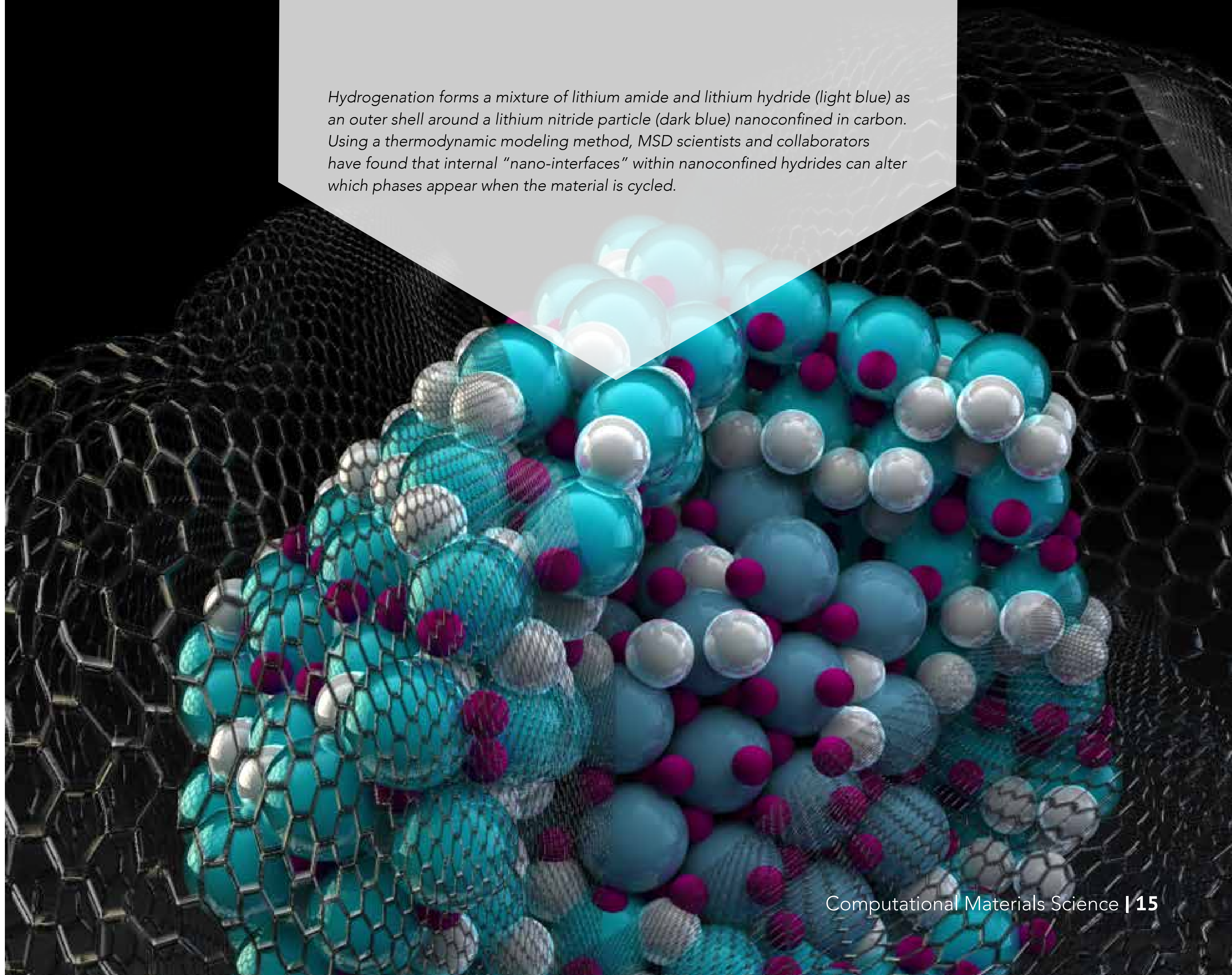
Home to some of the world's most powerful supercomputers, LLNL is a leader in predictive modeling and simulation of materials and complex interfaces. Using high-performance computing (HPC) resources, MSD experts build versatile, massively parallel computing capabilities for investigating chemical, electronic, structural, and kinetic properties of materials. These tools address critical challenges in clean energy, nuclear nonproliferation, and extreme-condition science. Some of our simulations use more than a million processors on LLNL supercomputers, and our expertise includes developing mesoscale codes like ParaDiS (see *Spotlight*), the AMPE3D phase field code, and the Gordon Bell Prize–winning atomistic codes ddcMD and Qbox.

To support both basic science and programmatic missions, we strive to ensure that MSD's computational resources provide reliable, accurate results for use in theoretical and experimental research and discovery. We also participate in LLNL's Exascale Co-Design Center for Materials in Extreme Environments, a joint effort with Los Alamos National Laboratory to address the Department of Energy's (DOE's) exascale computing goals. Sierra, LLNL's next supercomputer, will reach peak speeds of up to 150 petaflops (1015 floating-point operations per second), and MSD codes will perform some of the first simulations on the machine.

Advanced Quantum Simulations

MSD combines state-of-the-art quantum simulation approaches with HPC resources for accurate prediction of a wide range of material properties, providing opportunities to discover new materials with specific targeted properties and to examine states of matter that are difficult to access experimentally. Some of our major research areas are the development and use of quantum simulations to determine the equation of state of materials under extreme conditions; the discovery and optimization of materials for energy storage and conversion technologies; the construction of realistic materials models for applications including radiation detection, quantum computing, and optical materials; and the development of advanced theoretical models for electronic structure.

For instance, MSD's computational specialists are developing advanced sampling algorithms for use with Qbox, an open-source quantum simulation code that is used to predict properties of new materials for batteries, solar-energy conversion, light-emission devices, dielectric materials, and optical storage phase-change materials. While typical theoretical analyses of phase transition mechanisms often take a prohibitively long time to compute with standard simulation methods, these algorithms can characterize rare reactions with a more computationally efficient methodology. This innovative approach means we can accelerate the discovery and optimization of new materials properties, as well as produce data for augmenting other specialized codes.



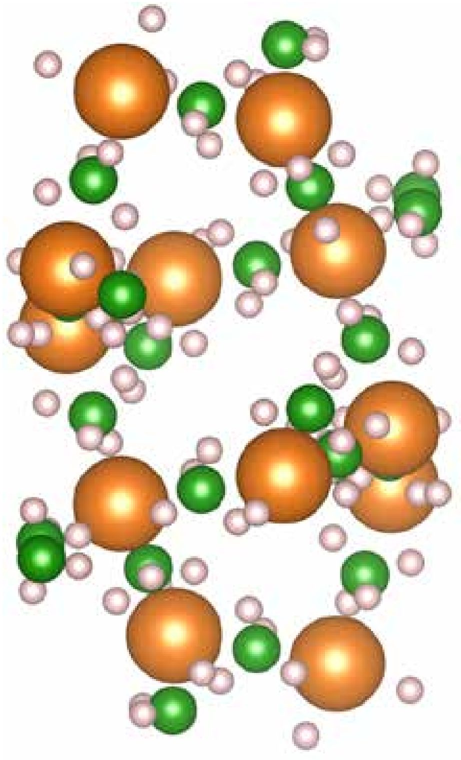
Hydrogenation forms a mixture of lithium amide and lithium hydride (light blue) as an outer shell around a lithium nitride particle (dark blue) nanoconfined in carbon. Using a thermodynamic modeling method, MSD scientists and collaborators have found that internal "nano-interfaces" within nanoconfined hydrides can alter which phases appear when the material is cycled.

Our quantum simulations for energy security include investigating the atomic-scale defects in thin-film solar cells, the electrode performance of carbon-based supercapacitors, and the potential of nanostructured materials for fuel conversion efficiency. To help optimize electrolyte/anode systems for lithium-ion battery designs, we employ large-scale molecular dynamics simulations of solid-electrolyte interphase formation. Beyond energy-related modeling, we also simulate electronic properties of glassy materials as hosts for scintillator detectors and explore the excited-state optical absorption of ion-doped solutions and optical glasses.

Leadership through Collaboration

LLNL's collaborative priorities rely on MSD's experience in computational materials science. LLNL belongs to the DOE's Energy Materials Network through the HydroGEN Advanced Water Splitting Materials Consortium, the HyMARC Hydrogen Materials Advanced Research Consortium, and the LightMAT Lightweight Materials Consortium. LLNL also directs modeling activities within the DOE's Critical Materials Institute and through the HPC4Mfg (HPC for Manufacturing) program. Our researchers maintain active roles in each of these initiatives.

For instance, as one of three leadership laboratories for HyMARC, LLNL advances the foundational understanding of materials for solid-state hydrogen storage. In this effort, MSD scientists draw upon the multiscale integration of methods such as quantum Monte Carlo, density functional theory, *ab initio* molecular dynamics, kinetic Monte Carlo, and phase-field modeling. Our HyMARC research includes nonequilibrium mass transport through bulk, surface, and interfacial environments; effects of solid–solid interfaces, phase nucleation, and growth processes on the kinetics of hydrogen chemisorption in metal hydride materials; theoretical spectroscopy simulations; and chemical bond kinetics and correlated transport processes in hydrides.



MSD researchers study the potential of magnesium tetrahydroborate and lithium imide, shown in this quantum mechanical model, for hydrogen storage systems.

Spotlight on ParaDiS

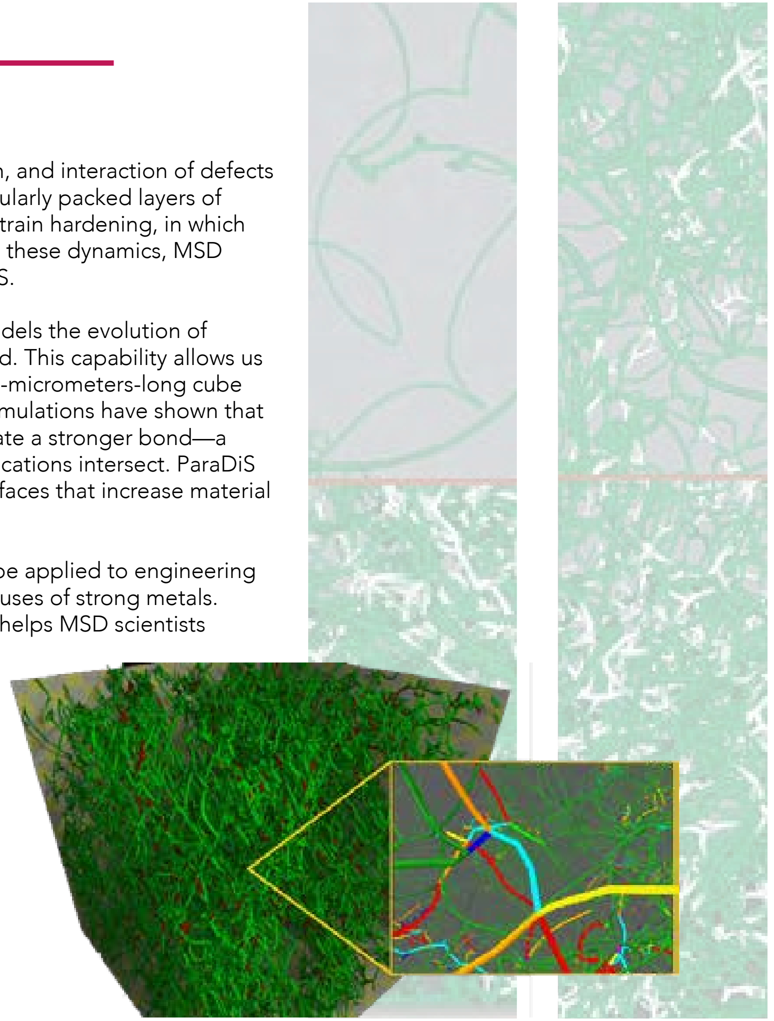
The strength of most metals derives from the motion, multiplication, and interaction of defects called dislocation lines. These defects are displacements of the regularly packed layers of atoms within the crystal structure. Dislocations are responsible for strain hardening, in which a material's strength increases as deformation increases. To explore these dynamics, MSD researchers developed the Parallel Dislocation Simulator, or ParaDiS.

Designed to run on massively parallel supercomputers, ParaDiS models the evolution of dislocations into highly complex microstructures under external load. This capability allows us to follow, for instance, tens of thousands of dislocations in a several-micrometers-long cube over several seconds with periodic boundary conditions. ParaDiS simulations have shown that three or more dislocation lines in the crystal structure of metals create a stronger bond—a nearly indestructible locking mechanism—than when only two dislocations intersect. ParaDiS also accounts for how dislocations interact with inclusions and interfaces that increase material strength.

Hardening mechanisms demonstrated by ParaDiS simulations can be applied to engineering and materials design for bridges, ships, armor, and other structural uses of strong metals. Predicting a material's performance under extreme conditions also helps MSD scientists support stockpile stewardship, as in simulations of nuclear weapon detonations.

Key features:

- Simulation of individual dislocation lines without calculational obstacles
- Accounts for boundary conditions, surface effects, and inhomogeneous loadings
- Part of a multiscale approach to predict material strength
- Run on up to 131,072 microprocessors on LLNL's BlueGene/Q machine



ENERGETIC MATERIALS

Energetic materials—high explosives (HEs), propellants, pyrotechnics—store and release large amounts of chemical energy. They are made by mixing solid oxidizers and fuels to produce a composite energetic material, such as gunpowder, or by creating a molecule that contains both oxidizing and fuel components. MSD staff, as part of the Energetic Materials Center (EMC), specialize in the modeling and experimentation surrounding the development, characterization, and effectiveness of energetic and reactive materials. We explore the energy released during energetic chemical reactions, such as in comparing composites to single-molecule materials, the mechanical response of those materials, and their long-term aging and chemical compatibility. We improve the safety, performance, and understanding of energetic materials and investigate advanced manufacturing techniques and new energetic material development.

MSD staff leverage a range of technologies in this field. We use *in situ* dynamic transmission electron microscopy to capture material response to rapid heating, while high-speed videography and time-resolved x-ray imaging shed light on combustion and deflagration processes. Through additive manufacturing, we can control and optimize the energy release of reactive materials. Our staff have created novel energetic materials, scaled them up to custom feedstocks, manufactured them into unique systems, and tested their performance.

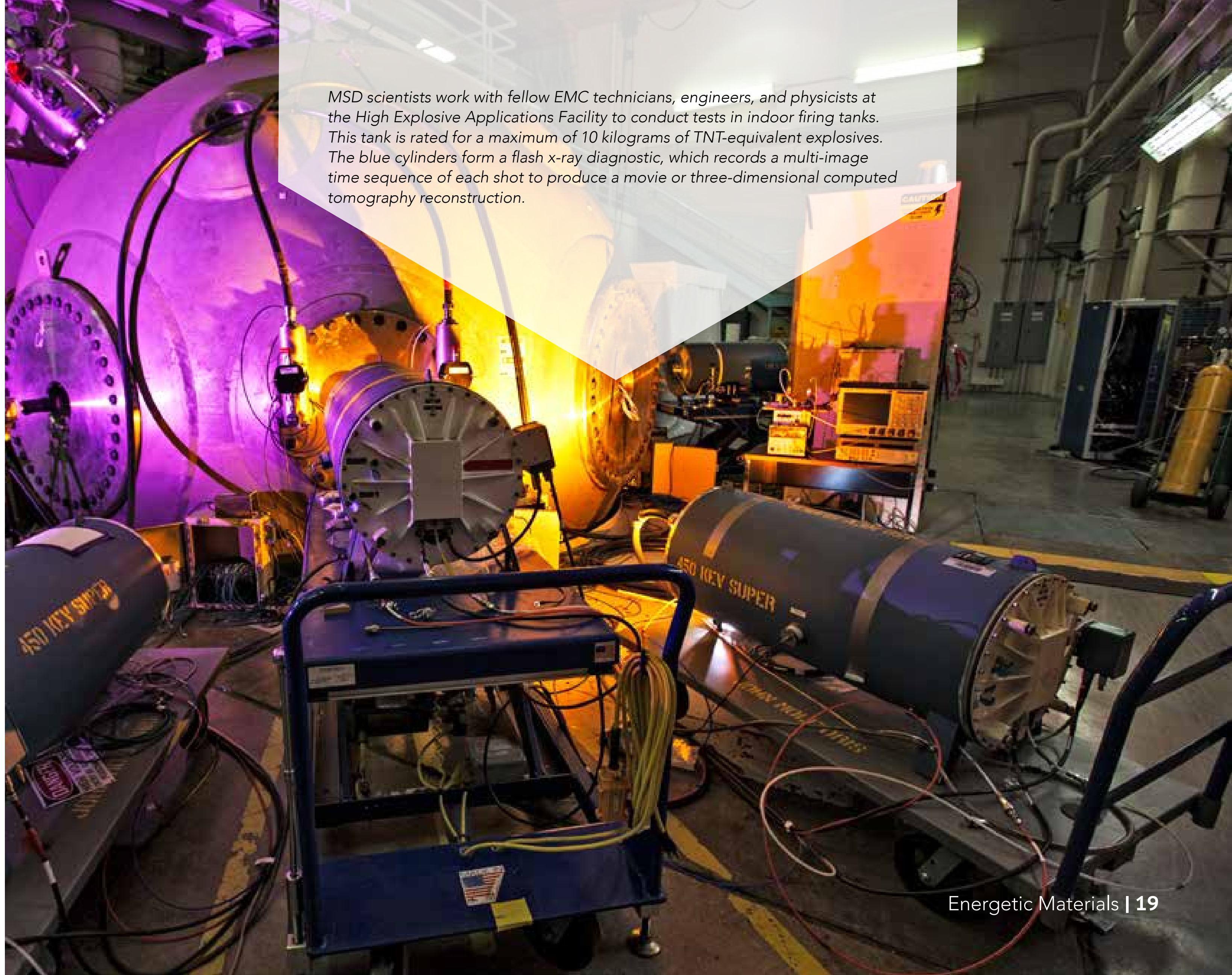
Extreme Conditions

Subjecting small material samples to extreme pressure and temperature is a mainstay of MSD research within the EMC. We tightly couple modeling and experimental efforts to understand chemical decomposition and synthesis that occur under extreme conditions. Observing chemical reactions, phase changes, and other behaviors of materials in "stressful" situations helps us strengthen the nation's security through science-based stockpile stewardship, counter-proliferation, advanced munition development, and transportation security.

Experiments driving chemical reactions with long- and ultrashort-pulse lasers, ultrafast lasers, gas guns, and explosive detonations access different regions of high temperature and pressure, where materials can change phase (see *Spotlight on Detonation Science at User Facilities*). LLNL's dynamic compression platforms and techniques span seven orders of magnitude in strain rate and support a range of experiments—from hydrogen experiments at the National Ignition Facility (NIF) and gas-gun studies on overdriven high explosives to low-speed impact safety research. The firing tanks at the High Explosives Applications Facility (HEAF) and Site 300 resources accommodate an extensive range of initiation, detonation, and hazard response. MSD researchers also drive the field forward with new diagnostics and more powerful platforms for HE research.

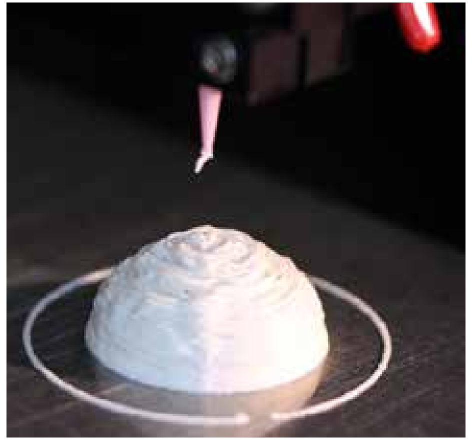
Dedicated Facilities

Operated by LLNL's Weapons and Complex Integration Directorate, the onsite HEAF provides a high-tech



MSD scientists work with fellow EMC technicians, engineers, and physicists at the High Explosive Applications Facility to conduct tests in indoor firing tanks. This tank is rated for a maximum of 10 kilograms of TNT-equivalent explosives. The blue cylinders form a flash x-ray diagnostic, which records a multi-image time sequence of each shot to produce a movie or three-dimensional computed tomography reconstruction.

venue for research and development on the performance of HEs. At this facility, MSD theoretical and experimental scientists work together toward a detailed understanding of the chemistry and physics of energetic materials for our national security customers. The EMC's interdisciplinary teams study how HE characteristics (detonation performance, mechanical response, chemical compatibility) change over time. This research advances development of nuclear and conventional munitions as well as rocket and gun propellants for applications in warhead science, homeland security, demilitarization, and industrial uses.



Additive manufacturing, or three-dimensional (3D) printing, holds great promise for customizing material behavior. MSD staff have demonstrated that 3D printing can be used to tailor the dynamic behavior of materials.

Site 300 is home to kilogram-scale processing for a range of energetic materials. There, MSD scientists and their Engineering counterparts scale new energetic material compounds up to 50 pounds and formulate pressed parts for large-scale integrated science experiments. Thermal control units house experiments that quantify chemical mechanisms associated with long-term aging. We measure and model sorption, transport, and chemical reaction kinetics to predict system-level aging, outgassing, and chemical compatibility. This work increases confidence in fielded systems and improves design and surveillance programs.

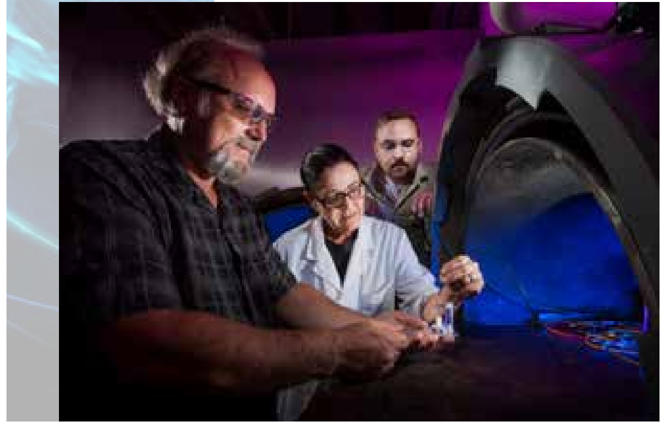
Experiments conducted at HEAF and Site 300 benefit from precision diagnostics such as x-ray radiography and embedded particle velocity/pressure measurements. HEAF provides multiple firing tanks, a propellant-driven gun tank, a laser machining center with femtosecond pulse speed, and other material characterization laboratories. These facilities enable MSD to respond to federal and industry demands for energetic materials applications.

MSD staff also nurture collaborations at external facilities. At the University of Rochester's Omega Laser Facility, we investigate new physics regimes with laser-initiated dynamic compression studies. Argonne National Laboratory's Advanced Photon Source provides synchrotron radiation beams for HE experiments, including high-resolution imaging for detailed MSD-designed studies of detonation processes. Stanford's Linear Accelerator, the Linac Coherent Light Source (a free electron laser), is the home for joint studies with LLNL Physics staff where we apply phase-contrast imaging to evaluate strain fields in collapsing HE hot spots.

Spotlight on Detonation Science at User Facilities

Key aspects of stockpile stewardship include fine-tuning and experimentally observing high-explosive (HE) detonation processes and developing computer models to predict the behavior of different HEs. MSD's energetic materials research answers long-standing questions in detonation science concerning the mechanisms of initiation, HE morphologies, and models of energy release and chemical reactions. We explore ways of characterizing, measuring, and imaging HE detonation processes, pushing toward higher temporal and spatial resolution within our experimental and modeling capabilities.

To improve our understanding of the physical and chemical processes in HE materials, we employ chemical equilibrium and kinetic modeling informed by experiments and simulations. We use state-of-the-art resources including LLNL's thermochemical code called Cheetah as well as the intense, pulsed x-rays generated by the Advanced Photon Source (APS). At the APS, MSD staff explore the evolution of condensate morphologies and compositions generated by different explosives, which create a unique fingerprint for each explosive type and detonation pressure. This work enables munitions design, detonation forensics, and rapid assessment of existing, newly synthesized, and hypothetical energetic compounds. Advances in HE science also reduce costs and accelerate the development cycle for new explosives.



Key features:

- Three-dimensional algorithms to reconstruct detonation systems
- X-ray imaging to observe nanoscale detonation phenomena with unprecedented resolution
- Predicting the size and phase of carbon nano-condensates
- Applying carbon condensation kinetics to modeling of energy release during detonation

OPTICAL MATERIALS

From high-power laser systems to groundbreaking telescopes, optics are critical to many national security missions. MSD's priorities are to improve optical performance and extend the lifetime of optics while reducing unit cost. We pursue innovations affecting the mirrors, lenses, gain media, diffraction gratings, protective coatings, and other optical components that enable multiple LLNL national security programs.

Our expertise in fundamental optical materials science encompasses all stages of an optical component's life—from design to fabrication and use. Many of MSD's homegrown technologies have transferred into production both onsite and offsite. As high-profile examples, we support National Ignition Facility (NIF) experiments through research in properties of optical materials and in the initiation and propagation of optical damage due to high photon fluence. As part of an international collaboration, MSD scientists developed processes to enable deployment of specially designed, titanium-doped sapphire amplifiers for the High-Repetition-Rate Advanced Petawatt Laser System via a dedicated, multi-year process.

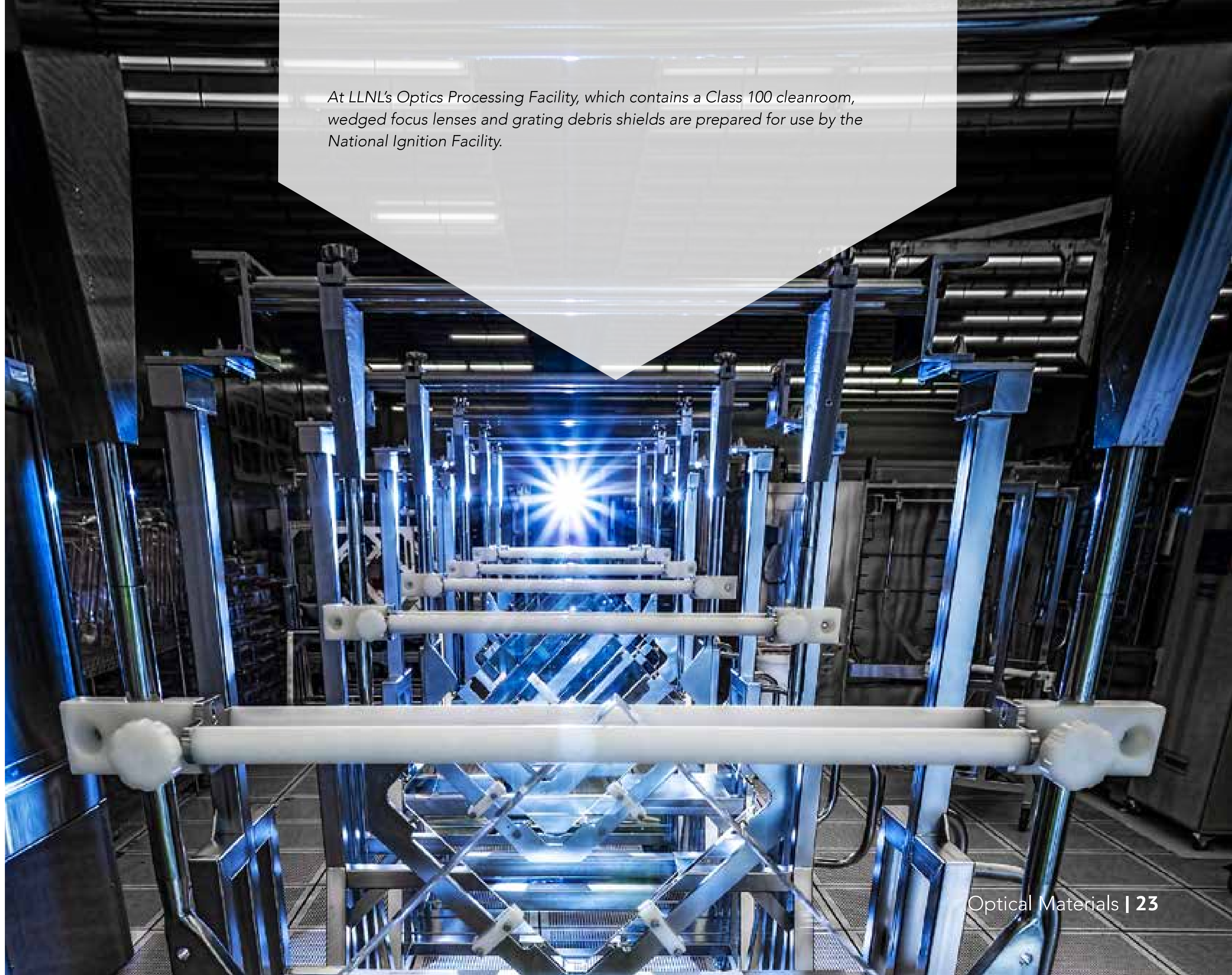
Enabling Design Breakthroughs

Opportunities abound for innovation in the optical fabrication field. MSD's research and development in novel bulk materials include glass melting, crystal growth, and additive manufacturing (AM) combined with ceramics processing. With new technologies, we aim to transform optical system design by providing access to optical components in previously unavailable formats. For instance, we have begun developing a new class of bulk optical materials and components with structural and compositional gradients that cannot be created by conventional methods. These components have functionally graded material properties—that is, refractive and other properties resulting from changes to composition or structure, not shape. In a breakthrough for AM technology, our scientists use direct-ink writing to print optical-quality glass, lenses with a gradient refractive index, and gradient-composition laser gain media. With other AM techniques, we can produce ultralight, ultrastiff microlattice supports for mirrors.

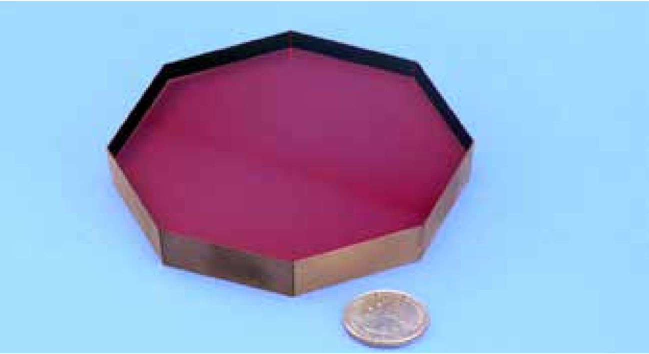
MSD scientists work with partners at NIF to manufacture a variety of specialty diffractive optics for researchers worldwide. This roster of components includes multilayer dielectric and gold-overcoated diffraction gratings for laser pulse compression, multilevel-etched Fresnel lenses and phase plates, segmented Fresnel lenses, and continuous-contour optics. These custom materials span a range of length scales.

Processing and Perfecting

Most advanced laser systems are limited by optical damage, which can affect a mission's success. MSD takes a science-based approach to understanding laser–matter interactions (that is, how laser light



At LLNL's Optics Processing Facility, which contains a Class 100 cleanroom, wedged focus lenses and grating debris shields are prepared for use by the National Ignition Facility.



Optics such as this titanium-doped sapphire amplifier slab are prepared to exacting specifications—in terms of shape, surface finish, and final assembly tolerances—using methods developed by MSD staff and collaborators.

interacts with optical materials at very high fluence) and develops ways to improve the damage resistance of optical components. We use simulations and experiments to understand optical processing and finishing techniques and their effects on material removal, surface shape and quality, and damage resistance. We have designed novel laser- and chemical-based post-processing methods that, along with other damage mitigation techniques, improve the lifetime and performance of LLNL's optical systems (see *Spotlight on Convergent Polishing*). For example, a chemical-etching method uses optimized hydrofluoric acid to remove damage precursors, such as the defect layers associated with fine scratches or surface impurities. This method reduces defects by more than two orders of magnitude and enables a 60 percent increase in the amount of energy that can pass through an optical element. Another technique called meter-scale reactive ion beam etching uses both physical (ion sputtering) and chemical (ion reaction at surface) etch processes during fabrication of high-resolution grating structures. MSD scientists have also created a nanometer-precision technology called magnetorheological finishing, which improves the damage resistance of freeform optics. This technology has been used to imprint high-gradient topological features of corrective optics for high-power laser systems.

Additional efforts include using high-sensitivity, high-resolution characterization tools to detect contaminants while improving optical designs. Sensitive multimodal and photoluminescence imaging methods measure the effects of repeated exposure to high- and low-fluence laser pulses. This work yields valuable information for predictions of contamination scenarios and debris-removal techniques.

Spotlight on Convergent Polishing

Polishing glass optics to their final shape using conventional full-aperture methods is labor intensive with multiple process iterations. MSD's innovative convergent polishing technology reduces the cost, effort, and time required to polish optical components. This technology won an R&D 100 Award in 2014 and is critical for manufacturing optics used in high-power lasers, imaging systems, and lithography.

LLNL scientists have developed the CISR (convergent, initial-surface-independent, single-iteration, rogue-particle-free) polisher in which a workpiece "converges" to the desired shape and size. Any flat or spherical workpiece can be polished in a single iteration without operator intervention. Initial and intermediate metrology measurements, which add to personnel time and workpiece handling risk, are not required.

The CISR polisher does not sacrifice quality for efficiency. Convergence technologies are built into its design, eliminating the need for real-time feedback, diagnostics, or computer control without risk of over-polishing. The system provides high surface quality by controlling particle-size distribution in the polishing slurry and by preventing the introduction of rogue particles that can cause scratches. For example, surface height variation can be reduced to 330-nanometer peak-to-valley flatness for a 26-centimeter workpiece.

Key advances:

- Custom-weighted septum to enable convergence stability and uniform temperature and slurry distribution
- Hermetically sealed, high-humidity polishing chamber
- Innovative bulk acid etching, pitch button blocking, and radial stroke functionality
- Precision-engineered filtration and chemical slurry stabilization systems

TARGET MATERIALS

To further LLNL's national security mission, MSD scientists develop novel materials and precision assembly and characterization techniques for experiments at the National Ignition Facility (NIF) and other high-power laser facilities. Different types of targets exemplify the range of scenarios we are called upon to address—from investigating the physics of inertial confinement fusion (ICF) reactions to supporting high-energy-density (HED) science. Our target materials are even used to research the early stages of star formation.

With colleagues both internal and external, MSD conducts basic and applied research to support target fabrication with innovations in nanofoams, coatings, adhesives, thin films, condensed hydrogens, advanced material processing and characterization. For example, our extensive work in target capsule support and suspension technologies has yielded new techniques and materials, such as silk-like nanotube yarns and reinforced fill-tube structures, that must be strong enough to survive handling and hold the capsule in place without interfering with experimental results.

The small-scale phenomena and extreme conditions that targets encounter during experiments make the results highly susceptible to any manufacturing imperfections. All targets must meet precise specifications for density, thickness, uniformity, shape, roughness, internal microstructure, accuracy of joints and parts, surface finish, and other factors. Accordingly, MSD scientists are developing equipment, processes, and procedures needed to field these experiments, including new material fabrication, measurement, handling, and inspection methods. Materials science expertise is essential for designing, commissioning, and enhancing capabilities for target systems.

High-Performance Coatings

As a vessel for the nuclear fuel, an ICF target's capsule must be completely spherical and impervious to leaks. A capsule may also contain internal layers with dopants that increase x-ray absorption, and we strive for precise control over dopant concentrations and uniformity. MSD researchers develop coating technologies to fabricate ICF fuel capsules with exquisite control of geometry and elemental composition. Our coating work spans a broad range of materials, including different metals, diamond, and plastics. We use a broad range of coating techniques, including evaporation, ion sputtering, chemical vapor deposition, electroplating, and spin-coating.

Our staff study polymer behavior in various chemical and thermal environments. We produce strong, freestanding, ultra-thin polymers for multiple applications (*see Spotlight on PEEL Technology*). These films can be made only a few nanometers thick and support more than 10,000 times their own weight. MSD also develops novel sputter coating and electroplating techniques. In one key initiative, we combine the

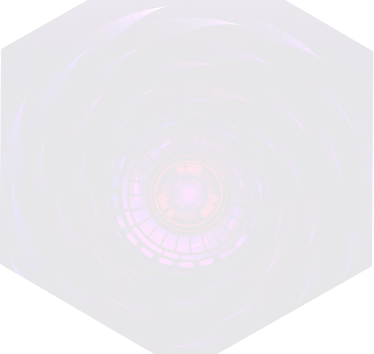
Each target undergoes a series of fabrication tests, including materials testing to measure specific properties and determine feasibility, assembly testing to check for centering and static stability, dynamic testing for vibration and other factors, and cryogenic layering tests.

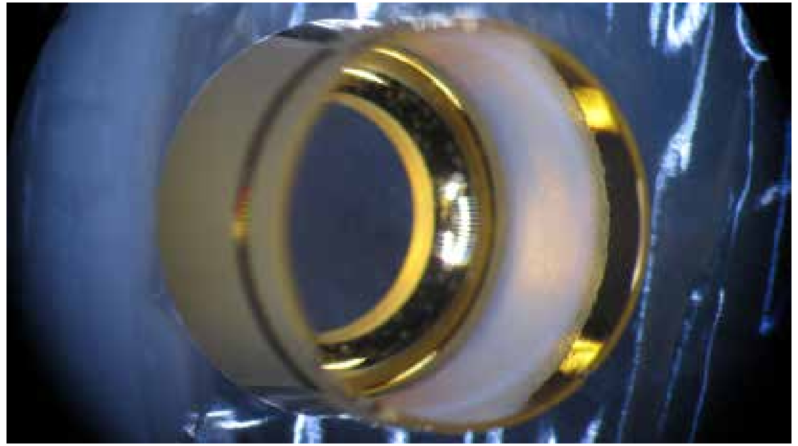
processing advantages (conformable, pure, and scalable) of chemical vapor deposition with the tailored material properties of traditionally synthesized polymers to create chemically stable, optically transparent polymers that simplify target fabrication and improve target performance. Beyond targets, these polymer coatings may be useful for optical, electronic, biomedical, or sensing devices.

Nanofoams

Foams play critical roles in target design, whether as ultrabright x-ray source targets, a capsule cushion or a hohlraum liner in ICF targets, or as part of the physics package for HED experiments. Density, shape, and spatial uniformity are important foam characteristics—especially at the small length scales required for laser targets—and MSD scientists explore these properties in different materials including pure metals, oxides, and polymers. We are developing new material synthesis techniques to expand the ranges of material composition, foam density, and homogeneity than are possible with the current technologies.

We are exploring both traditional sol-gel chemistry and emerging foam fabrication methods that involve the self-assembly of nanoscale blocks (such as nanowires and nanosheets) and submicron-scale additive manufacturing. These nanofoams are also attractive for other applications, including sustainable energy solutions such as hydrogen and electrical energy storage.





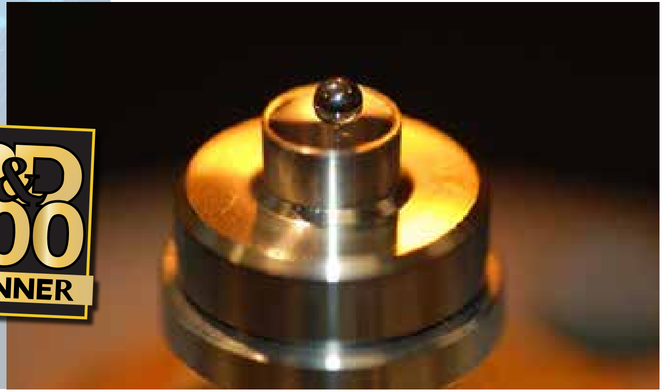
Computer simulations suggest that hohlraums lined with low-density foams could improve hohlraum drive symmetry in ICF experiments by mitigating wall motion and other issues. With new materials and additive manufacturing technology, MSD target designers can tailor the desired physics characteristics by varying foam densities and compositions.

Spotlight on PEEL Technology

Thin polymer films are typically made by dissolving a polymer material into a solvent and depositing the mixture onto a substrate. To address challenges in liftoff—the process of lifting the film from its deposition substrate—MSD staff experimented with direct delamination of the film by pretreating the substrate with a layer of an electrically charged polymer known as polyelectrolyte.

In collaboration with General Atomics, MSD scientists developed a novel technology called polyelectrolyte enabled liftoff (PEEL), which produces freestanding polymer films that are larger, stronger, and thinner—as thin as 6 nanometers—than those made conventionally. Moreover, PEEL's water-based, self-optimizing surface chemistry can create films with areas of 100 square centimeters or more. In the image below, the stainless-steel ball weighs 80,000 times more than the film supporting it.

PEEL has earned an R&D 100 Award and a Federal Laboratory Consortium technology transfer award. The process is scalable in size and quantity and applicable to a variety of scenarios. For example, NIF scientists rely on 30-nanometer membranes to suspend fuel capsules inside hohlraums. PEEL-engineered films allow researchers to study how film thickness affects fuel capsule performance, leading to improved target design.



Key features:

- Membranes for catalysis, sensing, wound healing, and laser targets
- Optical gating devices
- Reverse-osmosis filtration
- Tissue engineering for fragile assemblies
- Transferable films for microelectromechanical systems

ACTINIDES AND LANTHANIDES

Actinides (elements 89 through 103), both naturally occurring and synthetically produced, are complex, scientifically interesting elements that play an important role in national security and nuclear energy production. Rare-earth lanthanide elements are found in many high-tech devices, and actinides are key components in our enduring nuclear stockpile. LLNL's role in the National Nuclear Security Administration's Stockpile Stewardship Program requires radiation detection technologies, materials science experiments, predictive modeling, high-energy-density science, and nonproliferation strategies.

With expertise spanning the gamut from surface science to magnetism to metallurgy, MSD scientists support these global and national security missions through experimental and theoretical work on actinide and lanthanide materials. We strive to understand the structural, chemical, mechanical, magnetic, and electronic properties of 4f- and 5f-electron systems.

Actinides and the Stockpile

Plutonium stands at the transition point at which 5f electrons change from forming bonds with other elements to being chemically inert. Its isotopes vary in stability and behavior during decay, and the element is sensitive to changes in temperature, pressure, and composition. To help ensure the reliability and safety of the nation's nuclear stockpile, MSD researchers study the effects of plutonium's chemical and metallurgical properties as it ages and undergoes radioactive decay (see *Spotlight on High-Performance Probes).*

Uranium also plays an important role in the country's enduring stockpile. We use characterization techniques such as transmission electron microscopy, scanning electron microscopy, x-ray diffraction, optical metallography, and x-ray photoelectron spectroscopy to understand the atomic-, nano-, and microstructures that determine the properties important for stockpile applications. As these structures are strongly influenced by the materials' processing route, we investigate advanced fabrication techniques, such as near-net-shape casting and other manufacturing routes.

MSD's uranium research also includes alloy studies. Recent work reveals complex mechanical properties when the element is alloyed with 14-atomic-percent niobium, a superconducting material. We are investigating phase transformations that occur with slow and rapid cooling of uranium–niobium, as well as conditions under which its shape-memory behavior can be manipulated.

In addition to a wide variety of laboratory experiments, MSD scientists use state-of-the-art computational facilities at LLNL to predict the behavior of actinides and lanthanides under a variety of conditions. For example, MSD scientists use these high-performance computing resources to simulate structural and strength changes that occur in plutonium isotopes and other actinides over time. Coupled with experiments, these simulations inform

MSD's transmission electron microscopy (TEM) capabilities support many experimental needs including compositional analysis, microstructural imaging, and studies of material aging. Our high-resolution instrumentation, such as the R&D 100 Award–winning DTEM (dynamic TEM), enables direct observation of unique mechanical properties controlled by features at the nanoscale.

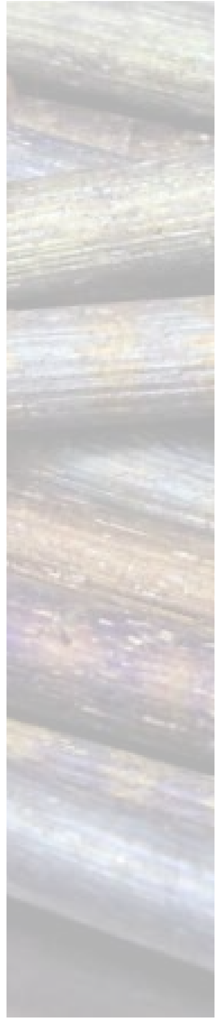
MSD researchers developed a new transparent ceramic scintillator for detectors in high-energy radiography. The GLO (gadolinium–lutetium–oxide) scintillator uses lanthanide elements and earned an R&D 100 Award in 2016.

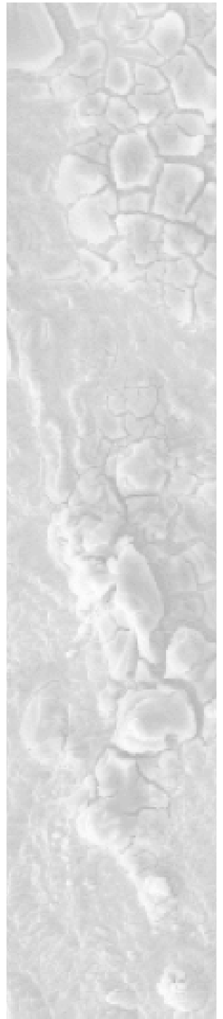
decisions about the future of the nation's stockpile.

Energy Breakthroughs with Lanthanides

Lanthanides are the "special sauce" of advanced technology. From phosphors in modern lighting to high-strength magnets and new classes of structural materials, small quantities of rare-earth elements are essential to many clean-energy material innovations in the last 50 years. Interest in these elements will increase as additive manufacturing (AM) enables deployment of multifunctional and functionally graded materials.

As members of the Department of Energy's Critical Materials Institute (CMI), MSD scientists enable innovation in U.S. manufacturing and enhance the nation's energy security. The CMI aims to reduce dependence on rare-earth and other critical materials through diversifying supply, developing substitutes, and improving recycling strategies. Working with external partners, we have developed new formulations for substitute materials with equivalent or superior properties to those found in rare-earth elements. For instance, standard phosphors used in fluorescent lighting consume more than 1,000 metric tons of rare-earth oxides each year. MSD staff have created a red-light emitting phosphor that is rare-earth free. Similarly, we are working to develop reduced rare-earth content permanent magnets and use AM for the production of net-shape magnets, minimizing waste and enabling difficult shapes. Another CMI team has developed a new class of lightweight aluminum–cerium alloys for use in high-temperature applications.





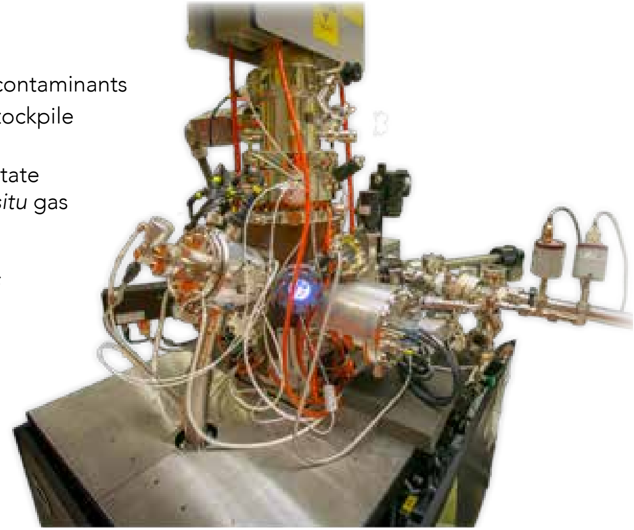
Spotlight on High-Performance Probes

MSD's actinide research relies on high-performance tools to investigate these elements' properties. A pair of new experimental capabilities, the scanning Auger nanoprobe (SAN) and the x-ray photoelectron spectroscopy microprobe (XPS), came online at LLNL's plutonium facility in 2016–2017 to explore key questions in this field.

SAN and XPS provide definitive, high-resolution identification and distribution of chemical species on solid material surfaces. These advanced analytical electron spectroscopies can detect elements of lithium to plutonium with spatial resolution less than 8 nanometers, so MSD scientists investigate the elemental composition and chemical bonding on surfaces with sub-micron spatial resolution. With these tools, we can also study catalytic reactions in other materials with superior resolution at grain boundaries and surfaces to quantify defects and validate data models that predict the degradation of material properties.

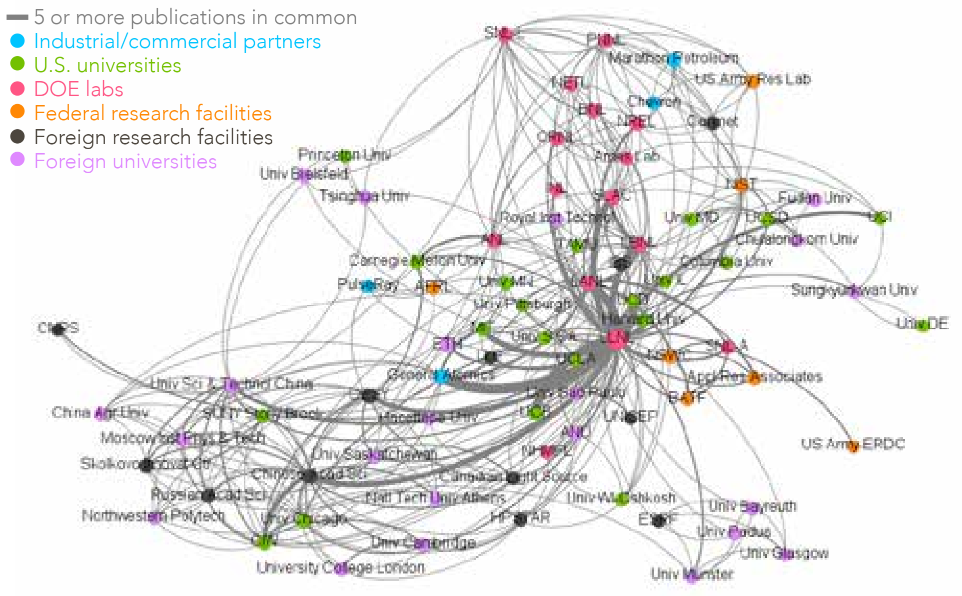
Key applications:

- Analyze surface and background contaminants
- Characterize aging processes in stockpile materials
- Perform elemental and chemical state mapping, depth profiling, and *in situ* gas reactions
- Measure the density of occupied electronic states and uniformity of elemental composition



MATERIALS SCIENCE BEYOND THE LABORATORY

As ambassadors of LLNL's materials science and technology, MSD nurtures strategic collaborations and partnerships with academia and industry. We also work with other national laboratories to advance the Department of Energy's (DOE's) and National Nuclear Security Administration's national security objectives. Working with LLNL's Innovations and Partnerships Office, our research often produces patents with licensing potential for commercial applications. Our technology-transfer successes help sustain economic security—not only for our regional neighbors in Silicon Valley, but also the whole nation.



As part of the High Performance Computing for Manufacturing (HPC4Mfg) Program, MSD researchers and collaborators use LLNL's high-performance computing to understand impacts of manufacturing processes on part performance and to enable the design and building of new devices and materials with unique physical and microstructural properties. The program's goals are to advance clean-energy technologies, increase the efficiency of manufacturing processes, accelerate innovation, reduce the time-to-market for new technologies, and improve the quality of products.

Energy security is a crucial part of LLNL's missions. The DOE's Office of Energy Efficiency and Renewable Energy established the Energy Materials Network to tackle clean energy challenges—hydrogen storage, fuel efficiency, improving photovoltaic modules, biomass conversion, among others—with materials science solutions. Over the years, our scientists have researched water–materials interactions, solid–solid interfaces, electrochemical interfaces, and non-equilibrium processes.

MSD works with local, national, and international collaborators.

MSD also invites collaborators onsite, regularly hosting scores of undergraduate and graduate student collaborators and interns. Visiting professors and staff from U.S. and international laboratories are frequently found working side by side with our staff. LLNL's Livermore Valley Open Campus (LVOC), a group of publicly accessible facilities, includes the High Performance Computing Innovation Center and the Advanced Manufacturing Laboratory. With expertise in computational materials science and materials design and fabrication, MSD maintains an active presence in LVOC's programs and outreach.

MSD scientists publish regularly, frequently with external research partners.

THE FUTURE OF MATERIALS SCIENCE

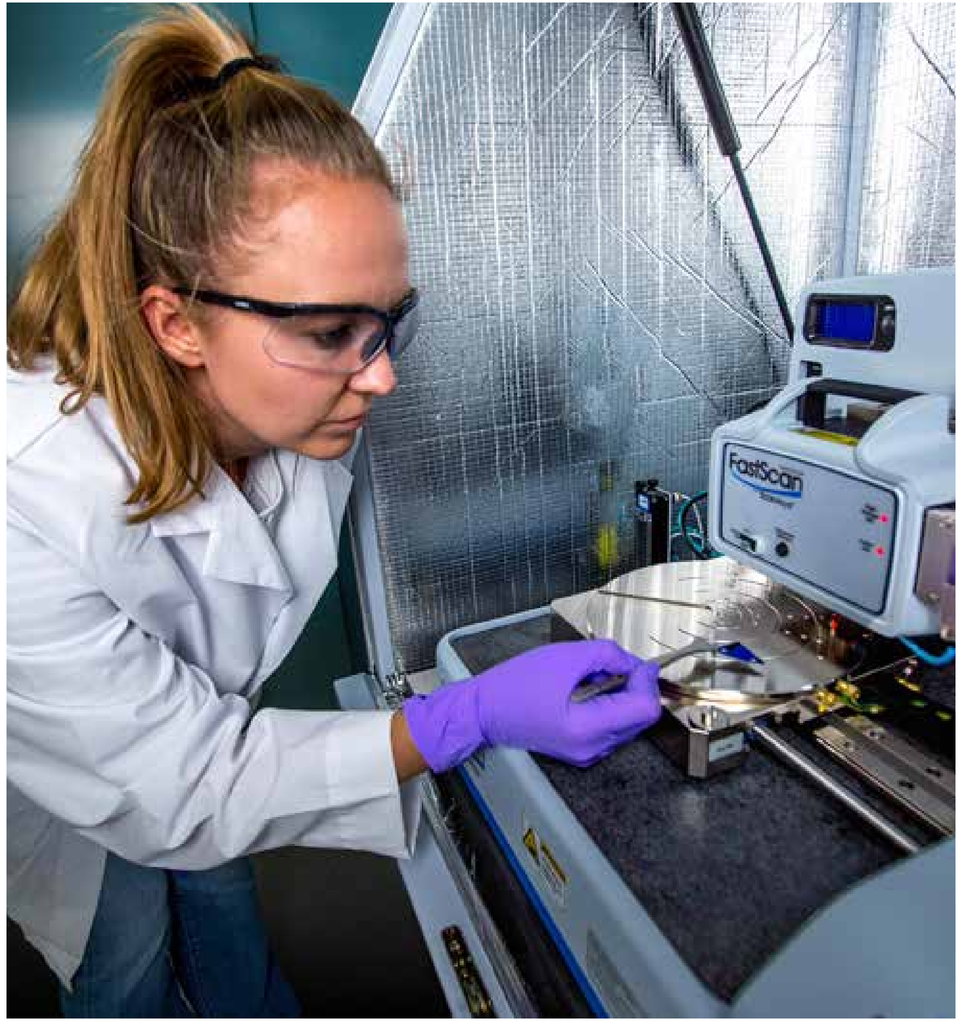
MSD is, and aims to remain, at the forefront of materials science. Our laboratories house leading-edge instruments and equipment, which MSD scientists augment with in-house innovations, such as a tabletop shock compression system for ultrafast characterization and a safe encapsulation system for laser micromachining of highly hazardous materials. To increase the rate of scale-up and adoption of new materials, another key pursuit is the computationally enabled acceleration of materials discovery, scale up, qualification, and certification.

MSD continues to invest in experimental resources across numerous areas, including nanoscale feedstock development, accelerated aging methodologies, advanced high-explosive synthesis and diagnostics, and functionally graded optical materials. We are advancing research in metallurgy, material corrosion and degradation, additive manufacturing methods using novel multifunctional feedstocks, and nanomaterial design and scale up. We also see a future for new characterization tools—from observing grain-scale kinetics to identifying defects within multi-layer materials.

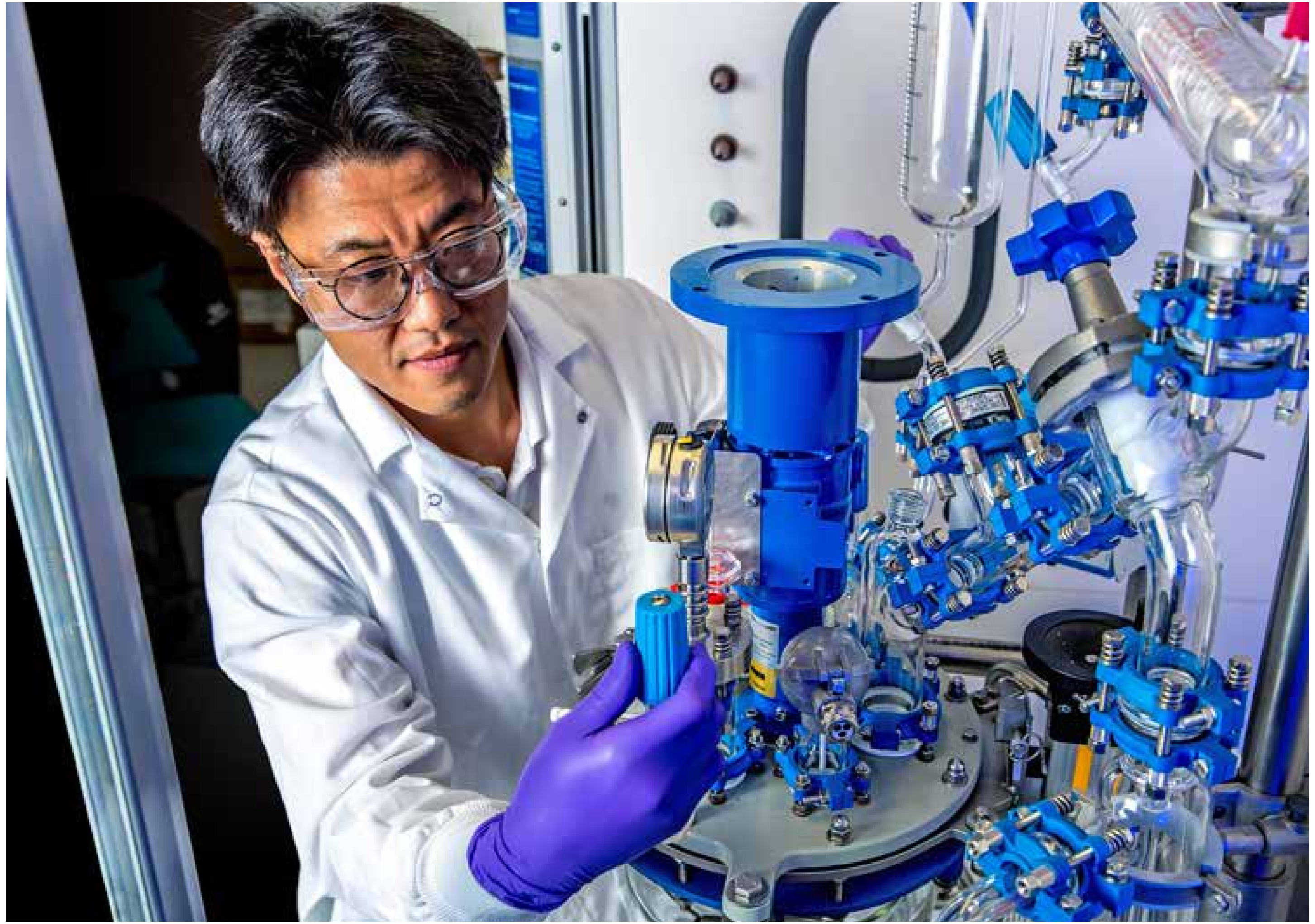
Ranked among the world's most powerful supercomputers, LLNL's Sequoia supports many of MSD's modeling and simulation projects.

LLNL is bringing exascale computing power online as the field of predictive modeling grows. To further investigate materials in harsh or extreme environments, our staff will extend coding capabilities to additional time and length scales. High-throughput modeling that leverages big data, informatics expertise, and integrated machine-learning algorithms will facilitate materials discovery and manufacturing.

Above all, MSD's future depends on a strong multidisciplinary workforce to maintain our commitment to LLNL's missions. We look forward to welcoming and developing the next generation of materials scientists through ongoing recruiting efforts and our dynamic postdoctoral and internship programs. Mentoring is vital to this strategy, as is participation in the larger scientific community. MSD encourages involvement in scientific associations, boards, symposia, and other professional opportunities. Thanks to our staff, mission-driven materials science is more than a possibility at LLNL—it is reality.



MSD's feedstock development requires several high-resolution technologies for nano- and micron-scale particle analysis.



Lawrence Livermore
National Laboratory

MSD

pls.llnl.gov/msd
materialsscience@llnl.gov

Prepared by LLNL under Contract DE-AC52-07NA27344. LLNL-BR-749986