PROGRESS AND PLANS OF NATIONAL NANOTECHNOLOGY INITIATIVE (NNI) AGENCIES

February 2018

Department of Defense (DOD)

Summary

The Department of Defense continues to aggressively pursue nanotechnology and nanomaterials to meet the needs of our warfighters on the battlefield, both for current conflicts and for the challenging missions the U.S. military will face in the future. In that vein, the department recognizes the need for strong efforts in foundational nanoscience research, and the need to maintain a solid nanoscience infrastructure within the DOD service laboratories. Joint work across the services in Synthetic Biology for Military Environments, much of which occurs at the nanoscale, has ramped up within the past year, and will continue to be a point of emphasis for DOD. Reaching across Federal agencies, the Air Force has worked with NIST and Brookhaven National Laboratory to develop new a world-unique nanoscale characterization technique, polarized resonant soft x-ray scattering for soft nanomaterials, thereby enhancing the fundamental nanoscience infrastructure for DOD and the Nation.

DOD must constantly transition state-of-the-art nanotechnologies for the benefit of our warfighters. Technologies developed in the academic or commercial sectors, or technologies developed anywhere within the DOD research and engineering enterprise, should transition rapidly when the welfare of the fighting force is at risk. DOD expects that the use of DOD ManTech (Manufacturing Technology), Defense Production Act Title III, Defense Innovation Unit Experimental (DIUx), and Small Business Innovation Research (SBIR) programs will continue to drive more nanotechnologies into the DOD industrial base. Examples of these programs include Advanced Functional Fabrics of America (AFFOA),[1] a DOD-sponsored institute under Manufacturing USA, as well as several Title III programs to include carbon nanotube production and POSS® (polyhedral oligomeric silsesquioxane) nanotechnology.

The U.S. Army Corps of Engineers plays a key role in national efforts to understand the environmental, health, and safety (EHS) effects of nanomaterials, as well as the exploration of methods in which nanomaterials can benefit EHS. The U.S. Army Engineer Research and Development Center (ERDC) has developed (and continues to upgrade) suites of tools to assess the EHS risks and potential liabilities of nanomaterials and the systems that utilize them. Finally, DOD clearly recognizes that a workforce skilled in nanotechnology is critical to national defense. DOD is a leading supporter of national science, technology, engineering, and mathematics (STEM) activities that reach from grade school to graduate school, and that include scholarships, internships, and a wide variety of events nationwide.

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[1] http://go.affoa.org/

Key Technical Accomplishments by NNI Goal

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

DOD/Navy: Navy scientists have developed and reduced to practice the use of new super-bright, photo-stable nanometer-scale voltage sensors for imaging brain activity with 20- to-40-fold greater sensitivity than currently possible. This advancement has paved the way for the design of new voltage-sensitive probes for deeper tissue imaging of brain activity for the diagnosis of brain disease and injury. The diagnosis and treatment of traumatic brain injury continues to be a major challenge for DOD medicine, and the tools developed here will allow for deeper tissue imaging with greater signal than is currently possible with conventional brain imaging probes and techniques.

DOD/Navy: Using reconfigurable DNA structures, Naval Research Laboratory (NRL) scientists have demonstrated a system able to detect two enzymes within the same sample. The DNA structures alter their conformation in response to the presence of enzymes; dyes attached to the DNA provide a real-time readout enabling monitoring of the system. This is an important milestone towards the future construction of "smart" nanomaterials able to sense, respond, and report from inside living systems. These materials can be integrated into sensors able to monitor warfighter health in the field.

DOD/Army: The U.S. Army Research Laboratory (ARL) is using computational chemistry and micromechanics analysis to design two-dimensional (2D) polymer ensembles that should be stiffer and stronger than linear aramids, but tougher than brittle 2D materials like graphene. Collaborative partnerships with academia are being used to synthesize the most promising computationally designed materials. These materials will be mechanically characterized using nanoscale indentation and shear experiments, with the best-performing materials down-selected for scaled synthesis and evaluation. The use of computational chemistry as a materials-by-design tool for high-performance structural materials represents a new paradigm in materials discovery for DOD applications, and holds promise to accelerate the development of new materials.

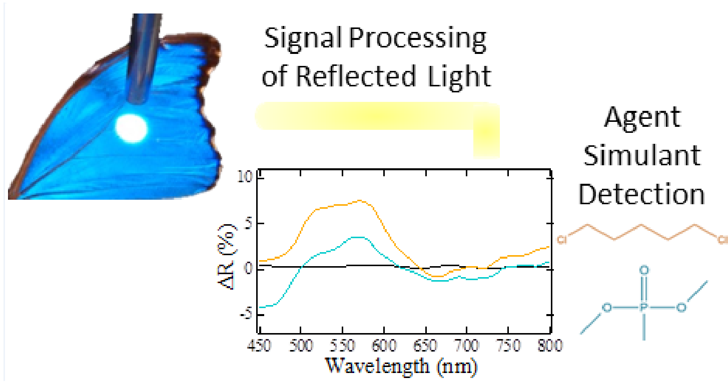
DOD/Air Force: *New Chemical Method for Exfoliation of Layered Transition Metal Dichalcogenides*. Layered transition metal dichalcogenides (TMDs) have attracted considerable attention for coatings, energy storage, and multifunctional composites due to their diverse property suites relative to other low-dimensional nanomaterials (e.g., graphene, aluminosilicates). For these bulk applications, solution exfoliation techniques, rather than vapor-phase growth favored for thin-film electronic applications, is required. Although various solution methods have been developed for powders, reproducibility and scale-up of the diverse array of TMDs (40+ compositions) in a broad range of solvents has been an issue, and has limited development of TMD films, inks, and composites. To address these issues, a new chemistry-based approach to layered TMD exfoliation was developed with characteristics critical for scaled-up production, including quiescent, bench-top conditions using mild redox chemistry; reduced reaction time; use of reagents safer than alternative solution-based approaches; compatibility with a broader range of solvent systems that were previously inaccessible due to large differences in surface energy between solvent and TMD; improved stabilization without the addition of surfactants; generalizability (MS_2, MSe_2, and MTe_2, M = Group IV-VII); and ability to prepare high concentration (> 10 mg/mL) dispersions with narrow layer thickness distributions. Patent applications have been filed.

DOD/Air Force: *Stabilization of Biomolecules in NanoScopic Ionic Liquids for Refrigeration-free Storage*. The successful implementation of biological materials for use in biosensors, diagnostics, biomedical devices, as well as composite-based materials and structures, is severely limited by their poor stability; the loss of biological activity/functionality over time (i.e., short shelf life); low tolerance to elevated temperatures; and increased sensitivity to different processing conditions (i.e., pH, salts, solvents). In all, these issues restrict the utilization of biological materials in an operational setting without the use of strictly controlled environmental conditions (i.e., refrigeration). More importantly, the need for cold chain logistics is a major barrier in resource-limited settings, as well as for military medivac operations where equipment weight and accessibility are major tactical concerns. As a result, researchers at the Air Force Research Laboratory (AFRL) have developed and patented a means towards enabling refrigeration-free storage and handling by creating protein ionic liquids. In total, protein ionic liquids represent new nanoscale multifunctional systems that are well suited towards addressing these challenges. As an example, researchers have created an ultra-stable antibody ionic liquid that is water-free, resistant to extreme temperatures (~150ºC), biologically active, exhibits a long shelf life, possesses a high protein titre, is in a processable form for printing and fabrication, and does not require "cold chain" logistics.

DOD/Air Force and academia: *First On-chip Nanoscale Optical Quantum Memory.* For the first time, an international team led by Air Force Office of Scientific Research (AFOSR)-funded scientists and engineers at Caltech has developed a computer chip with nanoscale optical quantum memory, a breakthrough with major computational implications. Quantum memory stores information in a similar fashion to the way traditional computer memory does, but on individual quantum particles—in this case, photons of light. This allows it to take advantage of the peculiar features of quantum mechanics (such as superposition, in which a quantum element can exist in two distinct states simultaneously) to store data more efficiently and securely. To store photons, the team created memory modules using optical cavities made from crystals doped with rare-earth ions. With a footprint of approximately 10 square micrometers, the memory can be integrated with other chip-scale photon source and detector devices for multiplexed quantum and classical information processing at the network nodes. The lead PI states that such a device is an essential component for the future development of optical quantum networks that could be used to transmit quantum information.

DOD/Air Force and academia: *Metalens.* AFOSR-sponsored researchers within the Harvard University Capasso Research Group used computer chip patterning techniques to create the first metamaterial lens, or metalens, that can focus the full spectrum of visible light. Metalenses are cheap to produce, thinner than a sheet of paper, and far lighter than glass. Potential applications include camera modules for cell phones and laptops, wearable optics for virtual reality and augmented reality, and telescopes in space. The work was recognized as runner-up for *Science* Magazine's Breakthrough of the Year.

DOD/DTRA: Defense Threat Reduction Agency (DTRA) funding and collaboration has facilitated basic research into nerve agent simulant sensing at the U.S. Air Force Academy Chemistry Department along two general efforts: (1) sensing based on light reflection from butterfly wings and (2) development of chemical materials that enable deposition of organometallic polymers for agent sensing. Analyzing data from light reflected from butterfly wings (natural photonic crystals) during exposure to nerve agent simulant vapor proved a viable means of detection (see image below). This demonstrated that vapor sensors based on photonic crystals could enable a long-term, passive, cheap sensor for nerve agents.



Distinct optical reflectance signals from a butterfly wing in the presence of simulants of mustard and nerve agents

DOD/Army: ERDC has developed novel nanocomposite materials using carbon nanofibers (CNFs) as an additive along with PA6 matrix material. This new composite was developed as part of basic research on force protection materials. The addition of CNFs, as opposed to carbon nanotubes and graphene nanoplatelets, has been found to be much more feasible and scalable for manufacturing, while also leading to remarkable improvements in strength and orders-of-magnitude improvements in toughness and ductility.

DOD/Army: ERDC's advanced multifunctional magnetically-responsive materials have been developed as part of military engineering basic research, with magnetic properties of composites controlled by synthetic and biologically-produced iron oxide nanoparticles. The integration of these materials into polymeric nanocomposites and fabrics has enabled the development of materials where strength and stiffness can be controlled with an externally applied magnetic field. Novel biological synthesis approaches are being developed as part of this research, to control ferromagnetic/paramagnetic properties along with particle size and morphology.

DOD/Army: ERDC has developed nanocomposites with controlled nanostructure that imparts piezoelectric properties, using nanoscale additives and bacteria-induced synthesis procedures. This work includes new applications of nanoscale modeling and simulation as well as new characterization methods for monitoring nanostructure evolution and the impact of nanostructure on properties.

DOD/Navy: The Office of Naval Research (ONR) is sponsoring a university research team to develop methods to integrate nucleic acid nanostructures with dynamic protein machines. Design methods for hybrid nanostructures would facilitate the construction of more sophisticated molecular nanostructures that are inspired by Nature's biopolymers and the dynamic formation of multi-polymer complexes. The effort involves extending computer-aided design tools to accommodate hybrid nanostructures made from combinations of nucleic acids and proteins in a unified graphical interface.

DOD/Navy: ONR has supported a university team to invent and manufacture graphene-based, stretchable, breathable, transparent, multimodal, electronic tattoo skin sensors that offer increased signal fidelity, less susceptibility to motion artifacts, and medical-grade data quality, compared to current graphene-based sensors. These electronic tattoo sensors are thinner than current graphene-based sensors (460 nm versus tens or hundreds of micrometers thick), designed in a filamentary serpentine shape, and fabricated on tattoo paper by "wet transfer, dry patterning," a method that minimizes the chemical contamination of graphene, and is quicker and cheaper than the photolithographic method used currently to pattern graphene-based biosensors. Also, these graphene electronic tattoo sensors can be directly transferred on human skin from the tattoo paper using water and fully conform to the microscale morphology of skin without any fracture or delamination for several hours if bare, or several days with liquid bandage coverage. They have been successfully used for measuring the electrical activity of the brain (electroencephalogram), heart (electrocardiogram), and muscles (electromyogram), and for measuring electrophysiological signals, including skin temperature and skin hydration.

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

DOD/Navy: Quantum sensing of motion will enable applications of accelerometry valuable to the Navy and DOD, including inertial navigation and gravitational detection of massive objects. An interdisciplinary team of scientists and engineers from NRL has incorporated semiconductor quantum dots into micrometer-scale mechanical resonators and has used the spin of a single hole to make highly sensitive measurements of mechanical motion. Strain-induced changes to the quantum dot affect the quantum spin states, which are read out using optical emission from the quantum dot.

DOD/Navy: At present, medical science is far better at sensing biological activity than actuating it. NRL's protonics program is learning to speak to biology using its most important word, the proton. One can think about protonics as the equivalent of electronics, except protons are moving instead of electrons. NRL has significantly advanced protonics by gaining a full understanding of what is happening at every interface of a protonics device. NRL researchers have used theory and modeling, confirmed by experimentation, to understand proton mobility and electrochemistry at every step. This work is laying a foundation for communication with any type of cell, not just electrically responsive cells. Such communication is an important step towards better outcomes for wounded warriors.

DOD/Navy: A significant roadblock to advancing materials for wounded warrior healing and regeneration is the intrinsic variability within live cell populations, as well as the surfaces with which they interact. Such variations result in data with large error bars, making the material design process difficult, if not impossible. Scientists at NRL have developed highly reproducible nanopatterned surfaces for investigating single cells in a variety of chemical and structural contexts. By challenging individual cells with a range of environments incorporated on these chips, researchers have significantly reduced the fluctuations inherent in cell/surface interaction studies, enabling an improved design and discovery process for regenerative materials.

DOD/Air Force: *Scale-up Fabrication of Plasmonic NanoRods*. The extremely large optical extinction coefficient of gold nanorods (AuNRs) enables their use in a diverse array of technologies, ranging from plasmonic imaging; therapeutics and sensors; to large-area coatings, filters, and optical attenuators. Development of the latter technologies has been hindered by the lack of cost-effective, large-volume production. This is due in part to the low reactant concentration required for symmetry breaking in conventional seed-mediated synthesis. Direct scale up of laboratory procedures has limited viability due to excessive solvent volume, exhaustive post-synthesis purification processes, and the generation of large amounts of waste. AFRL researchers have developed a new route to highly concentrated synthesis of monodispersed AuNRs by separating the two key steps in growth, using their recent improved understanding of the mechanism of AuNR growth. The significance is a 100-fold increase in concentration and resource efficiency without sacrificing independent control and narrow distribution of nanoparticle dimensions, aspect ratio, and volume. This results in an approximately 10-fold decrease in synthesis time and approximately 4-fold decrease in cost per gram of AuNRs. Patent applications have been filed.

DOD/Air Force: *Flexible RF circuits from NanoMembrane GaN.* AFRL has pioneered and patented the development of flexible gallium nitride (GaN) radio frequency (RF) devices that can be easily integrated into more effective wireless communications systems, the Internet of Things, autonomous vehicles, and radar applications. By making the high-performance devices flexible and conformal, more compact and mobile platforms can be realized without compromising performance. The AFRL team was the first to demonstrate a flexible RF transistor device based on GaN that can operate in a strained state by optimizing a transfer layer just six atoms thick underneath the device to effectively "lift off" high-performing RF transistor devices and move them to flexible platforms. These devices are being developed for military applications, including wearable human performance monitoring systems and future conformal radar concepts.

DOD/Air Force, academia, and industry: *CMOS Integrated Memristor and Nanophotonic Devices.* The Air Force is collaborating with academia and the SEMATECH semiconductor manufacturing consortium to develop both hybrid complementary metal-oxide semiconductor (CMOS)/memristor circuits and integrated CMOS with on-chip nanophotonics by leveraging the multi-billion dollar nanomanufacturing facility in Albany, NY. Advancements in autonomous systems requires dynamic learning by neuromorphic computers. This is only feasible using hybrid CMOS/memristor integrated circuits. The Air Force has brought together leading scientists and engineers to develop the world's only front-end-of-the-line memristor manufacturing process that utilizes commercial CMOS materials and processes. This significantly shortens the time from design to manufacturing to fielding to the warfighter. The Air Force is also developing CMOS integrated nanophotonics capabilities for ultra-high data transmission rates, both on-chip and chip-to-chip. This is a critical technology in today's Internet of Things environment.

DOD/Air Force and academia: *New Printing Technique for Solar Photovoltaic and Optoelectronic Devices.* AFOSR-funded researchers at the Georgia Institute of Technology (Georgia Tech) recently reported on the creation of a new printing technique (meniscus-assisted solution printing, or MASP) that enables the control of crystal size and orientation during perovskite film formation. Perovskites are key materials used in a variety of solar photovoltaic and optoelectronic devices, and controlling crystal size and orientation in thin films is critical to tuning and optimizing such devices. Solar cell power conversion efficiency has been shown to be boosted by nearly 20% by using MASP. While other fabrication techniques can also prepare similar perovskites, they require high temperatures to evaporate the processing solvent; however, this new low-temperature process now allows the use of polymer materials that are potential substrates for stretchable and flexible devices. This approach to making novel nanocomposites aligns well with current AFRL development activities in the areas of soft electronics and additive manufacturing.

DOD/Air Force and academia: *New Graphene Manufacturing Technique.* An international team of scientists (including AFOSR-funded researchers at Georgia Tech) has developed a new way to produce single-layer graphene from a simple precursor: ethene—also known as ethylene—the smallest alkene molecule, which contains just two atoms of carbon. Because of its low cost and simplicity, the technique could open new potential applications for graphene, which has attractive physical and electronic properties.

DOD/Air Force and academia: *Nano-Enabled Additive Manufacturing of Composites.* AFRL, in collaboration with academia, is developing novel nanoscale rheology modifiers that enable processing of aerospace-relevant resin systems in extrusion-based additive manufacturing. 2D nanoparticles allow three-dimensional (3D) printing of epoxy matrix resins that are highly filled with reinforcement fillers such as chopped carbon fibers and silicon carbide whiskers. The thixotropic behavior of these "nanofilled" polymer matrix formulations facilitates gelation, setting, and simple post-processing. Similar technology is being used to print high-temperature refractory materials with greatly reduced defects compared to conventional processing of ceramics.

DOD/Air Force and industry: *Production of Carbon Nanotube (CNT) Sheet, Tape, Film.* General Nano, partnering with AFRL, has developed Veelo—a class of lightweight CNT sheet, tape, film, and array products that original equipment manufacturer (OEM) and Tier 1 suppliers can seamlessly integrate into existing composite manufacturing processes for improved structural composite mechanical and electrical properties. General Nano has demonstrated continuous manufacturing of 300+ ft. CNT rollstock using a 13" wide wet-laid nonwoven pilot line and 25 $ft.^2$ of continuous carbon nanotube synthesis for a 1 kg per day CNT manufacturing capability. This enables such potential applications as de-icing, electromagnetic interference (EMI) shielding, lightning strike protection, and directed energy protection. For example in partnership with Boeing Research and Technology, Veelo has demonstrated adequate fracture toughness with improved (100x) electrical conductivity over the baseline composite currently being used in many aircraft composite structures. The new product is being evaluated by Boeing as a lighter-weight lightning strike protection material system.

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

DOD/Air Force, NIST, and DOE/Brookhaven National Laboratory: *Polarized Resonant Soft X-ray Scattering for Soft NanoMaterials, Devices, and Manufacturing*. The National Institute of Standards and Technology (NIST), the Department of Energy (DOE) Brookhaven National Laboratory (BNL), and AFRL Materials and Manufacturing Directorate (AFRL/RXA) are developing a world-unique polarized resonant soft x-ray scattering (P-RSoXS) facility at the National Synchrotron Light Source II (NSLS-II). P-RSoXS can readily probe nanomaterial and biomolecular interactions at the atomic level in aqueous environments by using tunable x-ray energies matching resonant energies of functional groups found throughout soft-matter and biological molecules. This energy-dependent scattering provides enhanced x-ray contrast from the chemical moieties of interest. The polarization of x-rays also provides information on molecular alignment and orientation at the interface or within large assemblies. Though commonly performed in high-vacuum environments, the developing capability at NSLS-II will incorporate liquid cells (first of their kind in the world), enabling P-RSoXS experiments under conditions relevant to biological and nanoscopic self-assembling systems. By using x-ray energies capable of selectively probing functionalities containing C, N, O, P, and S atoms in a polarized fashion in liquid environments, P-RSoXS can probe the local structure of individual chemical moieties in biological samples, which can then be reconstructed to yield local structural details needed to appropriately assess structure/function relationships.

DOD/Air Force: *Nano-Bio Aerospace Fuels Research & Test Facility.* AFRL is investing internal funds to refurbish an existing facility to become a state-of-the-art bio/nano fuels research laboratory. The project will result in about 12,000 $ft.^2$ of renovated lab/office space, half of which will be dedicated to nanoenergetics research.

DOD/Army: ARL has recently made significant progress in the science (and related processing) of stable nanocrystalline materials. ARL developed a divergent, bulk nanocrystalline copper–tantalum alloy that is able to achieve and retain high strength and creep resistance at elevated temperatures—a combination unexpected based on conventional wisdom and a true example of a revolutionary finding. These published results will also lead to advances in designing nanocrystalline alloys with order-of-magnitude increases in elevated temperature strength and creep resistance compared to single crystals and alloys currently used in turbine engines and hypersonics applications. Critical to the success of this work was the aim from the outset to develop a robust methodology for designing thermodynamically stable, nanoscale microstructures across a broad range of alloy types (e.g., aluminum, iron, nickel, vanadium, niobium, tantalum, molybdenum, and tungsten alloys). It is this inherent stability of the nanoscale grain structure that ultimately results in these excellent properties. Recent data indicate that the same creep-resistant properties have been passed on to Ni-based alloys. The potential of increasing the engine operating temperature 100-200 degrees Celsius by using nanocrystalline nickel, without a coating, or several hundreds of degrees with nanocrystalline refractory metal alloys, at stresses/strengths an order of magnitude higher than currently accessible, has the potential to revolutionize engine and flight technology on a global scale. ARL plans to extend its work in stable nanocrystalline materials to new alloy systems for a variety of applications. Some alloys under consideration are directed towards high-strength applications, some toward high temperature resistance, and others towards unique portable energy applications. A key component is the establishment of world-class powder processing and consolidation facilities at ARL, targeting a broad range of nanometallic systems.

DOD/Army: ERDC has pioneered new developments in nanocalorimetry, geochemical analysis, and particle sizing to advance understanding of nanoscale amorphous/poorly ordered silica additives for use in concrete. These materials are essential in the production of high-strength concrete materials for structural hardening of critical facilities. Developments of advanced characterization techniques are being executed as part of basic research, with implementation of knowledge generated being directly used by applied research programs including modeling of hydration and pozzolanic reaction mechanisms.

DOD/Army: ERDC has developed novel, multiscale modeling approaches using wavelet-based transformation methods that allow for the rapid mathematical up-scaling of nanoscale phenomena. These approaches enable implementation for high-performance computing for multiple applications, and are being extended for use in applied materials research.

DOD/Navy: ONR is funding a collaborative academic effort to establish a methodology for the massively parallel manufacture of nanoscale electronic devices. The approach involves the assembly of organic semiconductor building blocks into DNA-like organic electronic active components, using synthetic techniques employed in automated oligonucleotide synthesis, followed by the self-assembly of the DNA-like organic nanowires on nanoimprinted molecular breadboards. The strategy has the potential to serve as a foundation for the scalable nanomanufacturing of the next generation of semiconductor devices.

Goal 4. Support Responsible Development of Nanotechnology

DOD/Army: ERDC has developed knowledge products on environmental sustainability, performance, and potential risk of nanotechnology-enabled materials including nanotube paints and photocatalytic cementitious materials. Materials have been subjected to a tiered sustainability framework approach to identify potential concerns and the test methods needed to understand manufacturing, use, and disposal environmental risks. Products are available[2] and will be updated in fiscal year (FY) 2018. Additional life cycle

[2] https://nano.el.erdc.dren.mil/sops.html

methods;[3] framework testing,[4] and nanotechnology-enabled product case investigations[5] have been published.

DOD/Army: ERDC has developed and released a software program called Nano Guidance for Risk Informed Deployment tool (NanoGRID v1.0) that implements a tiered-based approach for EHS testing and assessment of the potential for release of nanoscale materials from products, based on properties and uses. In addition, ERDC has developed the Nano-enabled Navigation for Product Acquisition and Liability tool (Nano NAV-PAL) software, which is designed to help producers and integrators of nanomaterials by enabling evaluation of EHS risks of integrating nanomaterials into existing products or developing new nanomaterials. Both tools will be available for download.[6]

DOD/Army: ERDC has fabricated chitosan (CS)-graphene oxide (GO) composite films that were characterized and evaluated as pressure-driven water filtration membranes. The evaporative phase inversion process allows for scale up, overcoming limitations of vacuum-assisted self-assembly. This published work[7] represents the first report of graphene oxide being tested in cross-flow conditions. Work on preliminary synthesis and flux enhancement of graphene oxide with hydrophilic polymers has also been published.[8] ERDC has also developed and demonstrated a process for recycling GO composites. This material application offers a significant advantage over traditional thermoplastics and thermoset polymers in which decomposition occurs prior to the melting point, preventing recycling. The graphene oxide composites can be macroscopically repaired to restore original tensile strength, filtration performance, and flux parameters. A patent application has been submitted.

DOD/Army, CPSC, academia, and industry: ERDC; the Army Armament Research, Development and Engineering Center; the Consumer Product Safety Commission (CPSC); Duke University; and EATON Corporation have been funded to generate modeling and simulation of additive manufacturing processes, including prototyping development of nanomaterial-modified materials for force protection. ERDC, CPSC, and Duke will also perform case studies on nanoparticle and volatile organic compound emissions from nanotechnologies (e.g., energetic casings, novel propellant manufacturing methods), including additive manufacturing of advanced materials by fused deposition modeling, stereolithography, and metal power 3D printing technologies. The mission is to better characterize and identify exposure concerns, and to disseminate methods to reduce worker, soldier, and environmental exposure vectors while advancing novel manufacturing capabilities for the Army and the Nation.

DOD/Army, NIOSH, and academia: ERDC, Texas A&M University, and the National Institute for Occupational Safety and Health (NIOSH) are developing an analytical framework for detecting carbon nanotubes in complex matrices that will provide a streamlined approach for increasing confidence in low-exposure risk assessment decisions for hard-to-detect carbon-based materials. This includes new analytical methods employing microwave excitation technologies and better defining analytical detection limits to compare to

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[3] doi:10.1038/nnano.2017.152

[4] https://doi.org/10.1080/17435390.2017.1317863

[5] https://doi.org/10.1016/j.impact.2017.06.006

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

[7] https://pubs.acs.org/doi/abs/10.1021/acsomega.7b01266

[8] https://ascelibrary.org/doi/abs/10.1061/%28ASCE%29EE.1943-7870.0001268

human health particle aerosolization concentrations of concern. Products will be disseminated as peer-reviewed publications and software.

Plans and Priorities by Program Component Area (PCA)

PCA 1. Nanotechnology Signature Initiatives and Grand Challenges

DOD/Army, industry, and academia: The Army's Institute for Soldier Nanotechnologies (AISN), an Army-sponsored University Affiliated Research Center, is structured as an alliance between academia, industry, and the Army. Recent significant accomplishments include advances in fundamental understanding that led to a molecularly detailed model of the interphase structure in semicrystalline polymers, more accurate analysis of dynamic fracture leading to high-fidelity failure models, advances in fundamental understanding of 2D materials for potential mid-infrared detection and light emission, and further testing of multi-component nanolayer self-assembled structures for wound healing. The Army is collaborating with a startup (Veloxint, Inc.) to further develop a lightweight nanocrystalline metal alloy that can be molded using 3D printing, leading to a significant reduction in weight while maintaining mechanical strength.

DOD/Navy: In the area of the Nanoelectronics for 2020 and Beyond Nanotechnology Signature Initiative (NSI), the Navy plans to investigate photonic approaches to quantum information processing, which include developing photonic coupling to cold atoms and highly entangled photon sources. In addition, researchers will develop novel 2D heterostructures for spintronic applications. For the “Nanotechnology for Sensors” NSI, NRL plans to investigate chemical sensor platforms for the cellular signals that control wound healing and “smart” molecular machines that can sense, report, and respond inside living systems. In addition, NRL is developing quantum sensors based on spin-mechanical coupling. For the Future Computing Grand Challenge, NRL plans to support an effort in nanophotonic-based reservoir computing.

DOD/DARPA, NIST, NSF, academia, and industry: In support of the Nanoelectronics for 2020 and Beyond NSI, a semiconductor industry technology research consortium has worked with 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. For example, the Applications and Systems driven Center for Energy-Efficient Integrated Nanotechnologies (ASCENT) will use research from 13 different universities to explore novel integration schemes, innovative device technologies, and hardware accelerators useful for surpassing the anticipated limits in traditional CMOS technology. ASCENT will address 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.

DOD/DARPA, academia, and industry: The DARPA JUMP Program also includes activities in support of the Nanotechnology-Inspired Grand Challenge for Future Computing. 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. For example, the Center for Brain-inspired Computing Enabling Autonomous Intelligence (C-BRIC), aims to deliver major advances in cognitive computing and future artificial intelligence through neuro-inspired algorithms, theories, and hardware fabrics.

PCA 2. Foundational Research

DOD/Air Force: *MetaSurfaces for Compact Imaging.* Nanophotonics at subwavelength scales is dominated by scattering processes that have little directionality, and this fundamentally limits performance and functionality in nanooptical devices. Controlling the direction of optical emission and generation at nanoscale dimensions requires complex structured nanoparticle elements with precisely balanced multipolar electromagnetic resonances. The subwavelenth features required and precise material and fabrication tolerances needed to engineer such systems push the capabilities of current approaches for fabrication of plasmonic and nanophotonic systems. Current work at AFRL to explore epitaxial routes to fabricate advanced plasmonic systems is showing promise for highly controlled linear and nonlinear scattering, which can dramatically improve the performance of metasurface optics and integrated photonic systems that rely on subwavelength structured materials. This work could lead to revolutionary advances in compact imaging systems and detectors.

DOD/Navy: NRL scientists demonstrated that the spin polarization generated by spin-momentum locking in the topologically protected surface states of Bi_2Se_3 can be used to modulate the magnetization of an adjacent ferromagnetic film by spin transfer torque arising from the flow of pure spin current from the Bi_2Se_3 into the ferromagnetic film. In next-generation memory devices based on magnetic tunnel junctions, the magnetization of the free magnetic layer is switched by spin transfer torque using a spin-polarized current flowing through a high-resistance oxide tunnel barrier, resulting in power dissipation and heat generation. This accomplishment eliminates this high-resistance oxide layer, and provides a path towards non-volatile random access memory with higher density and lower power consumption.

DOD/Navy: ONR anticipates continued strong support of PCA 2, particularly in the area of biological actuation, where it plans to develop "protonic" devices for actuating cells and nanoscale transducers for wireless control of living cells. Additional efforts are planned to investigate enhanced biological and multiscale integrated chemical catalysts, multifunctional nanophotonics, nanoscale phase transitions, the quantum control of chemical reactivity, and cyclic peptide polymers for tissue scaffolds.

DOD/Navy: ONR sponsored research at a university laboratory to develop a strategy to fold single, long DNA or RNA strands into unknotted, target shapes called single-stranded DNA origami or single-stranded RNA origami. The method uses partially complemented double-stranded DNA or RNA and parallel crossover cohesion for construction of such structures, and has been demonstrated with synthetic sequences ranging in length from approximately 1,000 to 10,000 nucleotides. Facile replication of the single strand *in vitro* and in living cells has also been demonstrated. The method expands the design space for bottom-up nanotechnology.

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

DOD/Army, industry, and academia: The Army Research Office (ARO) supported a joint effort between a small business (Applied Novel Devices) and an academic partner (the University of Texas at Austin) that succeeded in growing large single-crystal domains of monolayer MoS_2 2D nanomaterials with edge length >120 µm for novel high-performance RF transistors (RF FETs). ARO plans to continue to explore other extraordinary functional properties (such as color centers) in novel 2D nanomaterials and their heterostructures made by using different 2D nanomaterials.

DOD/DTRA: DTRA-sponsored researchers at the University of California, Merced, are exploring basic research entitled "Quantum-Enhanced Motion Sensing using Entangled Spins in Quantum Dots." In 2017, this work, in a collaborative effort with NRL and Sotera Defense Solutions, Inc., was recognized by the American Institute of Physics as an innovative potential development for sensing. Interest in future development includes, for example, a push toward developments in nuclear detection. Future plans include continuing to see if there are additional potential developments of scientific interest between nanotechnology and quantum science areas for sensing and other broad uses.

DOD/Air Force, industry: *Dielectric Metamaterials for Optical Components.* Singly negative metamaterials with exceptional reflectance (i.e., superior to all metallic mirrors in the shortwave infrared portion of the electromagnetic spectrum) using 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. Full-wave simulations provide a broad range of novel optical properties through tailoring geometry, orientation, and arrangement of sub-wavelength features. 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/Air Force: *Single-Photon Quantum Emitters*. The precise location of single-photon quantum emitters composed of single defects in crystalline materials is a major enabling technological milestone that is widely pursued. Current planar processing approaches using implantation randomly place defects such that yields are insufficient for highly integrated quantum photonic systems. Current work at AFRL is developing molecular seeds that can act as nanoparticle growth initiators in a chemical vapor deposition (CVD) process to create single defects centered within nanoparticles. Ongoing work to precisely position such particles within optical integrated circuits using laser-assisted transfer will allow for both selection and placement of uniform single-defect-containing nanoparticles in large arrays.

DOD/Air Force and academia: *Novel Photonic Plasmonic Interconnect.* George Washington University has developed a novel photonic plasmonic interconnect under the AFOSR-sponsored Dynamically Adaptive Hybrid Nanoplasmonic NoCs (DAHNN) project. A novel architecture was designed for autonomous, high-throughput, high-speed, low-latency, and ultra-low power for on-chip communication that supports multi-domain data coordination. A key enabler was the on-the-chip Dynamic Data-Driven Applications Systems (DDDAS) adaptation engine operating synergistically with the network; where the DDDAS engine senses both application demand changes and the status of the network, and adapts the network to improve performance and power consumption. Using the same traffic information, the DDDAS-augmented network-on-chip tunes itself in order to improve its future monitoring, decisions, and network adaptation strategies. The innovation has focused on hybrid nanoplasmonic devices and DDDAS-on-the-chip, in addition to directly contributing to next-generation processor architectures. Initial findings have resulted in three filed patents. Furthermore, the work is setting the foundation for an interdisciplinary area of nanophotonic-enabled computing from NSF and Semiconductor Research Corporation (SRC) grants, which aims at creating an analog reconfigurable optical computer (aROC) and a nanophotonic neuromorphic computer.

DOD/Air Force: *CNT Arrays as Smart Sensors for "Fly-by-Feel" Systems.* Researchers at the Air Force Materials and Manufacturing Directorate have invented, patented, and demonstrated a bio-inspired artificial hair flow sensor that predictably measures the air flow in, and above, the boundary layer of an airfoil using the piezoresistive properties of CNT arrays grown between a single glass fiber and an electroded glass capillary.

These cantilevered hairs have high sensitivities (0.5 to 17% per m/s vs. 0.1% for others), can be tailored to flow speed (1-100 mph demonstrated), and can sense the onset of turbulence. Working with researchers in the Aerospace Systems Directorate, sensors were integrated as arrays onto the surface of an airfoil and used to successfully detect airfoil angle of attack (AoA), speed, coefficient of lift, moment, and flow separation. As small, agile fliers continue to join the fleet, lightweight, distributed smart sensors (vs. bulky "bolted-on," single-point measurements) will be increasingly needed for "fly-by-feel" systems.

DOD/DTRA: Funded by DTRA's Joint Science and Technology Office (JSTO), researchers are leveraging nanoscience to combat organophosphate nerve agents (OPNA) for improved warfighter safety. The efforts are part of JSTO's Nanostructured Countermeasure Platforms for Chemical Warfare Agents (NCP-CWA) program, which explores enhanced delivery methods for prophylactics and therapeutics. Currently there are no approved broad-spectrum prophylactic countermeasures available to protect the warfighter against multiple chemical threats. The JSTO portfolio aims to fill this gap with its bioscavenger program.

DOD/DTRA: Sometimes the smallest technologies provide the biggest impact for protecting warfighters from chemical and biological attacks. Researchers working for the DTRA's Toxicant Penetration and Scavenging (TPS) portfolio are developing enzyme-DNA nanostructures to provide a foundation for understanding catalytic enhancement in nanostructured materials. The TPS program explores chemical and biological agent countermeasure development as well as structural relationships. For this project, DTRA's Chemical and Biological Technologies Department is exploring DNA nanomaterials and their ability to control molecular features of enzyme systems. This has proven effective in enhancing catalysis, creating efficient multistep cascades, and improving enzyme stability.

DOD/Navy: NRL scientists have demonstrated the utility of nanoscale coatings to entirely eliminate dangerous dendrite formation while simultaneously increasing capacity retention in nanoscale Li-ion battery electrode materials. Stabilizing the electrolyte/electrode interface and eliminating dendrite formation allows batteries to be charged and discharged repeatedly without loss of capacity and, more importantly, without regard for accidental overcharge and the consequent thermal runaway. This eliminates the need for "partial charge" protocols in the field that hamper full usage of battery capacity.

PCA 4. Research Infrastructure and Instrumentation

DOD/Army: A key DOD nanotechnology research infrastructure component is the establishment of world-class powder processing and consolidation facilities at ARL, targeted to a broad range of nanometallic systems.

PCA 5. Environment, Health, and Safety

DOD/Army: ERDC has authored research and offered perspectives demonstrating the utility of multi-criteria decision analysis approaches to nanotechnology-focused risk assessment, underscoring the need to continue the transition from traditional risk assessment towards risk-based decision making and alternatives-based governance for emerging technologies. Further, ERDC has developed the Nano Prioritization Framework and Software Tool to help screen and prioritize a diverse array of nanotechnology-enabled consumer products by evaluating each product's potential hazard and exposure, as well as additional criteria designated as important to the user, and then establishing a prioritization score.

DOD/Army: ERDC has become the lead of the quarterly Deputy Under the Secretary of Defense-sponsored DOD Nanomaterials Working Group. Objectives include integrating the ERDC-developed NanoGRID framework into the OSD Guidance Manual for the Collection of Chemical, Physical, and Toxicology Data

(CPT) to support DOD Systems Acquisition; modifying the focus of the working group and renaming it the Advanced Materials Working Group; and growing participation to include technology developer perspectives on environmental, safety, and occupational health impacts on Army/Navy/Air Force ability to provide solutions to safe and rapid acquisition of advanced materials technologies.

DOD/Army, industry, and academia: ERDC, Brewer Science, and Missouri State University have published a methodology[9] and a website[10] supporting the life-cycle assessment of nanotechnology-enabled products developed by small businesses. The effort is streamlining sustainability, safety, and insurance liability decisions. They have developed and will disseminate standard operating procedures (SOPs) on the preparation of nanomaterial-enabled technologies, including assessment of characterization, release fate, and hazard. Such information is critical to accomplish currently elusive, high-quality exposure determinations required in risk assessment. Additional SOPs were completed in FY 2017 and will be publically disseminated via the Defense Technology Information Center in FY 2018. These products are available now[11] and will be updated in FY 2018.

DOD/Army and NIOSH: These agencies are eliciting/surveying subject matter expertise in order to finalize a definition and classification methodology for advanced (nano)materials (which include some nanomaterials). This methodology will be integrated into a decision-support tool to help technology developers collect pertinent risk information when using or considering use of advanced materials. ERDC will continue to finalize a framework for conceptualizing the sustainability of advanced materials. The framework will help developers of "advanced (nano)materials" better understand product sustainability and will support decisions related to sustainable development, alternatives assessment, and safety-by-design, including a new point source nanomaterial fate and transport model (NanoTRAK).

DOD/Army, EPA, NIST, and industry: ERDC is collaborating with the Environmental Protection Agency (EPA), NIST, and industry to develop internationally recognized testing assessment standards. ERDC is leading development of five standardized guidance documents and methods to advance acquisition of consistent, high-quality data for nanomaterials and products. Final drafts are being developed for tiered testing frameworks (ASTM), aquatic toxicity testing (Organisation for Economic Cooperation and Development, OECD), and standardized characterization of nanomaterials release from products (International Organization for Standardization, ISO, Technical Committee 229).

DOD/Army, academia, and industry: ERDC; the Army Armament Research, Development and Engineering Center; Virginia Tech; and NanoSafe, Inc., are organizing a series of workshops to define the decision scape for addressing the potential EHS implications of nanomaterials, advanced materials, and additive manufacturing. The first workshop (EMERGE – Emergency Management of Emerging Technologies and Advanced Manufacturing) tool place in March 2017. An additional workshop (NanoBio Convergence) is planned for 2018.

DOD/Air Force and industry: "O*rgan-on-a-Chip" Project*. The vision of this project is to utilize next-generation toxicity testing to identify and reduce toxicity of advanced nanomaterials used in aerospace applications. Research is currently addressing issues to understand the mechanisms of nanomaterial-induced toxicity through the use of cutting-edge molecular techniques, linked organ *in vitro* models, and the addition of mechanical forces to simulate physiologically relevant tissues/organs. These techniques are

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[9] https://www.techconnect.org/proceedings/paper.html?volume=TCB2017v1&chapter=9&paper=645

[10] https://jvic.missouristate.edu/case/nanotechnology-initiative/

[11] https://nano.el.erdc.dren.mil/sops.html

being applied to next-generation *in vitro* models to enable migration to testing and evaluation of toxicity directly within the operational environment. Integration of this understanding into a portable, low-cost, disposable form (“Organ-on-a-Chip”) will reduce risk in advanced materials development by providing timely feedback on toxicology to influence material formulation, material down-selection, and risk mitigation.

DOD/DTRA: One of the challenges in developing medical countermeasures for chemical and biological warfare agents is addressing the effects on the central nervous system (CNS). DTRA’s program leverages several approaches to address this challenge. One approach centers around the development of correlated *in silico*, *in vitro,* and *in vivo* models of the blood-brain barrier (BBB), including *in vitro* models derived from human induced pluripotent stem cells incorporating 3D architectures and soft electronic materials. These enable improved recapitulation of the human BBB as well as real-time tracking of transport phenomena. A second approach of the program spearheaded by the University of Michigan focuses on challenging these BBB models with libraries of nanoparticulates of varied physical/chemical properties such as size, morphology, surface chemistry, and elastic modulus to understand the effect of these parameters in dictating entry into the CNS. The *Bioengineering and Translational Medicine* article, Engineering of nanoparticle size via electrohydrodynamic jetting,[12] describes the establishment of a technological approach to compartmentalized nanoparticles with defined sizes in order to modulate cellular uptake.

[12] https://doi.org/10.1002/btm2.10010