PROGRESS AND PLANS OF NATIONAL NANOTECHNOLOGY INITIATIVE (NNI) AGENCIES

February 2019

Department of Defense (DOD)[1]

Summary

DOD recognizes the importance of nanotechnology and nanomaterials to the ongoing modernization of the current force, and also recognizes the revolutionary changes that these technologies may bring to our future warfighting capabilities. The department is committed to maintaining a broad base of foundational nanoscience research across the department's laboratories, and will continue to collaborate with other Federal agencies in this arena. The department will continue to emphasize the transition of evolving nanotechnologies into the DOD industrial base through the use of DOD ManTech (Manufacturing Technology), Defense Production Act Title III, Defense Innovation Unit, Manufacturing USA institutes, and Small Business Innovation Research (SBIR) programs.

Air Force

Nanotechnology-Enabled Devices

DOD/Air Force Research Laboratory (AFRL) and academia: *CNT-Based Artificial Synapse.* A carbon nanotube (CNT)-based synaptic resistor ("synstor") has been invented by Air Force (AF)-sponsored research group at UCLA to emulate the analog convolutional signal processing, correlative learning, and nonvolatile memory functions of neurobiological synapses. This artificial synapse is made from organic materials with a semiconducting CNT network as its channel and ion-doped polymer as its gate dielectric layer. A synstor crossbar circuit was demonstrated to concurrently process and learn from the signals in parallel analog mode with an energy efficiency of 10^{15} floating-point operations per second per watt (OPS/W), which is more than six orders of magnitude higher than that of the Summit supercomputer. The follow-up work will connect the synstors with artificial neurons to form the spike neuromorphic intelligent circuit (SNIC) and then the SNICs with distributed networks of sensors/actuators to demonstrate multifunctional intelligent systems for aerial vehicles.

DOD/AFRL: *Novel Carbon Nanotube Isopropyl Alcohol Gas Sensor.* Breathing air quality in both DOD and commercial air flights has come under increased scrutiny due to the identification of volatile organic compounds (VOCs) from the engine bleed air used to provide oxygen to the pilots and passengers. Specifically, the exposure to isopropyl alcohol (IPA), a main component of ice-inhibitor and cleaning solvent, has been hypothesized to be a key contaminant leading to air sickness before, during, and after flight. AFRL developed a novel CNT IPA sensor by: (1) integrating a polymer as an IPA capture matrix, (2) adopting a redox chemical additive as an IPA oxidizer, and (3) fabricating a CNT transistor as an electronic sensing conduit. This research demonstrates the ability to not only detect IPA in unfiltered laboratory air, but also to selectively discriminate IPA from other contaminants in comparison to a state-of-the-art commercial VOC sensor. Ultimately, this study opens up the pathway to selective electronic sensors that can enable real-time monitoring in a variety of environments for force health prevention and protection. A patent application has been filed .

DOD/AFRL and industry: *Dielectric Metasurfaces for Optical Components.* Singly negative metamaterials with exceptional reflectance (i.e., superior to all metallic mirrors in chosen portions of the electromagnetic spectrum) using a single array-layer of silicon nanopillars were developed and fabricated, in conjunction with SRI. Such single-layer metamaterials can augment current multiline filter designs and create mirrors with no chromatic aberrations, which are currently seen in broadband reflectors composed of multilayer dielectric stacks. Rapid simulations are enabling the population of a database with optical properties resulting from various geometries and compositions of such metasurfaces. Machine learning tools are being applied to the database to efficiently discover designs for desired optical properties. Through tailored designs for nanoresonators and transmissive/reflective optics, such all-dielectric (i.e., non-metallic) metamaterial designs have promise in intelligence surveillance and reconnaissance (ISR) and directed energy (DE) applications.

DOD/AFRL and academia: *Nano-Optic Endoscope for High-Resolution Optical Coherence Tomography* In Vivo*.* Acquisition of high-resolution images from within internal organs using endoscopic optical imaging has numerous clinical applications. However, difficulties associated with optical aberrations and the trade-off between transverse resolution and depth of focus significantly limit the scope of applications. An AF-funded Harvard University team integrated a metalens, with the ability to modify the phase of incident light at subwavelength level, into the design of an endoscopic optical coherence tomography catheter (termed nano-optic endoscope) to achieve near diffraction-limited imaging through negating non-chromatic aberrations. Remarkably, the tailored chromatic dispersion of the metalens in the context of spectral interferometry is utilized to maintain high-resolution imaging beyond the input field Rayleigh range, easing the trade-off between transverse resolution and depth of focus. The team demonstrated endoscopic imaging in resected human lung specimens and in sheep airways *in vivo*. The combination of the superior resolution and higher imaging depth of focus of the nano-optic endoscope is likely to increase the clinical utility of endoscopic optical imaging. The metalens work has been pioneered by researchers at Harvard with substantial support through an AFOSR Metasurface MURI award. This AFOSR-funded work is detailed in a paper published in *Nature Photonics*.[2]

DOD/AFRL and industry (SBIR): *Bio-inspired, Nano-Enabled Air Flow Sensors.* Researchers at the Materials and Manufacturing Directorate, Air Force Research Laboratory, have developed a novel, lightweight artificial hair sensor that mimics those used by natural fliers—like bats and crickets—by using carbon nanotube forests grown inside glass fiber capillaries. The hairs are sensitive to air flow changes during flight, enabling quick analysis and response by agile fliers. The AFRL-patented technology will be tested within an F-16 weapons bay to understand its applicability to quantifying aerodynamic conditions in a realistic environment. The current method is to qualitatively observe tufts of cloth flapping within the bay. The technology will be further commercialized through the Air Force SBIR and Small Business Technology Transfer (STTR) programs in conjunction with the Aerospace Systems Directorate.

[2] https://www.nature.com/articles/s41566-018-0224-2

DOD/AFRL and academia (international): *Reconfigurable Carbon Nanotube Multiplexed Sensing Device Platform.* An AFRL-Queen Mary University of London team reported the fabrication of reconfigurable and solution-processable nanoscale biosensors with multisensing capability, based on single-walled carbon nanotubes (SWCNTs). The CNTs were functionalized with specific, and different, aptamer sequences that were employed as selective recognition elements for biomarkers indicative of stress and neuro-trauma conditions. Multiplexed detection of three different biomarkers was successfully performed, and real-time detection was achieved in serum down to physiologically relevant concentrations of 50 nM, 10 nM, and 500 pM for cortisol, dehydroepiandrosterone-sulfate (DHEAS), and neuropeptide Y (NPY), respectively. Additionally, the fabricated nanoscale devices were shown to be reconfigurable and reusable via a simple cleaning procedure. The general applicability of the strategy presented, and the facile device fabrication from aqueous solution, hold great potential for the development of the next generation of low power consumption portable diagnostic assays for the simultaneous monitoring of airman health and performance. The work was published in *Nano Letters*.[3]

Nanotechnology-Enabled Measurements & Metrology

DOD/AFRL: *Polymer Matrix Composites with Embedded Nanosensors.* Optically active nanoparticles are being developed and added to polymer matrix composites for real-time monitoring of key parameters during processing. The goal is to significantly reduce costs associated with resin cure cycle development, manufacturing flaws, and nondestructive evaluation. Plasmonic resonances in gold nanorods are used to report local temperature and dielectric constant of the matrix (associated with cure), and branched quantum dot structures are sensitive to local strains. Plexcitonic complexes of gold nanorods with a variety of molecular fluorophores are being developed to provide robust self-calibration of these sensors.

DOD/AFRL, industry, and national laboratories: *Physics-Based Approach to Optimizing Polymer Matrix Composite Cure Cycles.* Currently, empirical and trial/error methods are used to obtain optimal cure cycles during processing of polymer matrix composites, which leads to high failure rates in production with minimal understanding to the primary causes. Molecular and mesoscale modeling of the process carried out at Boeing show distinct dynamics of different phases that are dependent on heating rate, hold temperatures, number of temperature steps, and hold times in a typical cure cycle. The missing key is the coupling of modeling efforts to experimental validation of *in-operando* experiments. Collaboration under a cooperative research and development agreement (CRADA) between AFRL and Boeing and support by beamline scientists at the National Synchrotron Light Source II at Brookhaven National Laboratories led to new insights in the complex crosslink reactions of AF-relevant thermosetting resins by using nanoparticle probes in x-ray photon correlation spectroscopy experiments. Coupled with mesoscale modeling efforts carried out at Boeing, the AFRL team carried out cure cycle experiments to obtain dynamics and morphology in real time. Optimizing the processing steps leads to improved mechanical properties and thermal stability and overall life-cycle performance, and will ultimately reduce scrap rates in polymer matrix composite production.

DOD/AFRL and academia: *Axial Point Source Localization using Variable Displacement–Change Point Detection.* A three-dimensional (3D) point-source technique is demonstrated by a Penn State–AFRL team using two-photon photoluminescence and four-wave mixing from plasmonic gold nanorods (AuNRs), imaged at the single-particle level. Introduction of position-dependent latitudinal astigmatisms into the imaging system, in combination with a change point detection (CPD) algorithm, resulted in localization of

[3] https://pubs.acs.org/doi/full/10.1021/acs.nanolett.8b00856?

single particles with high precision in three dimensions (20 nm axial localization using a single imaging objective). Matching the fundamental wave localized surface plasmon resonance energies resulted in increased axial localizations. This advance will facilitate the in-depth study of photonic materials and complex biological environments that can benefit from increased axial position determinations. The work is detailed in *Journal of the Optical Society of America B*.[4]

DOD/AFRL and academia: *Structure of Water and Ice Next to the Single Atomic Layer Graphene.* Graphene is single atomic layer thin material with extreme mechanical strength and superb electrical and optical properties. The water-graphene interface has received considerable attention in the past decade due to its relevance in various potential applications including biosensing, desalination, energy, and catalysis. Most of our knowledge about the interfacial water structure next to graphene stems from computational simulations. A University of Akron and AFRL team used surface-sensitive infrared-visible sum frequency generation (SFG) spectroscopy to probe the interfacial water structure next to graphene supported on a sapphire substrate. The team revealed that (1) the water next to graphene is highly coordinated and ordered to form ice-like water; and (2) the solid ice on graphene is proton disordered to form water-like ice. Specifically, this research sheds light on water–graphene interactions relevant in optimizing the performance of graphene biosensors for DOD human performance monitoring and protection.

Nanotechnology-Enabled Materials

DOD/Air Force and academia: *Ultra-Strong and Tough, High-Temperature Thermoset Interfaces.* An AFRL-Stanford team fabricated high-temperature thermoset nanocomposites by filling a porous hybrid matrix with a thermo-oxidative stable and high service temperature AFRL-developed poly (amic ester) precursor. Successive imidization and crosslinking of the precursor under molecular hyper-confinement (7 nm pore size) toughened the nanocomposite by as much as 80%. Further improvement in the thermoset composition resulted in extreme toughness values much greater than currently known materials. The toughening effects have resemblance to well-known biological systems such as nacre in which hidden length plays an important role for toughening a mostly inorganic structure. This work is of high relevance to next-generation AF platforms that require bonding of dissimilar materials, and addresses demand for higher-temperature (>750 °F) and lighter weight composites (complex interlaminar bonding) for future jet engines (with improved range and fuel economy).

DOD/Air Force: *Nanofluid Development for Digital Microfluidic Optoelectronics.* Optofluidics is a relatively new research field that focuses on the intersection of optics and microfluidics, and it is only in the last decade that optofluidic applications have received significant attention. Most research has been dedicated to exploiting the simultaneous control of fluidic conditions and optical beams, but there is surprisingly little research exploring the precise control of optically active colloidal nano- and microdroplets. Digital microfluidics provides a method for rapidly and autonomously controlling multiple discrete droplets across an array of electrodes, and this technology shows promise as a platform for novel optoelectronic applications such as reconfigurable filters and electrically dimmable eyewear. Current work at AFRL is focused on electrically manipulating discrete droplets of nanofluids—i.e. engineered colloidal suspensions of nanometer-sized particles—and investigating the structure-property relationship between nanoparticles, wetting capabilities, and photophysical data.

DOD/AFRL and academia: *Plasmonic Nanocatalyst.* AF-sponsored researchers at Rice University have demonstrated a new catalyst that can convert ammonia into hydrogen fuel at ambient pressure using only

[4] https://www.osapublishing.org/josab/abstract.cfm?uri=josab-35-5-1140

light energy, mainly due to a plasmonic effect that makes the catalyst more efficient. The new catalytic nanoparticles, which are made mostly of copper with trace amounts of ruthenium metal, are an example of antenna/reactor structures. The plasmon-mediated catalyst benefits from a light-induced electronic process that significantly lowers the “activation barrier,” or minimum energy needed, for the ruthenium to break apart ammonia molecules. By using available light energy, hot carrier-driven photocatalysis could greatly reduce the external energy needed for many chemical processes.

DOD/AFRL: *Fabricating Ceramic Nanostructures with Ductile-Like Compression Behavior via Rapid Self-Assembly of Block Copolymer and Preceramic Polymer Blends.* An AFRL-team developed a rapid and scalable process for the fabrication of nanostructured silicon carbide (SiC)-based ceramics displaying mechanical metamaterial properties. These novel mesoporous structures are achieved through patterning at the nanoscale via block copolymer (BCP) self-assembly. In this facile process, a blend of preceramic polymers (PCPs) and BCP are dissolved in warm solvent, cast, and quickly solidify as an organogel comprised of a 3D micelle network. Significantly, these materials rapidly self-assemble and do not necessitate the annealing steps that are typically required for block copolymer self-assembly. The PCP nanostructure of the films is thermally stable and maintained through pyrolytic soft template removal and conversion to ceramic. Exploration of PCP, BCP, and PMMA homopolymer blends resulted in the discovery of a co-continuous wormlike micelle phase, which after pyrolysis translated into a ceramic nanocoral-like structure with a network of high-aspect-ratio ceramic struts punctuated with mesopores. *In-situ* nanomechanical compression testing reveals ductile-like deformation, complete strain recovery up to 14% strain, and enhanced energy absorption over bulk ceramics. The confluence of rapid self-assembly, affordability, and mechanical metamaterial properties offered by this system surmount many of the challenges associated with producing materials nanostructured over large areas. A patent application has been filed and the work is published in *ACS Applied Nano Materials*.[5]

DOD/AFRL: *Low-Energy, Nanoparticle Reshaping for Large-Area, Patterned, Plasmonic Nanocomposites.* Films with plasmonic properties are enabling for technologies including colorimetric sensors, filters, and gradient refractive index lens (GRIN) elements. Spatially multiplexing different plasmonic effects, however, is challenging. We demonstrate a post-film fabrication process that enhances AuNR reshaping with chemistry. Broadband non-coherent light provides sufficient heating to drive localized redox processes that lead to an isovolumetric reduction of the surface-to-volume ratio of cetyltrimethylammonium bromide (CTAB)- stabilized AuNRs in polyvinyl alcohol (PVA). Single crystallinity is retained. The reshaping rate occurs >100x faster (seconds) than previous reports that utilize increased surface diffusion as temperatures approach the particle melting point (days). Using the process’s dependency on reactant concentration and broadband power density, multiexposure optical processing preserves particle alignment, enables multicolor patterning, and produces gradients of the plasmon resonance of at least 0.01 eV/μm (3 nm/μm). The work is published in *J. Mater. Chem. C*.[6]

DOD/AFRL: *Liquid Crystal Elastomers Exhibit Anisotropic Mechanical, Thermal, and Optical Properties.* The director orientation within a liquid crystal elastomer (LCE) can be spatially localized into voxels (3D volume elements) via photoalignment surfaces. An AFRL team prepared nanocomposites in which both the orientation of the LCE and SWCNT are locally and arbitrarily oriented in discrete voxels. The addition of SWCNTs increases the stiffness of the LCE in the orientation direction, yielding a material with a 5:1

[5] https://pubs.acs.org/doi/10.1021/acsanm.8b01820

[6] https://pubs.rsc.org/en/content/articlelanding/2018/tc/c8tc00780b#

directional modulus contrast. Additionally, the SWCNTs sensitize the LCE to a dc field, enabling uniaxial electrostriction along the orientation direction. This demonstrates that localized orientation of the LCE and SWCNT allows complex 3D shape transformations to be electrically triggered. The work is detailed in *ACS Applied Materials & Interfaces*.[7]

Environmental Impact of Nanotechnology

DOD/AFRL: *Post-Detonation Sampling of Novel Explosive Solid-Phase Particulate for Nanoscale Generated Silica.* Silicosis arises from exposure to crystalline silica dusts, a well-known hazard in mining and other occupational environments. Phases of crystalline silica (e.g., quartz, cristobalite, and tridymite) are naturally occurring minerals in the Earth's crust, but under the correct thermal and pressure conditions they can be derived from amorphous silica, or can transition from one crystalline phase to another. In this work, four detonation tests were performed: ~84 g of pentolite sampled for 30 minutes post-detonation; ~160 g of AFX-260 sampled for 30 minutes post-detonation; and two more ~160 g AFX-260 samples, each sampled for 15 minutes post-detonation. Airborne post-detonation particulate was sampled onto polyvinyl chloride sampling filters for x-ray diffraction (XRD) analysis targeting crystalline silica. Transmission electron microscopy (TEM) was also used for analysis of particle size, morphology, and elemental composition. From the XRD scans, the primary crystalline component matches iron oxide (Fe_2O_3), although the primary peak for quartz is also evident. Approximate volume percent ratios of the quartz phase to the amorphous phase were calculated based on relative integrated intensities, and are ~1%. Although it is not a direct comparison, this estimate matches in-house powders comprised of known amounts of amorphous carbon black and crystalline Min-U-Sil 5 quartz standard. Furthermore, TEM analysis for crystalline vs. amorphous morphologies showed that crystalline particles were metallic rather than silica, confirmed with energy dispersive x-ray spectroscopy (EDS). Most particles were spherical and not electron-dense, matching amorphous morphologies. The average aggregate size, considering total projected area measured and calculating a diameter assuming spherical particles, with a cutoff of 20 nm diameter, is < 100 nm for the particulate sampled for 30 minutes post-detonation and ~140 nm for the AFX-260 sampled for 15 minutes post-detonation. Overall, there is a minimal presence of crystalline silica detected in the post-detonation particulate sampled and analyzed via XRD.

Navy

NRL Nanoscience Program

FY 2020 Signature Initiatives and Grand Challenge

In the area of the Nanoelectronics for 2020 and Beyond Nanotechnology Signature Initiative (Nanoelectronics NSI, PCA 1b[8]), in fiscal year (FY) 2020 NRL plans to investigate photonic approaches to quantum information processing, which include developing highly entangled photon sources. In addition, NRL plans to develop heterostructures of two-dimensional (2D) materials for spintronic applications.

For the Sensors NSI (PCA 1d), NRL plans to investigate chemical sensor platforms for detecting the cellular signals that control wound healing.

---

[7] https://pubs.acs.org/doi/10.1021/acsami.7b13814

[8] For a complete list of NNI Program Component Areas (PCAs), see: https://www.nano.gov/about-nni/what/vision-goals.

For the Future Computing Grand Challenge (PCA 1f), NRL plans to initiate an effort in nanophotonic-based reservoir computing.

FY 2020 Foundational Research

NRL anticipates continued efforts in the area of Foundational Research (PCA 2). This research includes efforts in phonon-polariton lattices, controlling magnetism in metamagnetic nanostructures, enhanced optical properties in hybrid nanostructures, and bio-inspired quantum-coherent networks in DNA origami structures.

FY 2020 Nanotechnology-Enabled Applications, Devices, and Systems (PCA 3)

NRL will develop new approaches to interface with and control biological systems. These approaches include the development of "protonic" devices for actuating cells and self-assembled nanoscale transducers that can wirelessly control living cells. Additionally NRL is developing dimensionally-confined biological catalysts and multiscale architectures for chemical catalysts.

Accomplishments

DOD has significant interest in new technologies with which to stimulate electrically excitable cells such as neurons in the brain or muscle cells in tissue for new diagnostics and therapeutics to treat battlefield injury. NRL scientists, in collaboration with university neuroscientists, have developed the technology to interface gold nanoparticles (NPs) with the plasma membrane of neurons. Upon photoactivation of the membrane-tethered NPs, modest local heating of the plasma membrane bilayer opens ion channels that induce action potentials; the basis of neuron activation and communication in the brain. Given the established biocompatibility of gold NPs in the clinic, this novel technology opens the possibility of new, noninvasive therapies for the treatment of traumatic brain injury, post-traumatic stress disorder (PTSD), and depression.

Two-photon lithography enables writing of arbitrary nanoarchitectures in photopolymers. This design flexibility opens almost limitless possibilities for biological studies, but the acrylate-based polymers do not allow for adhesion and growth of some types of cells. NRL scientists have reacted OrmoComp® structures with several diamines, thereby rendering the surfaces biocompatible and directly permissive for neuron attachment and growth. This treatment presents a surface coating similar to the traditional cell biology coating achieved with poly-D-lysine (PDL) and laminin. However, in contrast to PDL-laminin coatings that cover the entire surface, the amine-terminated OrmoComp® structures are orthogonally modified in deference to the surrounding glass or plastic substrate, adding yet another design element for improving warfighter treatment regimens.

NRL and AFRL scientists have developed a way to directly write quantum light sources, which emit a single photon of light at a time, into monolayer semiconductors such as tungsten diselenide (WSe_2). Single-photon emitters are key components in a wide range of nascent quantum-based technologies relevant to the DOD mission, including secure communications, sensing, and computation. Quantum-based communication between distant DOD assets is not vulnerable to eavesdropping or decryption, an essential requirement for dominance of the battlespace. Quantum computation implemented in a solid-state host provides onboard capability to rapidly analyze very large data sets acquired by sensor arrays, reducing data transmission and bandwidth requirements. This new quantum calligraphy technique paves the way for the use of single photon emitters in solid state hosts for these DOD applications.

NRL scientists have fabricated a novel bilayer structure comprised of two different monolayer materials, molybdenum diselenide ($MoSe_2$) and WSe_2, to create a new electronic state called an "interlayer exciton" formed between the two layers. They further developed a detailed model of the interlayer interaction to enable purposeful design of such heterostructures with tailored properties. These results provide new fundamental insight into the basic science of these emerging semiconductor materials, and enable use of the subsequent heterostructures for a wide range of technologies important to the DOD, including novel optoelectronic devices such as nano-lasers and photodetectors.

Scientists and engineers at NRL have incorporated pairs of coupled quantum dots into micromechanical resonators and shown that they are sensitive to motion. The interaction between spins in each dot results in entangled states with an interaction energy that changes with motion-induced strain. Quantum sensing of motion should enable sensitive accelerometry for applications valuable to the Navy and DOD, including inertial navigation and gravitational detection of massive objects. These results can also be used to better control quantum systems, couple multiple quantum bits, and access the quantum limits of motion.

NRL scientists have begun to develop a new class of nonlinear infrared optical devices that respond on the picosecond (i.e., THz) timescale and whose performance may be electrically modulated by the user. These achievements, based on strong cavity coupling to molecular vibrations, enable optical devices such as saturable absorbers and tunable filters that operate in the infrared.

Curing severe blast-induced wounds will require a thorough understanding of the environment into which cells migrate to regenerate the damaged tissue. It has recently been postulated that cells secrete nanovesicles called exosomes to help guide the wound healing process, but these vesicles have proven exceedingly difficult to detect. NRL has invented novel nanosensors, comprised of gold capped nanopillars, which enable single exosome detection in a massively parallel format for the first time.

NRL scientists have designed nanoscale assembly lines capable of biosynthesizing high-value commodity chemicals without needing cells. These modular systems, consisting of a series of enzymes arrayed around quantum dots, access channeling processes to catalyze multiple sequential chemical reactions with efficiencies hundreds of times better than the enzymes alone. By utilizing different enzymes in a plug-and-play manner the system can be reordered to make different products. Such emergent systems can provide a chemical analog to 3D printing or additive manufacturing by allowing on-site biosynthesis of food, fuel, and medicine at points of need such as a deployed ship or forward operating base.

NRL scientists have designed and demonstrated several schemes for enzyme detection based on reconfigurable DNA structures. These sensors are able to detect multiple enzymes and respond based on the composition of the sample. Dyes attached to the DNA facilitate monitoring of the system in real time. Utilizing a DNA “egg” configuration enables both the sensing of multiple enzymes as well as the release of a cargo. The developed sensors are a step towards the construction of “smart” nanomaterials that are able to sense, report, and respond from inside living systems. These materials can be integrated into sensors able to monitor warfighter health in the field.

ONR Bionanotechnology Program

Programmatic Highlights and Changes for FY 2020 by PCA

<u>PCA 2. Foundational Research</u>

The Office of Naval Research (ONR) will continue to support bionanotechnology research with emphases on fabrication techniques for hierarchical, biologically-based materials with defined properties, DNA nanotechnology and application for functional device platforms, synthesis and patterning of materials by microorganisms, and design and fabrication of bio-inspired and biomimetic materials and devices using Nature's design principles.

Key Technical Achievements and Accomplishments by Goal

Goal 1. Advance a World-Class Nanotechnology Research and Development Program

Researchers supported by the Office of Naval Research have used machine learning and pattern recognition with data generated from physics-based simulations to accelerate the design of new biologically inspired hierarchical materials optimized for specific properties (e.g., toughness and strength), and validated the approach using three-dimensional printing and testing of these new materials. The new approach accelerates the search for high-performing hierarchical materials by orders of magnitude and is applicable to other material systems for optimization of a variety of properties. This research was highlighted in a special focus on 3D printing in *R&D Magazine*.[9]

Researchers supported by the Office of Naval Research developed a new spinning method for the production of synthetic regenerated silk fibers that possess both the structural hierarchy and mechanical properties of natural silk, since prior approaches fail to allow production of synthetic silk fibers as strong as the natural version and microstructure is known to provide silk with its stiffness and stretchy qualities. The new process affords cheaper silk thread and fabric, the production of fibers with desired properties (e.g., mechanical strength) and features (e.g., color, shape), and the production of fibers with enhanced functionalities added through applied coatings, facilitating numerous new uses.[10]

Researchers supported by the Office of Naval Research have developed a small, conformal, radio frequency sensor that when mounted on a tooth and communicating wirelessly with a mobile device can continuously transmit information about analytes of interest in the oral cavity. The sensor consists of a sensing layer, which is a porous silk film or a hydrogel that absorbs the analyte to be detected, sandwiched between individual split-ring resonators. The tri-layer sensor continuously collects and transmits waves in the radio frequency spectrum, and transmits a different spectrum of radio frequency waves, with varying intensity, when the analyte of interest is present in the sensing layer. Multiplexed sensing can be achieved by the integration of multiple sensing layers, and potential applications include tracking nutrient intake and monitoring biomarkers found in saliva indicative of disease, inflammation, stress, or fatigue.[11]

Researchers supported by the Office of Naval Research have enhanced their DNA brick design strategy for self-assembly of three-dimensional nanostructures to allow tens of thousands of components to self-assemble into gigadalton-sized structures, which is a 100-fold increase in nanostructure complexity compared to DNA nanostructures created with existing design methods (i.e., DNA origami or first-generation DNA bricks, which use hundreds of unique components for self-assembly of nanostructures on the megadalton scale). In conjunction with this research, the software *Nanobricks* was developed to facilitate the design of large 3D brick structures that contain around 10,000 components.[12] DNA nanostructures of this complexity are expected to afford new capabilities such as scaffolds for patterning complex inorganic nanostructures or for 3-dimensional positioning of diverse functional moieties.[13]

[9] https://www.rdmag.com/article/2018/12/r-d-special-focus-3d-printing

[10] https://www.nature.com/articles/s41467-017-00613-5

[11] https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201703257

[12] http://nanobricks.software/

[13] https://www.nature.com/articles/nature24648

Researchers supported by the Office of Naval Research developed a unimolecular folding strategy for construction of nucleic acid (DNA and RNA) nanostructures to enable the replication of nanostructures *in vitro* or in living cells, reduce production costs, increase formation yields, and reduce defects. This required the identification of new design rules that allow single nucleic acid strands to fold and pair up sequences distant from one another in an orderly and precise fashion so as to avoid tangles and knots. A design algorithm and web-based automated software based on those design rules was also developed to provide a general platform for producing complex structures from a single long strand.[14]

ONR Power Electronics Program

Key FY 2020 Plans and Priorities by PCA

PCA 3. Nanotechnology-Enabled Applications, Devices, and Systems

ONR plans investments in FY 2020 to continue research into nanoclay insulation materials to further develop and characterize materials and their manufacturing processes.

Key Technical Accomplishments by NNI Goal

Goal 1. Advance a World-Class Nanotechnology Research and Development Program

ONR-funded nanoclay electrical insulation materials research has resulted in completion of a composition Design of Experiment (DOE) based on 22 formulation runs to identify the optimal nanostructured insulation with thermal conductivity of 0.8-0.9 W/mK, breakdown strength of 1000–1100 VPM, dissipation factor <3% and dielectric constant <5.

Goal 2. Foster the Transfer of New Technologies into Products for Commercial and Public Benefit

ONR-funded research has direct commercial applicability to support improved power density of electrical machines that are used in numerous applications including electric vehicles.

Goal 3. Develop and Sustain Educational Resources, a Skilled Workforce, and a Dynamic Infrastructure and Toolset to Advance Nanotechnology

ONR-funded efforts supported two faculty members and four graduate students/postdocs.

ONR-funded efforts developed research/testing facilities and advanced manufacturing capabilities for nanotechnology materials.

Goal 4. Support Responsible Development of Nanotechnology

All ONR-funded nanotechnology research is conducted with high regard for environmental, health, and safety considerations.

[14] http://science.sciencemag.org/content/358/6369/eaao2648

Additional Highlights

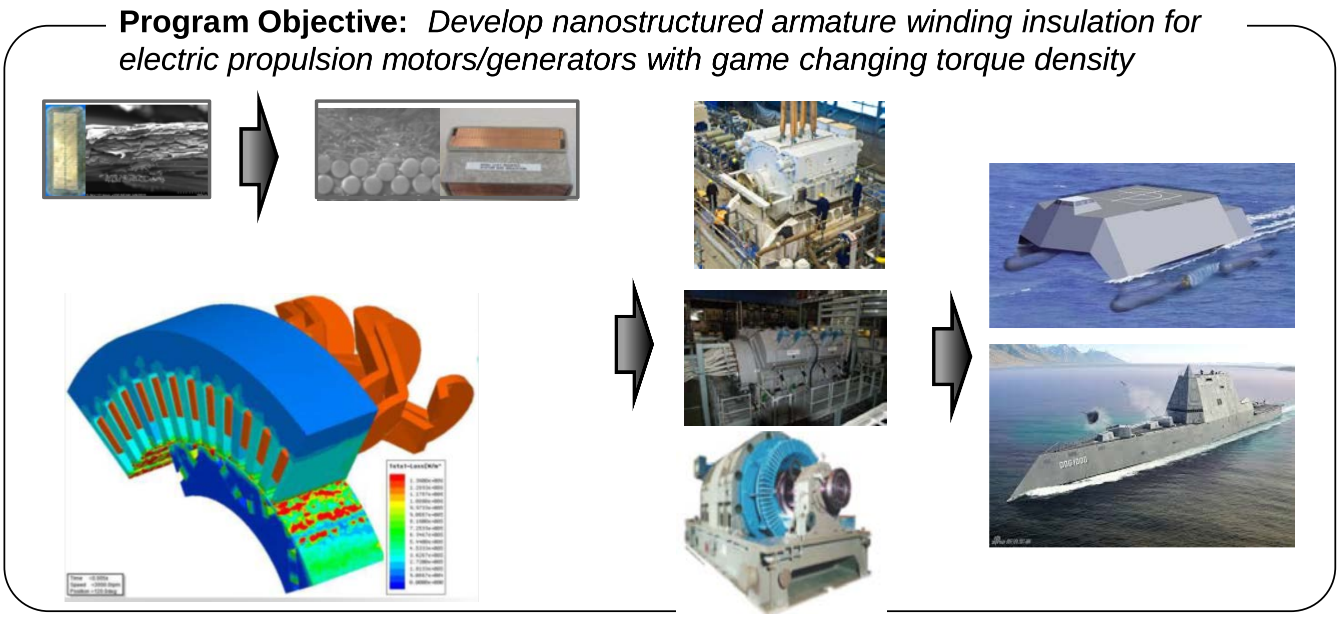

Figure 1. Improved electrical machine insulation systems can significantly improve power density to meet increasing demands for electrical energy on space- and weight-constrained Navy ships.[15] The research team has filed a patent application for this innovation and is preparing a journal publication. Image credit: Yang Cao, University of Connecticut.

ONR Nano-Engineered Materials Program

Key FY 2020 Plans and Priorities by PCA

PCA 2. Foundational Research

The Office of Naval Research will continue to support programs on electrically assisted materials manufacturing of lightweight alloys (e.g., aluminum and titanium alloys) and ultra-high melting point ceramics with increased hardness and low density (e.g., B_4C). This significant basic research effort will provide a comprehensive scientific basis along with predictive modelling tools of nanoscale processing phenomena defining macroscopic material properties.

The Office of Naval Research will continue to support programs on understanding the scientific phenomena that define the unique properties of structural and multifunctional nanomaterials. A special emphasis is on identifying material systems and processes enabling the assembly of these materials at mesoscale and beyond while preserving and potentially enhancing the material properties, initially defined at the nanoscale. There is a specific interest in understanding the limits imposed by the physical and chemical characteristics of a material in creating these nanomaterial ensembles with desired properties.

Key Technical Achievements and Accomplishments by Goal

Goal 1. Advance a World-Class Nanotechnology Research and Development Program

An ONR-supported Purdue University team discovered that at room temperature, flash-sintered yttria-stabilized zirconia (YSZ) micropillars can sustain giant strain (~8%) compared with their bulk counterparts

[15] https://today.uconn.edu/2018/05/uconn-researchers-advance-submarine-power/

(~2%) due to stress-induced martensitic transformation toughening. Brittle-to-ductile transition of fracture mode is observed at 400 °C in flash-sintered YSZ, much lower than the ~800 °C reported in conventional bulk YSZ. The enhanced plasticity at elevated temperatures arises from the transition from phase transformation toughening to dislocation creep as the dominant inelastic deformation mechanism, due to the existence of a high density of dislocations in flash-sintered YSZ and/or to early initiation of grain boundary sliding of ultrafine grains. This discovery provides the first evidence of superior mechanical properties of flash-sintered ceramics and establishes an important way to fundamentally understand the densification and mechanical properties of ceramics.[16]

An ONR-supported Northwestern University team demonstrated a patterning strategy to create functional nanostructured surfaces that enable tunable wetting states with reversible transitions. By stretching and reshrinking polymer nanoridges, structural features could be controlled without cracking or delamination, and different wetting transitions were achievable starting from a single surface in a programmable manner. This parallel, lithography-free technique can rapidly prototype surfaces with customizable wetting states for diverse applications in advanced water collection, self-cleaning systems, and directed water transport. The team anticipates that high-aspect-ratio surface patterns with dynamic topographical control can function as flexible platforms for biosensors, actuators, and antibiofouling surfaces.[17]

An ONR-supported Northwestern University team reported that crumpled paper-ball-like graphene particles can readily be assembled to yield a scaffold with scalable Li loading up to 10 mA hr. cm-2 within tolerable volume fluctuation. High Coulombic efficiency of 97.5% over 750 cycles (1,500 hr.) was achieved. Plating/stripping Li up to 12 mA hr. cm-2 on crumpled graphene scaffold does not experience dendrite growth, which points to a solution to a long-standing problem with dendrite growth plaguing Li anode performance in Li-ion batteries.[18]

ONR Nanoelectronics Program

Key FY 2020 Plans and Priorities by PCA

PCA 2. Foundational Research

The ONR Nanoelectronics program will continue to foster and encourage high-risk innovative research in nanoscience that will enable revolutionary new electron devices to achieve their ultimate limits of high speed, light weight, and low power consumption, and that interactively combine sensing, processing, computation, and communications functions. The research challenges the program seeks to address are: the fundamental building block of information handling beyond transistors; novel computing architectures that are suited for the new paradigm after "Moore's Law" CMOS scaling has ceased; and reliable and cost-effective means to synthesize and fabricate electronic circuitry at atomic resolution. In FY 2019, ONR will launch a new MURI program entitled, "Molecularly Programmable Graphene Architecture," focused on bottom-up synthesis of functional graphene electronic devices and circuits with atomic precision.

[16] *Nature Communications* (2018) 9:2063; DOI: 10.1038/s41467-018-04333-2

[17] *Adv. Mater.* 2018, 30, 1706657; DOI: 10.1002/adma.201706657

[18] *Joule* 2, 184–193, (2018); DOI:10.1016/j.joule.2017.11.004

Key Technical Accomplishment by NNI Goal

GOAL 1. Advance a World-Class Nanotechnology Research and Development Program

Top Physics Honors. At the March 2018 American Physical Society (APS) meeting, five out of a dozen total awardees were current or past ONR-funded PIs in the Nanoelectronics Program.

DOD Vannevar Bush Faculty Fellowship. ONR Nanoelectronics Program PIs from Harvard University were among 10 winners of the 2018 DOD Vannevar Bush Faculty Fellowship.

NRL Hulburt Award. An ONR Nanoelectronics Program PI and NRL scientist was promoted to the rank of Senior Scientist (ST), and awarded the 2018 E.O. Hulburt Annual Science Award—NRL's highest honor in science and technology.

Topological Graphene Nanoribbons (GNR). In the August 9, 2018, issue of the prestigious scientific journal *Nature*, two articles appeared back to back reporting the observation, and successful engineering with atomic precision, of highly nontrivial topological states in bottom-up synthesized graphene nanoribbons (GNRs). The two breakthrough projects were carried out under two separate ONR grants, a MURI project led by UC Berkeley researchers and a separate award to EMPA in Zurich, Switzerland. Topological states, particularly the capabilities to engineer their structures and properties, hold promise for entirely new classes of information-processing capabilities based on novel quantum mechanical principles.

Army

Engineer Research and Development Center (ERDC)

Key Plans and Priorities

DOD/Army/ERDC: New work has been initiated focused on use of nanomaterials to modify polymers and coating systems for controlled optoelectronic properties as part of Army basic research. The work focuses on spectral tenability for a variety of future applications.

DOD/Army/ERDC: Efforts will continue under many Army applied research programs focused on the use of advanced materials, including materials that incorporate aspects of nanotechnology in materials, modeling, and characterization, to support requirements for advanced force protection systems.

DOD/Army/ERDC and academia: New collaborations between the ERDC and the University of Southern Mississippi include research activities that leverage nanotechnology. These include focus areas on nanomaterial additions to construction materials such as asphalt and composites to improve mechanical properties and durability, as well as controlled optoelectronic properties for a variety of future sensing and coating applications. These efforts utilize advanced modeling and synthesis approaches to produce prototype materials for ERDC evaluation and transitions to support Army applied research programs.

DOD/Army/ERDC and academia: Advanced materials for force protection will be developed as part of collaborative research with the University of Mississippi. These will utilize combinations of nanomaterials including nanocellulose and carbon nanotube forests in multilayered composite assemblies. Computational modeling will be used to optimize the design of prototype composites for ERDC evaluation and potential transitions to support Army applied research programs.

DOD/Army/ERDC: ERDC is characterizing emissions of nanoparticle additives and volatile organic compounds from fused deposition modeling 3D printers and stereolithography 3D printers, respectively. This information is critical to health and safety management for personnel working in remote locations and confined spaces. Future collaboration with the National Institute for Occupational Safety and Health (NIOSH) is anticipated.

DOD/Army/ERDC and academia: ERDC is working with Texas A&M University to validate a novel microwave detection method for determining presence of free nanotubes in paints, and will publish a framework for selecting different analytical methods for measuring carbon nanomaterial release from complex matrices.

DOD/Army/ERDC/NIOSH: ERDC, with feedback from NIOSH, generated a preliminary definition for advanced materials, including nanomaterials, within an environmental, health, and safety context. The definition was vetted by practitioners through survey and submitted for publication in the peer-reviewed literature and is expected to be published in 2019.

DOD/Army/ERDC, academia, and industry: ERDC, in collaboration with Missouri State University and Brewer Science, is investigating new methods for integrating 2D printed nanotechnology-enabled sensors into 3D printed parts (including drones) for detection of environmental conditions (temperature, humidity); this will enable flexibility and gas detection for greater deployability of low-cost environmental sensing in remote locations.

DOD/Army/ERDC, academia, and industry: ERDC, in collaboration with Missouri State University and Brewer Science, is developing and executing STEM projects for grade school students to engineer stronger and lighter bridges by computer aided design (CAD), 3D printing, and incorporation of nanotube-enabled flex sensors to predict failure.

Key Technical Accomplishments

DOD/Army/ERDC: New approaches for synthesis of hybrid polymer nanocomposites using a combination of functionalized carbon nanotubes, graphene, and graphene oxide were developed as part of Army basic research. These hybrid systems for nanoscale reinforcement of polymers enables improved tensile strength by up to 6X along with increases in toughness for Nylon6 polymer-based nanocomposites.

DOD/Army/ERDC: New molecular dynamics approaches have been developed for modeling of functionalization of carbon nanomaterials as part of Army basic research. These models have been directly utilized to guide synthesis of engineered nanomaterials for use in composite materials.

DOD/Army/ERDC: Multifunctional materials have been developed under Army basic research using paramagnetic and ferromagnetic nanomaterials incorporated into elastomers. These materials have been studied in fluids for rheological property control, but also for structural joints and panels wherein properties can be directly controlled by externally applied magnetic fields.

DOD/Army/ERDC: Novel nanoscale characterization method and synthesis approaches were developed as part of Army basic research to study biological systems and the self-assembly of nanoscale tubule structure. A bio-inspired synthesis approach was developed and successfully used to fabricate mm-scale hierarchical structure through a novel microtubule self-assembly process. This work has developed a new understanding of biological self-assembly mechanisms.

DOD/Army/ERDC: Nanosilica morphology, molecular structure, and defect chemistries have been characterized for the first time under Army basic research. This effort is focused on developing advanced nanomaterials and modeling capabilities for use in high-performance concrete materials for expedient protection and structural hardening. This effort is the first of its kind to fully characterize these complex and highly variable materials produced by industrial partners.

DOD/Army/ERDC: Novel characterization methods using electron microscopy and nanoscale-resolution x-ray computed microtomography were used to characterize damage in geomaterials under high-rate and high-pressure loading conditions as part of Army basic research. Understanding these damage mechanisms is critical to support future force protection research and material development.

DOD/Army/ERDC: Nanoceramic particles were incorporated into metal matrix composites using a novel additive manufacturing processes. These materials are being studied for high hardness coatings for metals as part of Army applied research on advanced force protection systems. The work couples novel materials, synthesis approaches, and modeling. The developed materials show significant improvements in performance compared with conventional metals used for force protection.

DOD/Army/ERDC: Carbon nanofibers and graphene were incorporated into resin systems used to fabricate composite materials for force protection. The additives successfully improved the properties of the matrix in composites and load sharing between fiber reinforcement. This work was conducted as part of Army applied research on advanced materials for force protection.

DOD/Army/ERDC and academia: The use of nanocellulose additives for concrete and polymer composites was studied as part of Army applied research with collaborators at the University of Maine. This work focused on functionalization approaches and composite synthesis methods to generate improvements in mechanical properties.

DOD/Army/ERDC, academia, and industry: ERDC, in collaboration with Missouri State University and Brewer Science, optimized research, development, and manufacturing of nanotube-enabled environmental sensors to reduce cost, emissions, and energy usage through materials purification and increased recycling using life cycle (inventory) assessment. This public-private partnership developed a tool called NanoNavPAL to connect small technology developers to regulatory information.[19]

DOD/Army/ERDC: ERDC has characterized the ultrafine and nanoscale particle emissions from fused deposition modeling 3D printers, specifically investigating thermoplastic feedstocks with metal additives. Understanding these emissions is critical to user safety in confined, unventilated spaces.

DOD/Army/ERDC, CPSC, and academia: ERDC, the Consumer Product Safety Commission (CPSC), and Duke University investigated new methods to characterize the release of nanoparticles from abrasion of 3D printed pucks containing nanosilver and nanotubes.

DOD/Army/ERDC and CPSC: ERDC and CPSC published a knowledge document on a risk prioritization framework and tool to group different nanomaterials in consumer products.[20]

DOD/Army/ERDC and NIOSH: ERDC and NIOSH published a knowledge document within which free carbon nanotubes were not found following abrasion of a nanotube-enabled anti-corrosive paint.[21]

---

[19] https://nano.el.erdc.dren.mil/tools.html

[20] https://pubs.rsc.org/en/content/articlelanding/2018/en/c8en00848e/unauth#!divAbstract

[21] https://www.sciencedirect.com/science/article/abs/pii/S2452074818300855

DOD/Army/ERDC: ERDC published a new protocol for consistent spiking of nanomaterials into environmental media, including water and sediment/soil.[22]

DOD/Army/ERDC: ERDC published a knowledge document on detection limits for carbon nanotubes and nanoscale TiO_2 from matrix abrasion protocols.[23]

Institute for Soldier Nanotechnologies (ISN)

ISN FY 2019 & Beyond Plans

The Army's Institute for Soldier Nanotechnologies at MIT, in collaboration with the Army Research Laboratory (ARL) and other Army engineering and research centers, will continue to perform basic research to help the Army enable high-impact and potentially game-changing protection and other capabilities for the soldier and the soldier's platforms and systems. The planned ISN research emphasizes exploration of novel phenomena associated with fundamental processes (physical, chemical, biological) at the nanoscale or arising from nanostructural features in materials and devices, recognizing that nanotechnology entails much more than making materials that are very small and have very low weight. The intrinsic properties of matter (e.g., dielectric, chemical, mechanical, transport, etc.) become size-dependent below a critical length scale of a few hundred nanometers. Thus, these properties can change each time the material is made smaller. This provides opportunities for the discovery of new effective materials and phenomena that are otherwise unattainable in Nature. Moreover, nanotechnology involves materials systems that can be categorized in terms four basic types of "dimensionality" (D): 0D: nanoparticles (e.g., quantum dots); 1D: wires with nanoscale diameter or fibers with nanoscale feature sizes (e.g., optoelectronic fibers, carbon nanotubes); 2D: thin films consisting of only a few atomic monolayers (e.g., single- and multilayer graphenes and 2D photonic crystals); and 3D: three-dimensional structures with nanoscale feature sizes (e.g., nanocrystalline metal alloys, gyroid photonic structures). All of these categories of nanostructured materials systems are essential and will be investigated in planned ISN research. They serve as building blocks for, and enable functionality in, diverse materials. With nanotechnology as the foundation, if ISN research discovers that extending to micro-, meso- or even macrotechnology is required to enable the best, most efficient, and low-cost pathway to a soldier capability, then that is what planned ISN research will endeavor to do.

The planned research emphasizes close collaborations of MIT and Army scientists and engineers to provide exceptional breadth and depth of expertise in basic research, Army relevancy, and accelerated transitioning. Army relevancy and transitioning are important elements of ISN operations, with planned ISN basic research supporting each of the six priorities of the new Army Futures Command, i.e., Long Range Precision Fires (ISN: compact and low power LIDAR, ultra-strong kinetic penetrator materials); Next Generation Combat Vehicle (ISN: materials for stronger, lighter weight armor; quantum-dot-enabled hyperspectral imaging; nanoparticle display technology); Future Vertical Lift (ISN; stronger, lighter-weight armor materials; quantum-dot-enabled hyperspectral imaging; nanoparticle display technology; lightweight electric power sources); Army Network/C3I (ISN: functional fibers and fabric networks; quantum dot UV tagging and communications); Air and Missile Defense (ISN: sensitive, portable detectors for fissile material); Soldier Lethality (ISN: quantum-dot-enabled hyperspectral imaging; small form factor, lightweight electric power generators; functional fibers and fabric networks; quantum dot UV tagging and communications; ultra-

[22] https://apps.dtic.mil/docs/citations/AD1055740

[23] https://www.sciencedirect.com/science/article/abs/pii/S2452074817301623

sensitive IED sensing; nanoparticle-enhanced obfuscation; health monitoring and treatment; biofidelic blast/ballistic modeling).

The planned research program includes 16 projects within three Strategic Research Areas (SRAs). SRA-1, Soldier Protection, Battlefield Care, and Sensing, focuses on studies to develop lighter-weight, stronger materials to protect the soldier and soldier-augmenting platforms and systems from mechanical damage owing to blast waves, ballistic impacts, and mechanical vibrations, using various mechanisms of energy absorption including phase transitions and materials deformation, as well as projects on medical treatment innovations for the soldier. SRA-2, Augmenting Situational Awareness, concentrates on providing the soldier and soldier platforms with the next level of capabilities for secure communications, multifaceted situational cognition and visualization, and invulnerability to enemy detection and potentially for some cases, immunity to enemy EMP (electromagnetic pulse) and spoofing technologies. SRA-3, Transformational Nano-optoelectronic Soldier Capabilities, primarily focuses on understanding fundamental optical, electronic, and transport/reaction phenomena in nanostructured materials and learning how to apply these phenomena to enable major advances in portable power, communications, neuromorphic computing, signal processing and detection. Taken together, the research in SRA-2 and SRA-3 emphasizes a broadly-based attack on diverse segments of the EM spectrum currently under-exploited owing to inadequate scientific understanding of the basic physics of novel electronic, optical, and electromagnetic phenomena or the unavailability of efficacious materials and devices to capitalize on recent progress in this understanding.

ISN FY 2018 Accomplishments

<u>3D-Printed Shape-Shifting Soft Robots that can Crawl, Jump, and Grab</u>

New 3D-printed robotic structures can squeeze in tight spaces like a crack in the wall of a cave, jump over trip wire, or crawl under a vehicle—all complex Army-relevant functions impossible for humans to perform safely. ISN researchers have developed novel and exciting nanostructured functional inks and an accompanying 3D printing platform that can enable both the modeling and design of complex magnetically actuated devices. The MIT-ISN team demonstrated this success using auxetic metamaterials—synthetic composite materials that have an unusual internal structure and the unusual property that when exposed to external magnetic actuation, they shrink in both longitudinal and transverse directions. This is different from typical auxetic materials that require direct mechanical contact, and when compressed they undergo contraction in the directions perpendicular to the applied force. The team's findings could lead to new biomedical applications, nanostructured magnetic ink optimized to strengthen soft robotic functionality, and new on-demand flexible material systems for integration into soldier systems. Such complex shape-morphing structures could have great potential for the Army, because they may help create soft robots—robots with pliable limbs similar to natural organisms. Compared to the current generation of rigid robots, soft robots could move much more dexterously on a complex battlefield terrain.

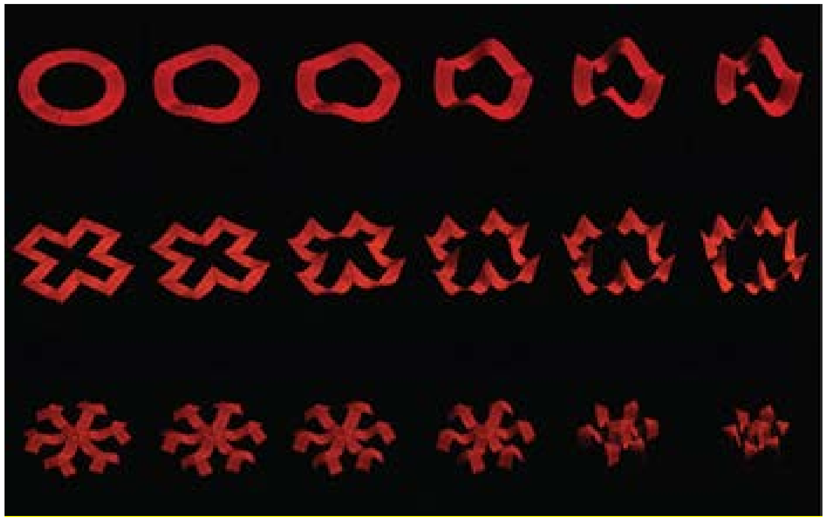

Figure 2. Time-lapse photo for various designs of developed magnetic active material. Image credit: Xuanhe Zhao, MIT.

Industrially Scaled 3D Printed Bulk Nanocrystalline Metal Parts

Many “nano” materials produced in the lab meet challenges in getting to industrial scales. So-called nanocrystalline metals have internal crystals that are only dozens of nanometers in size, rendering the metal very strong, hard, wear-resistant, and excellent at high loading rates and in extreme conditions. These materials are very successful in the laboratory, but are often so unstable that they cannot even be processed in bulk forms, much less put into service where their instability would compromise their properties over time. ISN researchers have pioneered a new paradigm in the design and production of nanocrystalline metals by developing the science of nanostructure stability. Using computation and experiment to design new metal alloys where the alloy chemistry thermodynamically favors a nanostructure, they have shown how such stable nanocrystalline metals can be processed with existing metals processing equipment, dramatically improving the scalability proposition. The MIT ISN team has conducted a significant collaboration in technology transfer with two partners: Veloxint Corporation has scaled the production of MIT-designed nanocrystalline powders, and Desktop Metal, Inc., has successfully incorporated those powders into a commercial 3D metal printer. The result is the first demonstration of bulk 3D printed nanocrystalline metal parts, with complex geometries, and stable high-strength nanocrystalline structures. Such parts now stand on the brink of commercial adoption, bringing nanocrystalline metals into wide usage in a variety of mechanical applications.

Nanostructural Response to Microparticle Impact

Nanostructured material networks offer unique prospects for ultra-lightweight mitigation of particle impact and shock. But how can one test the effectiveness of new nanostructures that are fabricated in tiny sizes (micron dimensions, less than 0.001 mm^3 total volume) before any scale-up is practical? ISN researchers have developed a laser-induced particle impact test (LIPIT) to investigate the dynamic behavior of nanomaterials under extreme loading. Individual microparticles are accelerated to supersonic velocities through a laser ablation process. Particle trajectories and material deformations caused by particle impact are monitored in real time using an ultrahigh-speed camera. In the example shown in Figure 3 below, the team records images of a 14-μm silica particle launched at about 500 m/s as it impacts a 3D nanotruss metallic glass sample, fabricated by collaborators at Caltech. Following impact, the particle rebounds with 25% of its incident energy (75% of the incident kinetic energy has been absorbed) and the nanotruss sample is damaged and delaminated from the substrate. In this research, the critical aim of the team is toward optimized energy absorption performance and toward fundamental understanding of the mitigation mechanisms.

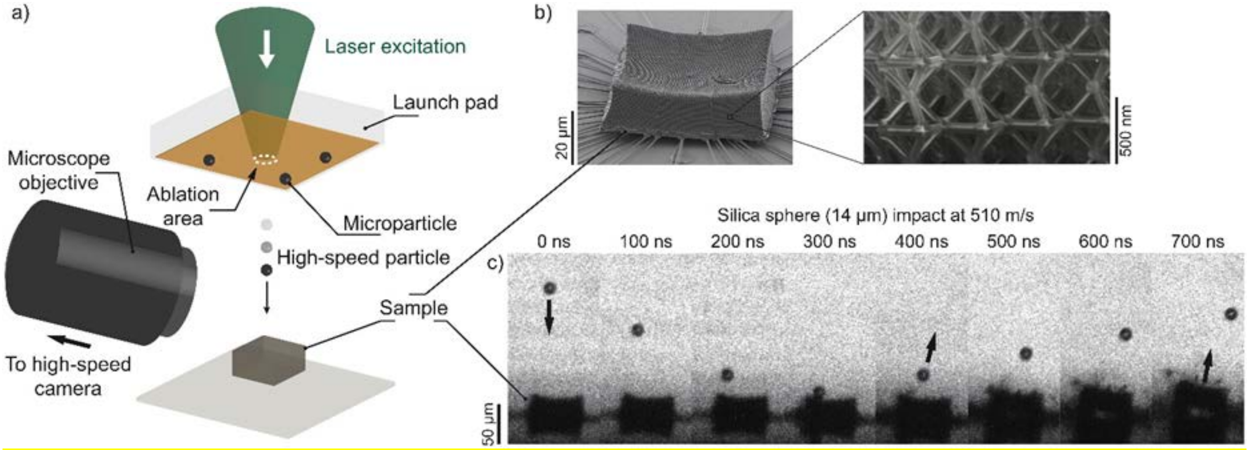

Figure 3. Schematic illustration and results of the laser-induced particle impact test. (a) Upon laser ablation of the gold film, microparticles are launched at speeds up to 3 km/s. The impact is imaged using a µs laser pulse and a high-frame-rate camera. (b) Nanotruss sample attached to a silicon substrate (left) and close-up view (right) of the truss structure. (c) Image sequence recorded using a high-speed camera with 5 ns exposure time for each image, showing particle impact at 510 m/s. The interframe time is 100 ns.
Image credits: the Keith Nelson Research Group, MIT, and the Julia Greer Research Group, Caltech.

A New Breed of Portable Nanostructured Energy Sources

Thermophotovoltaics (TPV) is an age-old approach for using heat to generate light (photons) which then excite electron-hole pairs in a photovoltaic (PV) cell to generate electricity. This process has been known for years to be notoriously inefficient. The reason is that the temperature of the heated object dictates the energies of the emitted photons and for typical object temperatures of around 1000 Kelvin, the vast majority of emitted photons have energies that are too low to excite electrons above the PV bandgap. In contrast solar cells work well because the source of photons is the Sun, which is at 6000 Kelvin. ISN researchers have succeeded in breaking this severe TPV bottleneck by designing nanostructured photonic crystals that can change the densities of states of the photon modes of an object at 1000 Kelvin to exist with energies primarily above the band gap of the PV cell. This changes the efficiency of TPV dramatically. The team's resulting demonstration, for the first time, of a nanophotonics-enabled portable power generator introduces a new ultra-high energy density wearable power source technology. It has potential to reduce the soldier's battery load by more than 75 percent in a 72-hour dismounted mission. This efficiency gets better for longer missions, as shown in Figure 4. The entire device (including fuel) will be roughly water-bottle-sized, safe to handle, have no moving parts, and will produce 20 W of power. The system design is scalable and should be able to produce up to 300 W of power for other applications. Currently the wearable generator uses propane or butane as fuel, but the burner could be designed to work with other fuels such as JP8 as well.

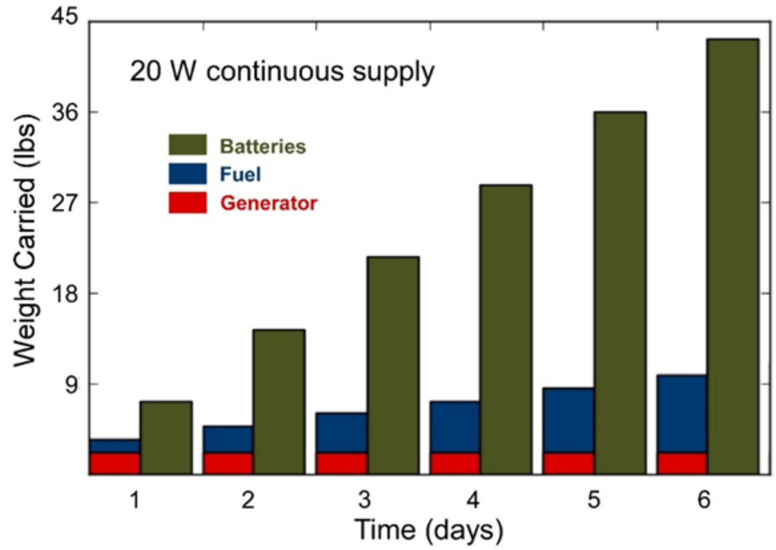

Figure 4. Projected weight requirements of ISN's novel nanophotonic TPV system (generator [red] and fuel [blue]) compared to the weight requirement of an equivalent power source using rechargeable batteries (green) as a function of soldier mission time. Image credit: John Joannopoulos, MIT.

Solving the Isomer Cataloging Problem for Nanopores in Two-Dimensional Nanomaterials

Two-dimensional (2D) materials, such as graphene and hexagonal boron nitride (hBN), which are capable of being synthesized as a single atomic layer, constitute an exciting area of nanotechnology, promising potential advances in application areas such as flexible electronics, lightweight composites, and membrane separation processes. These materials often contain inherent defects, known as nanopores, formed by several atoms being missing from the 2D lattice. Predicting the properties of real materials requires knowledge of the defects present in them. Moreover, the performance of 2D materials in gas separation and desalination processes depends on the shapes and sizes of the nanopores present in them. An ISN team has developed a computational framework based on electronic structure calculations, kinetic Monte Carlo (KMC) simulations, and chemical graph theory, to solve this isomer cataloging problem (ICP). Remarkably, the top four most-probable isomers (MPIs) of nanopores ranging in size from 6 to 20 atoms removed from the graphene lattice, as predicted by their solution to the ICP, are exactly the ones found in TEM images of graphene, reported in the literature, as well as those collected by their collaborators. Considering that the team's physically-motivated algorithm predicts up to 593 isomers (already down from the 11.7 million theoretically-possible ones for N=12), it is remarkable that only 4 MPIs are required to match experimental data. The set of predicted MPIs should considerably advance the application of nanoporous 2D materials by allowing for a direct link between theory/simulations and experiment.

Fluid-Like Self-Leveling 2D Nanomaterials with Superlubricity

Fluid-like graphenes with out-of-plane solid-like rigidity offer unique opportunities for achieving unusual physical and chemical properties for next-generation interfacial technologies. Of particular interest in the present study are graphenes with specific chemical functionalization that can predictably promote incommensurate sliding structures. ISN researchers have succeeded in demonstrating superlubricity between stainless steel (SS) and diamond-like-carbon (DLC) with densely functionalized graphenes displaying dynamic intersheet linkages that mechanically transform into stable tribolayers. The macroscopic lubricity evolves through the formation of a thin film of an interconnected graphene matrix that provides a coefficient of friction (COF) of 0.01. Mechanical sliding generates complex folded graphene structures wherein equilibrated covalent chemical linkages impart rigidity and stability to the films examined in macroscopic friction tests. This new approach to frictional reduction has very exciting broad implications for manufacturing, transportation, and aerospace.

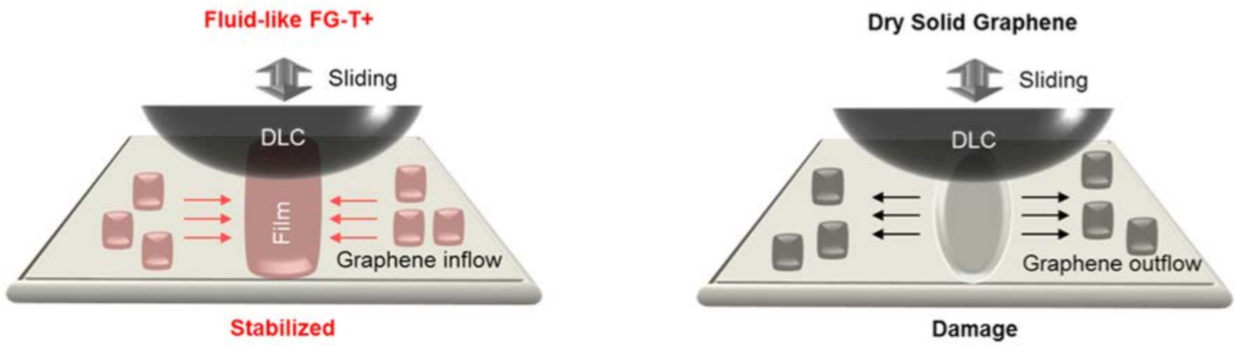

Figure 5. Mechanically induced chemical transitions of graphene films. Left: The tribo-layer of fluid-like FG-T+ is stabilized during sliding motion due to the influx of FG-T+ into contacting edges and self-leveling. Right: The solid-like FG and UEG undergo tribo-chemical damage. Image credit: Timothy Swager, MIT.

<u>Towards Broadly Tunable CMOS-Compatible All-Silicon Nanostructured Light Sources</u>

The efficient extraction of light from silicon is a long-standing challenge in modern engineering and physics. The difficulty arises from silicon's indirect bandgap and the short lifetime of non-radiative processes such as Auger recombination. The realization of an energy-efficient silicon-based light source could find broad applicability in areas such as ultra-large-scale integration (ULSI), telecommunications, mid-infrared sensing, optoelectronic displays, and lighting. Every practical solution proposed thus far to this fundamental yet technologically crucial problem relies on the chemical modification or physical patterning of silicon substrates, requiring fabrication steps or high annealing temperatures that are not compatible with conventional ULSI processes. An ISN research team has made a significant breakthrough by experimentally demonstrating the generation of tunable radiation in the near-infrared (800 to 1600 nm) from a nanostructured all-silicon grating. Their success relies on exploiting the Smith-Purcell (SP) effect, which is recorded when free electrons fly on top of a periodic structure. The SP effect provides exceptional tunability of the output wavelength (from the microwave regime to the near-ultraviolet) and versatility in the material platform (higher efficiencies with lossless dielectrics than metals). Light emission is generated by the spontaneous emission from these nanogratings interacting with low-energy free electrons (2–20 keV) and is recorded in the silicon transparency window. The team also theoretically investigated the feasibility of a compact, all-silicon tunable light source comprised of a silicon field emitter array (FEA) integrated with a silicon nanograting that emits at the telecommunication wavelengths. The results reveal the prospect of a CMOS-compatible electrically-pumped silicon light source for applications at the mid-infrared and telecommunication wavelengths.

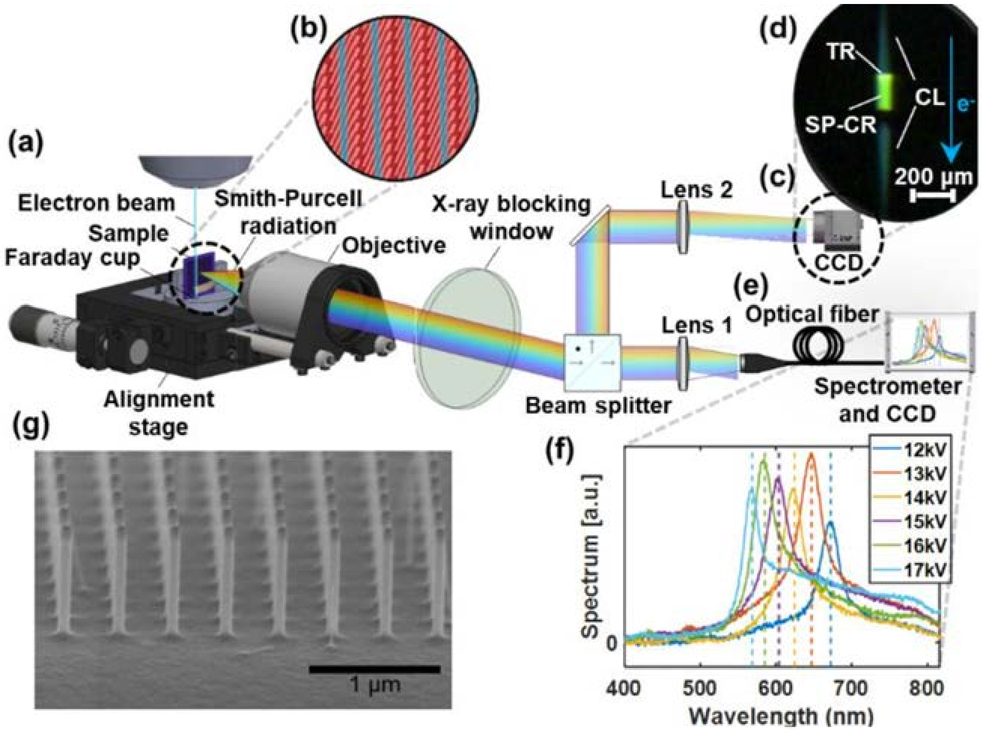

Figure 6. SEM-based experimental setup to observe SP radiation. (a) Inside the SEM vacuum chamber, the sample of (b) here, silicon nanowires (schematic), is held so that its surface is almost parallel to the path of the electron beam. The emitted light is collected by an objective, directed to a beam splitter that splits the optical beam to a (c) CCD camera, used to image (d) the surface of the sample that emits transition radiation (TR), SP-CR (Smith-Purcell-Cerenkov radiation) and CL (incoherent cathodoluminescence) and (e) a spectrometer fiber tip collector. (f) Third-order SP spectra for different acceleration voltages. (g) Scanning electron micrograph of a silicon nanowire photonic crystal with period of 400 nm. Image credit: Marin Soljačić, MIT.

Nanocomposites for Improved Hemostasis in Wounds

Topical hemostats are designed to accelerate or promote coagulation and hemostasis during hemorrhaging. The process may modify the clot architecture or distribution of blood components, resulting in reduced clotting times or minimal blood loss. Among a panel of known hemostatic materials, spatial distributions of individual blood components were quantified by an ISN scientist during contact with hemostatic materials. Hydrogel (gelatin, nanocomposite) and solid (QuikClot, chitosan) hemostats were systematically studied by measuring the spatial distribution of fluorescently labeled blood components surrounding the hemostat. Fibrin, platelets, and red blood cells were visualized separately to quantify their unique morphologies in the presence of hemostatic materials. Fibrin networks and plasma clots were generated using concentration-defined fibrinogen–thrombin solutions and heterogeneous human plasma samples, respectively. Among the blood components, fibrin exhibited the greatest differential response between hemostats, whereas the cell distributions showed minimal variability. The extent of fibrinolysis was independent of the hemostat, and the introduction of flow during clot formation reduced the differential effects of particular hemostats while maintaining qualitatively similar responses. A systematic approach taken to study these hemostats is being applied to develop new hemostatic materials, improve the determination of hemostatic mechanisms of action, and identify the signatures of modified clot structures generated at hemostat–clot interfaces.

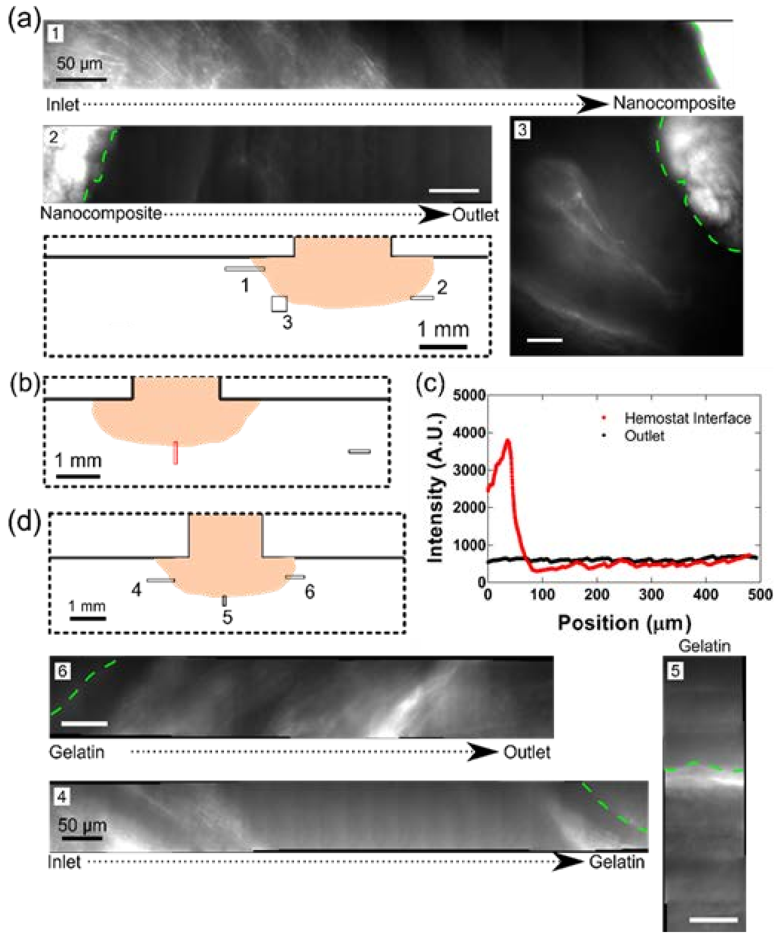

Figure 7. Fibrin profile of clot under flow: (a) Wide-field images of clots formed under flow in a nanocomposite-containing channel maintain the depletion region and high-intensity band surrounding and at the nanocomposite interface, respectively. Depletion regions were noted on both the inlet (image #1) and outlet (image #2) sides of the nanocomposite. A larger image (image #3) captures the depletion region and the non-uniform clot that was observed throughout the channel. Bands of fibrin are separated by regions without fibrin, in contrast to uniform networks that are generated under static conditions. (b) The approximate position and scaled size of the fibrin intensity profiles generated in nanocomposite-containing channels. (c) Profiles of fibrin intensity at the nanocomposite interface and in a region between the nanocomposite and outlet port. Away from the nanocomposite (outlet), the intensity is relatively uniform. The intensity increases near the nanocomposite interface followed by a reduction in intensity and an increase to a plateau value. (d) Schematic of gelatin-containing channel and a zoomed-in image of the relative positions of the stitched images taken. Stitched images at multiple sights shows clots up to the gelatin interface on the inlet (image #4), center (image #5), and outlet (image #6) side of the nanocomposite. Dashed green lines in fluorescent images indicate the approximate position of the hemostat interface. Image credit: Bradley Olsen, MIT.

Empowering Future Vaccines and Immunotherapies with Nanotechnology-Based Immunomodulators

Vaccines are a powerful defense against infectious diseases; however, generating effective vaccines against important pathogens including malaria, tuberculosis, HIV, and Ebola have remained unsolved challenges. Modern subunit vaccines do not typically elicit an immune response on their own and must be combined with immune stimulating adjuvants. Nanotechnology-based approaches that target vaccine adjuvants to lymph nodes have the capacity to enhance both the potency and safety of vaccines by focusing adjuvant activity to tissues where immune responses are initiated, while avoiding systemic exposure. ISN researchers have created a new class of adjuvant nanoparticles composed of lipids, immunostimulatory glycolipids, and cholesterol, which self-assemble into well-defined ~40 nm diameter nanoparticles. These particles are designed to efficiently traffic to lymph nodes and stimulate multiple innate immunity pathways to promote vaccine responses. The team has discovered that compared to standard adjuvants such as alum, these nanoparticles can elicit a 75-fold increase in antibody titers to a model diphtheria vaccine. Using intravital infrared imaging to visualize in live animals the mechanisms of action of this nano-adjuvant, the team discovered that saponin-MPLA NP adjuvants dramatically alter lymph flow: following injection of an infrared tracer dye alone in the leg of mice and imaging one hour later, most of the dye is found near the injection site. By contrast, injection of the tracer dye together with saponin-MPLA nanoparticles leads to the majority of the dye being delivered to the lymph node over the same time-course (right panel in part C of Figure 8). These data suggest that saponin-MPLA NPs promote antigen drainage and/or retention in the draining lymph node and could explain the striking immunostimulatory effects of this particulate adjuvant. The team is currently investigating how certain innate immune cells, such as neutrophils, may be influencing the lymphatic vasculature as well as overall lymphatic flow.

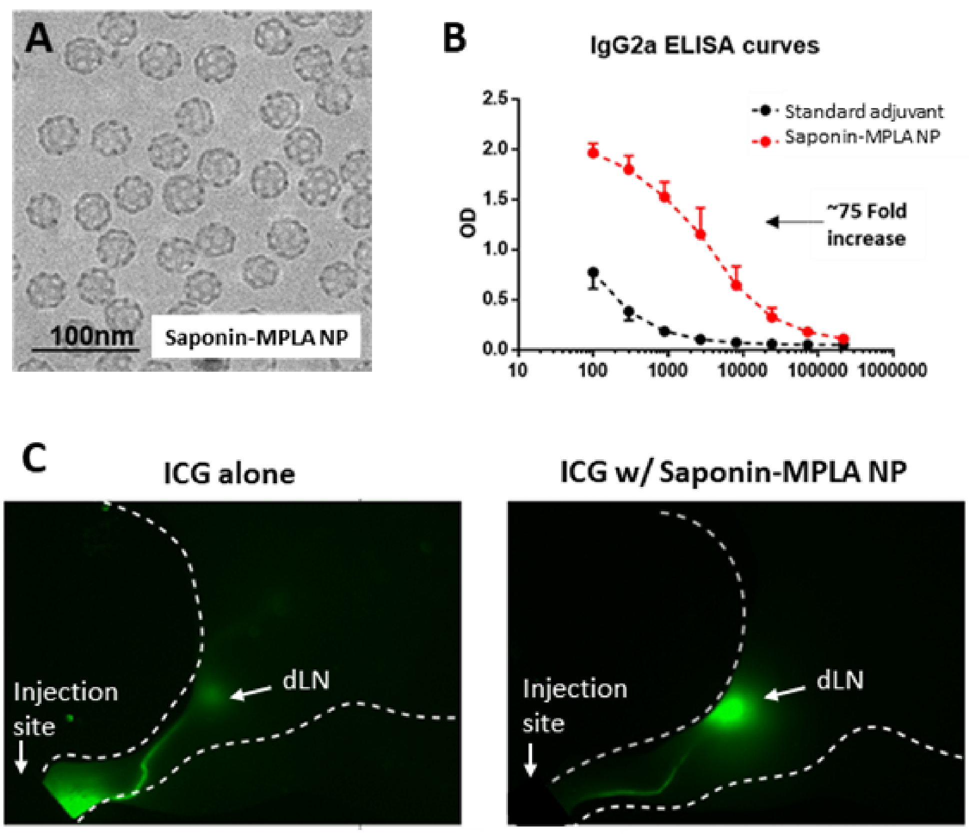

Figure 8. Highly potent self-assembling nano-adjuvants for next-generation vaccines: (A) TEM of saponin-MPLA nanoparticles. (B) Antigen-specific IgG2a antibody titer. (C) Intravital images of fluorescent dye (ICG) signal in draining lymph-node (dLN) 1 hr. post injection. Image credit: Darrell Irvine, MIT.

Deep Learning with Coherent Nanophotonic Circuits

Artificial neural networks are computational network models inspired by signal processing in the brain. These models have dramatically improved the performance of many learning tasks, including speech and object recognition. However, today's computing hardware is inefficient at implementing neural networks, in large part because much of it was designed for von Neumann computing schemes. Significant effort has been made to develop electronic architectures tuned to implement artificial neural networks that improve upon both computational speed and energy efficiency. Recently, an ISN scientist proposed a revolutionary new nanostructured nanophotonic architecture for a fully-optical neural network that, using unique advantages of optics, can result in a computational speed enhancement of at least two orders of magnitude over the state-of-the-art and three orders of magnitude in power efficiency for conventional learning tasks. The team has experimentally demonstrated various essential parts of its architecture using a programmable nanophotonic processor.

Nanophotonic Recurrent Ising Sampler

The difficulty of conventional electronic architectures in solving large combinatorial problems motivates the development of novel computational architectures. There has been much effort recently in developing photonic networks that can exploit fundamental properties enshrined in the wave nature of light and of its interaction with matter: high-speed, low-power, optical passivity, and parallelization. However, unleashing the true potential of photonic architectures requires the development of featured algorithms that exploit these fundamental properties. ISN researchers have introduced an exciting solution: the Photonic Recurrent Ising Sampler (PRIS). This is a technique tailored for photonic parallel networks that can sample combinatorially hard distributions of Ising problems in a fast and efficient manner. A variety of practical tasks including scheduling, circuit design, and artificial intelligence rely on discrete combinatorial optimization problems whose solutions cannot be found efficiently using traditional algorithms. Many such non-deterministically-polynomial-hard (NP-hard) problems can be mapped to the Ising problem. The PRIS solves general Ising problems. In addition to the attractive features of photonic networks, the PRIS relies on intrinsic dynamic noise to find ground states more efficiently.

Inverse Design of Large-Area Nanostructured Metasurfaces

Need for a computational framework for efficient optimization-based “inverse design” of large-area “metasurfaces” (subwavelength-patterned nanostructured surfaces)—for applications such as multiwavelength and multiangle optimizations and demultiplexers—is of critical importance. To optimize surfaces that can be thousands of wavelengths in diameter, with thousands (or millions) of parameters, the key is a fast approximate solver for the scattered field. An ISN research team has succeeded in developing a novel computational “machine learning” design approach capable of optimizing nanopatterned surfaces over thousands or even millions of parameters to automatically discover the best pattern for any given optical device. They employ a clever “locally periodic” approximation in which the scattering problem is approximated by a composition of periodic scattering problems from each unit cell of the surface, and validate it against brute-force Maxwell solutions. This is an extension of ideas in previous metasurface designs, but with greatly increased flexibility, e.g., to automatically balance tradeoffs between multiple frequencies, or to optimize a photonic device given only partial information about the desired field. The team’s approach even extends beyond the metasurface regime to non-subwavelength structures where additional diffracted orders must be included (since scalar diffraction theory is not applicable).

Electron-Current Rectification in Quantum Materials: Energy Harvesting & IR Detection

ISN researchers have discovered a new mechanism for electron current rectification utilizing intrinsic quantum properties of materials. Unlike conventional rectifiers using semiconductor diodes, the new mechanism enables rectification at small voltage or high frequencies, leading to a sensitive, efficient and tunable rectifier up to the infrared frequencies. Sensitive and efficient detection of infrared radiation invokes applications in a variety of fields: medicine, biology, meteorology, telecommunication, surveillance, military, etc. To date, there has been a difficulty in utilizing such frequency range because it lies between the electrical and optical ranges. Promising candidate materials include two-dimensional materials such as graphene and transition metal dichalcogenides. The teams finding proposes a new platform for functional energy harvesters and infrared detectors.

Additional Army Research Office (ARO) Activities

Accomplishments

ARO-funded researchers from the University of Michigan showed that radiative heat transfer between planar membranes with sub-wavelength dimensions can exceed the blackbody limit in the far field by more than two orders of magnitude. They achieved this result by using custom-fabricated calorimetric nanostructures with embedded thermometers. The heat-transfer rates were observed to be in good agreement with calculations based on fluctuational electrodynamics. This work highlights the potential of using nanoscale membranes for enhancing and controlling thermal absorption and is directly relevant to various fields, such as energy conversion, atmospheric sciences, and astrophysics, in which radiative heat transfer is important.[24]

Army Research Laboratory

FY 2018 Accomplishments

DOD/ARMY: The U.S. Army Research Laboratory has recently developed a nanogalvanic aluminum alloy powder that has demonstrated the ability to generate large volumes of hydrogen gas when mixed with any liquid that contains water (e.g., tap water, wastewater, energy drinks, urine, etc.). This is a major breakthrough in the ability to generate power at the point of need. Researchers discovered that specifically alloyed, nanostructured aluminum powders readily react (through a galvanic reaction) with water at room temperature, without any use of catalysts, to instantly produce large quantities of hydrogen gas. The reaction is very straightforward and results in the production of hydrogen gas, water, heat, and non-toxic byproducts. These patent-pending powders produce hydrogen at a rate that currently is one of the fastest reported in the literature for aluminum + water reactions, and without the need for hazardous and/or costly materials. The hydrogen gas generated can act as fuel to produce power on demand at the point of need via fuel cell and/or internal combustion engine systems. ARL is currently working with the Army Tank Automotive Research, Development and Engineering Center to evaluate this material for use in hydrogen vehicles. ARL also has CRADAs with numerous companies including General Atomics, H2 Power, React Power, Kymera, Cerion, etc., for evaluating this material for power generation. ARL is currently in negotiations for licensing this technology to industry.

DOD/ARMY and academia: ARL developed two-dimensional polymers that have the potential to achieve bulk mechanical properties that surpass commercial high-performance ballistic fibers for soft armor applications. A theoretical framework was created to design and screen potential molecules for excellent mechanical properties, and several desirable chemistries were downselected and were synthesized. Experimental characterization and process refinement are ongoing, with preliminary mechanical results on the first synthesized films showing high stiffness and high strength, albeit less than commercial products.

---

[24] https://www.nature.com/articles/s41586-018-0480-9

DOD/ARMY and academia: ARL scientists have developed a bismuth chalcogenide-graphene hybrid material for enhancing thermoelectric figure of merit. Compared to non-hybrid systems of standalone bismuth telluride nanoplates, the Seebeck coefficient of the hybrid system is higher by a factor of 2. The present method of synthesis proves to be simple, facile, low cost, and scalable for fabrication of large-scale devices.

DOD/ARMY and academia: ARL scientists and academic partners have achieved high saturation magnetization (Ms) in cobalt ferrite/multilayer graphene (MNG) and cobalt ferrite/CNT composites. The achieved high saturation magnetization is attributed to the proximity effect caused by hybridization of carbon pi-bonds and metal d-bands, which results in short-range exchange forces. The proximity induced MS is more than 3 times that of pristine cobalt-ferrite and 70 times that of pristine CNTs. The developed materials have important applications in sensors, data storage, and communication systems.

DOD/ARMY and academia: ARL and an academic partner have developed bio-templated Au, Fe, and mixed AuFe clusters that exhibit very high non-linear fluorescence and absorption. The non-linear absorption, especially two-photon absorption, is highly relevant for high-intensity laser protection applications. The synthesized fluorescent metal nanoclusters exhibit a very high degree of chemical and photo stability and can be embedded in a wide range of media for different applications.

DARPA/MTO

PCA 1b. Nanoelectronics for 2020 and Beyond

DOD/DARPA, NIST, NSF, academia, and industry: A semiconductor industry technology research consortium has worked with the National Institute of Standards and Technology (NIST) and the National Science Foundation (NSF) in a public–private partnership (called the Nanoelectronics Research Initiative—NRI—before December 2016 and nanoelectronic COmputing REsearch—nCORE—after January 2017) to address key national priorities. Through research investments in centers across the United States, NRI/nCORE seeks the next device that will propel computing beyond the limitations of current technology. The nCORE program, with support from NSF beginning in 2018, has been developed based on learning from the NRI.

In January 2018, the Defense Advanced Research Projects Agency (DARPA) and its industry partners announced six new research centers under the agency's Joint University Microelectronics Program (JUMP). JUMP will not only push fundamental technology research but also establish long-range microelectronic research themes with greater emphasis on end-application and systems-level computation. In FY 2019, for example, the Applications and Systems-Driven Center for Energy-Efficient Integrated Nanotechnologies (ASCENT) is exploring vertical complementary metal–oxide–semiconductor (CMOS) transistors for novel memory-logic co-integration circuits, beyond-CMOS spintronics for brain-inspired computing, and in/near-memory hardware demonstrations for machine-learning workloads. ASCENT is addressing both device materials and the architectures required to use them.

Via the nCore and JUMP public–private partnerships, NIST, DARPA, NSF, and U.S. member companies continue to support major interdisciplinary research teams at academic institutions across the Nation. Benchmarking of new devices in order to optimize the selection of future technology is a component of these programs.

PCA 1f. Nanotechnology-Inspired Grand Challenge for Future Computing

DOD/DARPA, academia, and industry: Among the new research centers announced by DARPA and industry partners under the JUMP program in 2018 is the Center for Brain-Inspired Computing Enabling Autonomous Intelligence (C-BRIC). In FY 2019, C-BRIC is focusing on the stochastic-spiking networks algorithm and theory development for future artificial intelligence computing workloads. In addition, neuromorphic computing accelerators using emerging memory devices and in-memory circuit architecture are being explored for autonomous intelligence.