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Information Analysis Center

Special Nanotechnology Issue 2017

Nanotechnology

it's a Big Deal

DEPARTMENT OF DEFENSE
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Information Analysis Center

Special Nanotechnology Issue

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Message from the Science and Technology Advisor

On Dec. 29, 1959, the esteemed physicist and Nobel Laureate, Richard Feynman, gave a lecture at the California Institute of Technology titled, “There’s Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics.” In his speech, he addressed the fact that humanity has not exploited all there is in the known universe and suggested it would be possible in the coming years to dive deeper into matter than had ever been done before, to manipulate atoms and create machines and new materials at extremely small scales, and by doing so, usher in a new age of science. His presentation is largely accepted as the beginning of interest in a new field now known as nanotechnology, a term first used by Norio Taniguchi in 1974 and later popularized by Eric Drexler.

Nanotechnology is generally a set of tools and techniques used to manipulate matter on an atomic scale, between 1 and 100 nanometers, to produce new materials and structures, often referred to as engineered nanomaterials. Several major breakthroughs throughout the 1980s and 1990s demonstrated the potential that nanotechnology had in terms of revolutionizing various aspects of scientific discovery, technological advancement and economic development.

In 1981, Gerd Binnig and Heinrich Rohrer of IBM developed the scanning tunneling microscope, which allowed individual atoms to be imaged and manipulated. Two other IBM researchers, Donald Eigler and Erhard Schweizer, were able to spell out “IBM” by arranging 35 xenon atoms using an STM in 1989.

Research at Rice University in 1985 led to the discovery of buckminsterfullerene, usually referred to as a “buckyball,” a carbon compound composed of 60 carbon atoms arranged in a structure that roughly resembles a soccer ball. Harold Kroto, Robert Curl and Richard Smalley were awarded the Nobel Prize in Chemistry in 1996 for their discovery.

Finally, numerous researchers from as early as the 1950s into the 1990s, can take some credit for discovery and re-discovery of carbon nanotubes, which are hollow, cylindrical structures made of carbon that exhibit extreme thermal, mechanical and electrical properties.

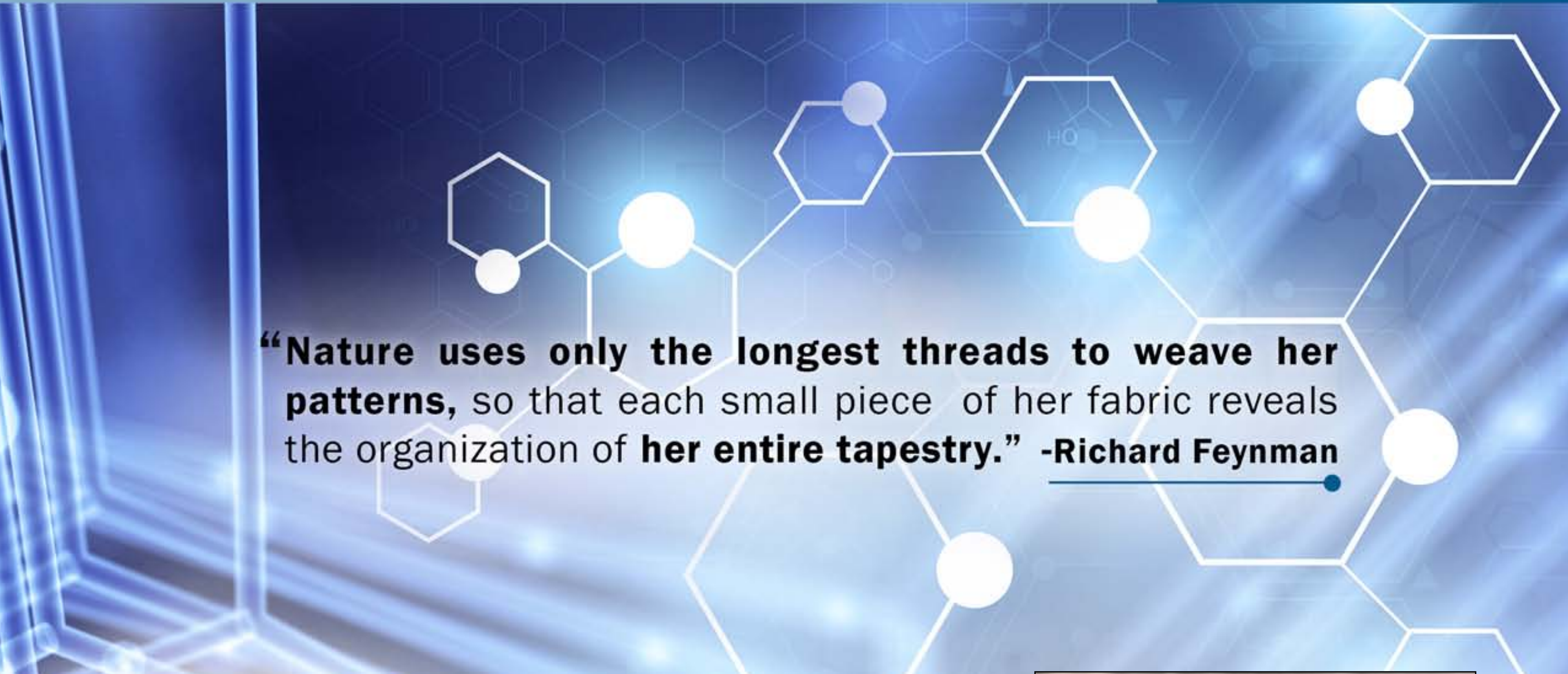
Seeing the strategic potential of nanotechnology, the Clinton administration decided to take action, and in 2000, under the guidance of Mihail “Mike” Roco, the U.S. government established the National Nanotechnology Initiative in order to “bring together the expertise needed to advance this broad and complex field.”

The NNI is a national research and development initiative involving 20 departments and agencies of the federal government, investing nearly $24 billion since 2001. Over the past 16 years, nanotechnology research and commercialization in the United States has grown rapidly, largely due to the investment and oversight of the NNI.

Approximately 1,200 companies, universities and government laboratories engage in nanotechnology research, development and commercialization in the United States. More than 750 products that incorporate nanotechnology/nanomaterials in their design in some way are currently available in U.S. markets. The proposed NNI budget for fiscal year 2017 is greater than $1.4 billion.

The early years of nanotechnology research in the United States were primarily theoretical, but much has changed in terms of what is now possible and what is practical. The pace of discovery in nanotechnology research has been blistering, leading to an explosion of roughly 2,000 different types of engineered nanomaterials, including the all-important graphene, a single layer of carbon atoms arranged in a hexagonal pattern. The significance of contributions in the field have been noteworthy enough to earn at least four Nobel Prizes, including the 2016 award in chemistry “for the design and synthesis of molecular machines” as well as the establishment of the Kavli Prize in Nanoscience, first awarded in 2008. Efforts to educate a future workforce in nanotechnology have led to the launch of nanotechnology programs at more than 100 academic institutions in the United States alone.

The Department of Defense has been actively engaged in nanotechnology research, development and, when applicable, commercialization, since before the founding of the NNI. Since 1999, the DoD has spent approximately $5 billion on nanotechnology research, including a proposed $131 million



> “**Nature uses only the longest threads to weave her patterns,** so that each small piece of her fabric reveals the organization of **her entire tapestry.”** **-Richard Feynman**

dollar budget for fiscal year 2017, with the majority dedicated to foundational research.

Most of the funding and research activities regarding the DoD’s nanotechnology enterprise are directed by eight key organizations, including the research laboratories of the Army, the Navy and the Air Force, as well as the Defense Advanced Research Projects Agency and the Defense Threat Reduction Agency. The DoD’s commitment to a sustainable nanotechnology program is evidenced by the founding of formal nanotechnology research institutes.

The Naval Research Laboratory established the Institute for Nanoscience in 2001 to conduct multidisciplinary research at the nanoscale. In 2002, the U.S. Army established the Institute for Solider Nanotechnologies at the Massachusetts Institute of Technology to conduct “basic research to create new materials, devices, processes, and systems, and on applied research to transition promising results toward practical products useful to the Soldier.” [1]

The Picatinny Arsenal, part of the U.S. Army Armament Research, Development and Engineering Center launched a nanomaterials class in 2015, further demonstrating the important role that nanotechnology is playing within the DoD. To further show that there is no sign of slowing down, the DoD announced in 2016 that it will be investing $75 million in the Revolutionary Fibers and Textiles Manufacturing Innovation Institute at MIT to “accelerate innovation in high-tech, U.S.-based manufacturing involving fibers and textiles” where nanomaterials will play a significant role. [2]

Nanotechnology research within the DoD is slowly transitioning from basic to applied, and as this happens, more attention is being paid to how nanotechnology will benefit the individual warfighter and how to overcome challenges for implementing these technologies, such as facilitating technology transfer and minimizing environmental impacts.

The articles presented in this special issue not only exhibit applications of nanotechnology in the Homeland Defense and Security Information Analysis Center’s focus areas, but they also reveal the reach that nanotechnology has on so many aspects of science, technology, engineering and society.

As the DoD continues to invest in nanotechnology, it is now time to go beyond the possibilities of what basic research can offer and to consider what a healthy, thriving nanotechnology enterprise looks like. This collection of articles represents the future of thought in nanotechnology that must be present going forward. As more funding and resources are dedicated to understanding the nanoscale, a balance needs to be struck between pushing the boundaries and limits of science with being mindful of limiting potential impacts and anticipating unintended consequences.

Whether it is the invisible world of the nanoscale itself, or the state of affairs created by the use of nanotechnology, the words of the philosopher, Bertrand Russell (1872-1970), are a reminder that, “One must care about a world one will not see.” [3] ■

Gregory Nichols
HDIAC S&T Advisor

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2. Chandler, D. L. (2016, April 01). New institute will accelerate innovations in fibers and fabrics. Retrieved from **http://news.mit.edu/2016/national-public-private-institute-innovations-fibers-fabrics-0401** (accessed December 14, 2016)
3. Robertson, C., & Robertson, C. (1997). The Wordsworth dictionary of quotations. Ware, Hertfordshire: Wordsworth. (accessed December 14, 2016)

A Timeline of Nanot

1959

Richard Feynman, from California Institute of Technology, gave the first lecture called, "There's Plenty of Room at the Bottom" on technology and engineering at the atomic scale at an American Physical Society meeting at Caltech

National Nanotechnology Initiative. (2014). Nanotechnology Timeline. Retrieved from http://www.nano.gov/timeline (accessed December 8, 2016)

1981

Researchers at IBM's Zurich lab invented the scanning tunneling microscope. This allowed scientists to identify spatial images of individual atoms for the first time.

Nanotechnology Initiative. (2014). Nanotechnology Timeline. Retrieved from http://www.nano.gov/timeline (accessed December 8, 2016)

1974

Tokyo Science University professor coined the term nanotechnology to describe precision machining of materials to within atomic-scale dimensional tolerances.

Nanotechnology Initiative. (2014). Nanotechnology Timeline. Retrieved from http://www.nano.gov/timeline (accessed December 8, 2016)

2000

President Clinton launched the National Nanotechnology Initiative (NNI) to coordinate federal Research & Development efforts and promote U.S. competitiveness in nanotechnology.

Nanotechnology Initiative. (2014). Nanotechnology Timeline. Retrieved from http://www.nano.gov/timeline (accessed December 8, 2016)

1995

First publication, "Revolution in Military Affairs," regarding analysis of nanotechnology in military applications. It concludes that emerging technologies, including nanotechnology, will reshape the way nations use force to achieve national goals.

Foresight Institute. (1995). Hughes Aircraft Study of "Revolution in Military Affairs" Sees Possible Role for Nanotechnology Devices. Retrieved from https://www.foresight.org/Updates/Update23/Update23.3.html (accessed December 8, 2016)

Researchers at Rice University discovered the Buckminsterfullerene (C60) or The buckyball. Buckyball is a molecule resembling a soccer ball in shape and composed entirely of carbon like graphite and diamond.

Nanotechnology Initiative. (2014). Nanotechnology Timeline. Retrieved from http://www.nano.gov/timeline (accessed December 8, 2016)

1985

Researchers at IBM's Almaden Research Center manipulated 35 individual xenon atoms to spell out the IBM logo. This demonstration of the ability to precisely manipulate atoms ushered in the applied use of nanotechnology.

Nanotechnology Initiative. (2014). Nanotechnology Timeline. Retrieved from http://www.nano.gov/timeline (accessed December 8, 2016)

1989

Researchers at NEC discovered the carbon nanotube. CNTs' properties include high-strength, electrical and thermal conductivity.

Nanotechnology Initiative. (2014). Nanotechnology Timeline. Retrieved from http://www.nano.gov/timeline (accessed December 8, 2016)

1991

Graphene is isolated and characterized by researchers at the University of Manchester. Graphene's surface-to-volume ratio, optical properties and electrical conductivity make it a unique solution for sensor functions.

- *Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., & Frisov, A. A. (2004). Electric Field Effect in Atomically Thin Carbon Films. Science, 306(5696), 666-669. doi:10.1126/science.1102896*
- *Graphene-info. (2009). What is a sensor? Retrieved from http://www.graphene-info.com/graphene-sensors (accessed December 8, 2016)*

2004

echnology

2001

U.S. Army Institute for Soldier Nanotechnologies founded at MIT.

Foresight Institute. (2001). U.S. Army to Establish new center for "Soldier Nanotechnologies." Retrieved from http://foresight.org/Updates/Update47/Update47.2.html#SoldierNano (accessed December 8, 2016)

2002

Sean Howard warns of possible "devastation caused - accidentally, or by terrorists, or in open conflict - by artificial atomic and molecular structures capable of destroying environments and life forms from within."

Howard, S. (2002, July/August). Nanotechnology and Mass Destruction: The Need for an Inner Space Treaty. Disarmament Diplomacy, 65. Retrieved from http://www.acronym.org.uk/old/archive/dd/dd65/65op1.htm (accessed December 8, 2016)

2006

Fabrication of silicon nanowire devices for ultrasensitive, label-free, real-time detection of biological and chemical species.

Patolsky, F., Zheng, G., & Lieber, C. M. (2006). Fabrication of silicon nanowire devices for ultrasensitive, label-free, real-time detection of biological and chemical species. Nature Protocols, 1(4), 1711-1724. doi:10.1038/nprot.2006.227 Retrieved from https://www.ncbi.nlm t.nih.gov/pubmed/17487154 (accessed December 8, 2016)

2006

Prediction that the future of weaponry will be built ground-up from the microscale, and not the top down approach used to date. Nanotechnology weapons of mass destruction will likely be developed by a resource/science-rich nation, as the requirement to develop such weapons would exceed the capabilities of smaller nations. Furthermore, development of a novel nanotech WMD will likely remain a closely guarded secret by any state developing such a weapon, as revealing such a weapon would result in a loss of asymmetrical advantage.

Treder, M. (2006, December 14). Nukes and Nanotech. Retrieved from http://ieet.org/index.php/IEET/more/treder20061214 (accessed December 8, 2016)

2006

Chemical vapor detection using single-walled carbon nanotubes.

Snow, E. S., Perkins, F. K., & Robinson, J. A. (2006, May 24). Chemical vapor detection using single-walled carbon nanotubes. Chemical Society Reviews, 35(9), 790. doi:10.1039/b515473c Retrieved from https://www.nrl.navy.mil/estd/sites/edit-www.nrl.navy.mil.estd/files/pdfs/07-1226-3452.pdf (accessed December 8, 2016)

A gold nanoparticle-based chronocoulometric DNA sensor for amplified detection of DNA.

Zhang, J., Song, S., Wang, L., Pan, D., & Fan, C. (2007). A gold nanoparticle-based chronocoulometric DNA sensor for amplified detection of DNA. Nature Protocols, 2(11), 2888-2895. doi:10.1038/nprot.2007.419 Retrieved from https://www.ncbi.nlm.nih.gov/pubmed/18007624 (accessed December 8, 2016)

2007

Radiation Detectable and Protective Articles Patent granted to Radiation Shield Technologies. RST offers a protective material made from nanopolymeric compounds that protects against chemical, biological, radiological and nuclear incidents with flame protection. The protective suite has certified fabric for first responders to CBRN or terrorist incidents. The suit is made of liquid metal that is lightweight, flexible and foldable and has been deployed worldwide by NATO.

Business Wire. (2009). Radiation Shield Technologies Granted Key U.S. Nanotechnology Patent for World's First and Only Nuclear Radiation-Blocking, Anti-Chemical, Biological-Protection Fabric. Retrieved from http://www.businesswire.com/news/home/20090127005403/en/Radiation-Shield-Technologies-Granted-Key-U.S.-Nanotechnology (accessed December 8, 2016)

2009

The Defense Treaty Reduction Agency and scientists at Lawrence Livermore National Laboratory have developed a flexible, highly breathable material with carbon nanotubes with the ability to protect against viruses, bacteria and even small chemical agents. The fabric can block sulfur mustard agents, GD, VX never agents, toxins and biological spores. The membrane is expected to act like living skin and the fabric will exfoliate as a reaction to contact with chemical agents. The uniform could be deployed in the field in less than 10 years.

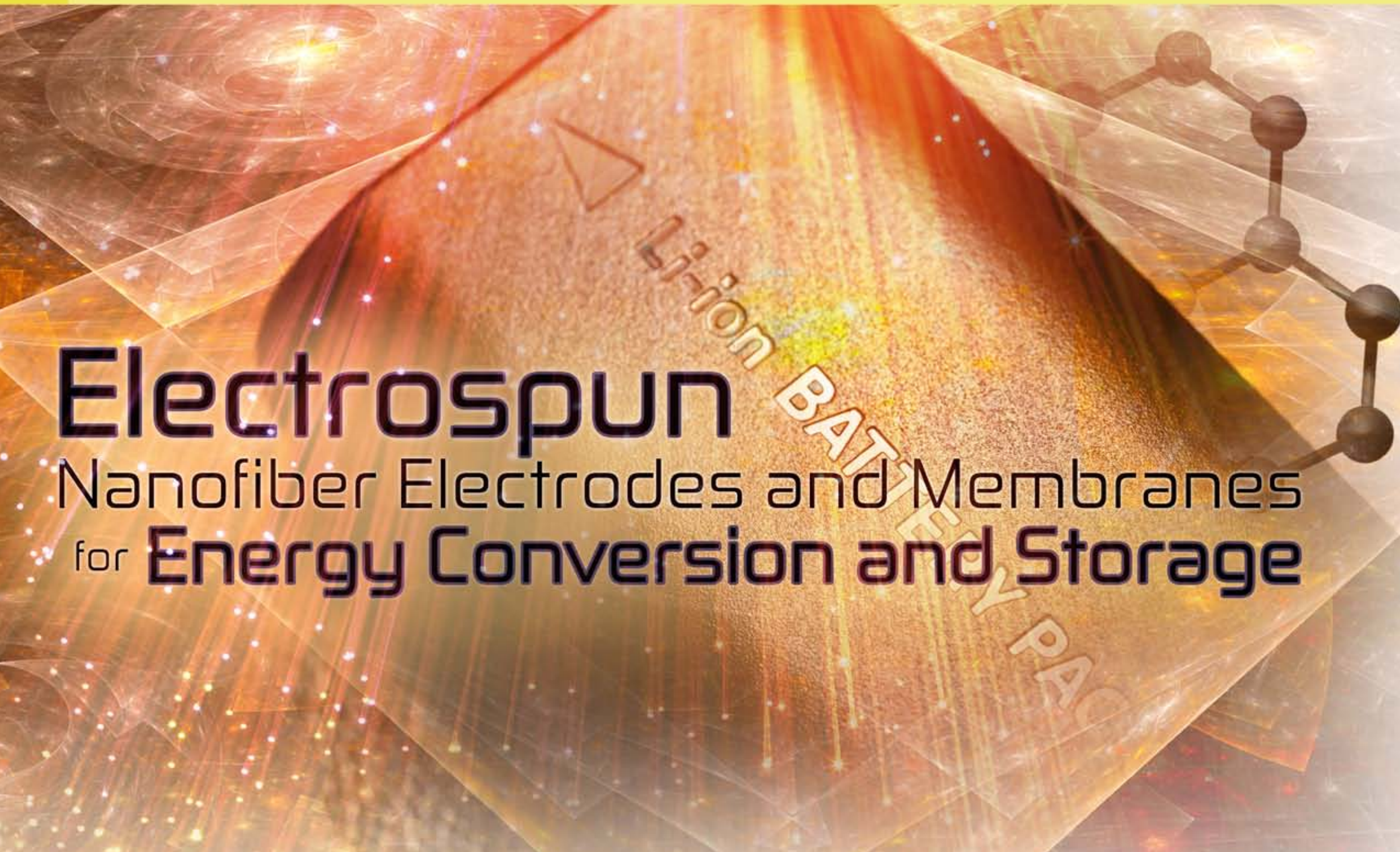
Global Biodefense. (2016). Novel Material Aims to Protect Military from Biological and Chemical Agents. Retrieved from https://globalbiodefense.com/2016/08/11/novel-material-aims-protect-military-biological-chemical-agents/ (accessed December 8, 2016)

2016

Graphene nanodevices utilized for DNA sequencing.

Heerema, S. J., & Dekker, C. (2016). Graphene nanodevices for DNA sequencing. Nature Nanotechnology, 11(2), 127-136. doi:10.1038/nnano.2015.307

2016



Electrospun Nanofiber Electrodes and Membranes for Energy Conversion and Storage

By: Ryszard Wycisk, Ph.D.,
Ethan Self
&
Peter N. Pintauro, Ph.D.

Separators and Electrodes in Fuel Cells and Batteries

The modern military relies heavily on portable electricity. The efficient generation, storage and distribution of electrical energy in a war zone are essential to sustaining military operations. New, highly mobile energy conversion and storage devices, like proton-exchange membrane fuel cells and next-generation lithium-ion batteries, will provide military forces with an energy-on-demand option for communications, logistical operations and weaponry. In this regard, continued research and development efforts are needed so the performance of such devices matches military needs.

Batteries store energy, whereas fuel cells convert a fuel (e.g., hydrogen) and oxidant (air) into electrical energy. While different in terms of their mode of operation, battery and fuel cells' main hardware components are quite similar. Both contain high surface area anodes and cathodes, with an inter-electrode membrane or electrolyte-filled separator, which prevents electrode contact and provides ion transport pathways.

The electrodes contain dispersed active material, such as carbon-supported platinum catalyst in fuel cells or lithium storage particles (graphite and $LiCoO_2$) in Li-ion batteries. In polymer electrolyte membrane fuel cells, a hydrated perflurorsulfonic acid polymer film (e.g., DuPont's Nafion®) separates the electrodes and allows for facile proton transport during current flow. The separator in Li-ion batteries is usually a porous film prepared from polyolefins (polyethylene/polypropylene), which is soaked in a liquid electrolyte during cell assembly.

At present, the high surface area porous electrodes in both batteries and fuel cells are fabricated by solvent evaporation from cast slurries containing active material and polymer binder. Dense fuel cell membranes are prepared from ionomer solutions by solvent casting or melt extrusion of the ionomer precursor, while porous battery separators are typically fabricated via a dry process involving extrusion of molten polymer (e.g., polyolefin) into a fabric which is then annealed and stretched under controlled thermal conditions to create the desired microporosity. While these fabrication techniques are commercially viable, they do not fully exploit the extraordinary performance characteristics of many newly developed nanomaterials.

Electrospinning is one option for the hierarchal organization of polymers and nanoparticles into membrane and electrode components for high-performance energy storage and conversion devices. Electrospinning processes are cost competitive and simple to realize on a commercial scale, with process equipment readily available for large-scale manufacturing. This paper provides a brief overview on the use of nanofiber electrospinning for fabricating fuel cell and battery components.

What is Electrospinning?

Electrospinning is a scalable technique for the fabrication of sub-micrometer diameter fibers composed of one or more polymers or mixtures of nanoparticles and a polymer binder. A standard electrospinning apparatus (See Figure 1) consists of a high voltage power supply, a fiber collector surface and

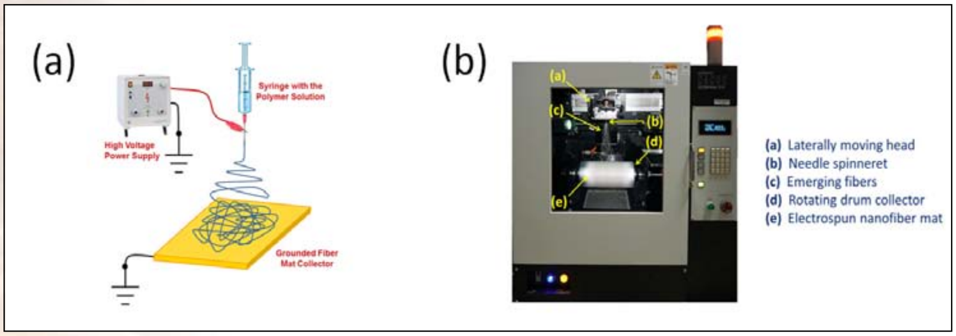


Figure 1: (a) Schematic diagram of the electrospinning process and (b) An example of a commercial lab-scale electrospinner from MECC, Japan. (Released)

one or more spinnerets. A polymer or particle/polymer solution or a polymer melt is supplied to the spinneret(s) at a controlled flowrate. With a sufficiently high electric field between the spinneret tip and grounded collector (on the order of 0.5-3 kV/cm), a Taylor cone forms, from which of a small-diameter fiber jet emerges. As the jet travels towards the collector, it dries in flight and elongates by a whipping process. The elongation and thinning of the jet leads to the formation of a fiber mat, where the average fiber diameter is typically in the 100-600 nm range.

Fiber electrospinning was invented in the early 1900s, but little interest was seen until the work of Reneker and co-workers in the 1990s. [1] In 2008, Pintauro and co-workers [2,3] used electrospinning to prepare nanocomposite fuel cell membranes as an alternative to traditional membrane fabrication methods and materials (e.g., cast polymer blends and copolymers).

In the resultant nanofiber composite membrane morphology, the proton conduction structure and function of the ionomeric material was decoupled from the mechanical support and swelling control functions of the uncharged polymer.

Recently, Pintauro's group introduced nanoparticle/polymer hybrid fiber electrospinning for the fabrication of fuel cell and battery electrodes. Here, a concentrated suspension of electrochemically active nanoparticles (e.g., Pt/C, $LiCoO_2$ or Si) and polymer binder in an organic solvent is electrospun to create a highly porous and robust fiber mat electrode. Such fiber mat electrodes exhibited superior performance in hydrogen/air fuel cells and Li-ion batteries compared to conventional electrodes prepared by slurry/tape casting or sprayed droplet deposition. In the remainder of this paper, recent work from the present authors on electrospun fuel cell membranes, Pt-based fuel cell electrodes, and Li-ion battery electrodes is reviewed.

Electrospun Nanofiber Composite Membranes for Fuel Cells

Over the past 15 years, there has been unprecedented research and development activity worldwide in the field of fuel cells involving both academia and commercial enterprises. [4] The search for low-cost, high performance fuel cell membranes has been a significant part of this overall effort. Low/moderate temperature hydrogen/air proton exchange membrane, or PEM, fuel cells are highly efficient, ecologically-friendly energy conversion devices.

The key membrane properties for PEM fuel cells are: (i) a high proton conductivity, especially at low relative humidity air conditions; (ii) mechanical robustness, including resistance to wet/dry cyclic stresses; (iii) good oxidative and thermal stability; (iv) low permeability to the fuel and oxidant; and (v) low cost. A perfluorosulfonic acid polymer, or PFSA, membrane, such as Nafion® by DuPont, fulfills some of these specifications, but their dramatic conductivity loss at low relative humidity and high price are serious barriers that need to be addressed.

Pintauro and co-workers introduced electrospinning as a novel platform for the fabrication of nanocomposite fuel cell membranes. [2,3,5,6] Such membranes were found to be viable alternatives to membranes based on polymer blends and block copolymers. Initially, the nanocomposite membranes were fabricated by electrospinning an ionomer fiber mat followed by mat impregnation by an uncharged, inert polymer.

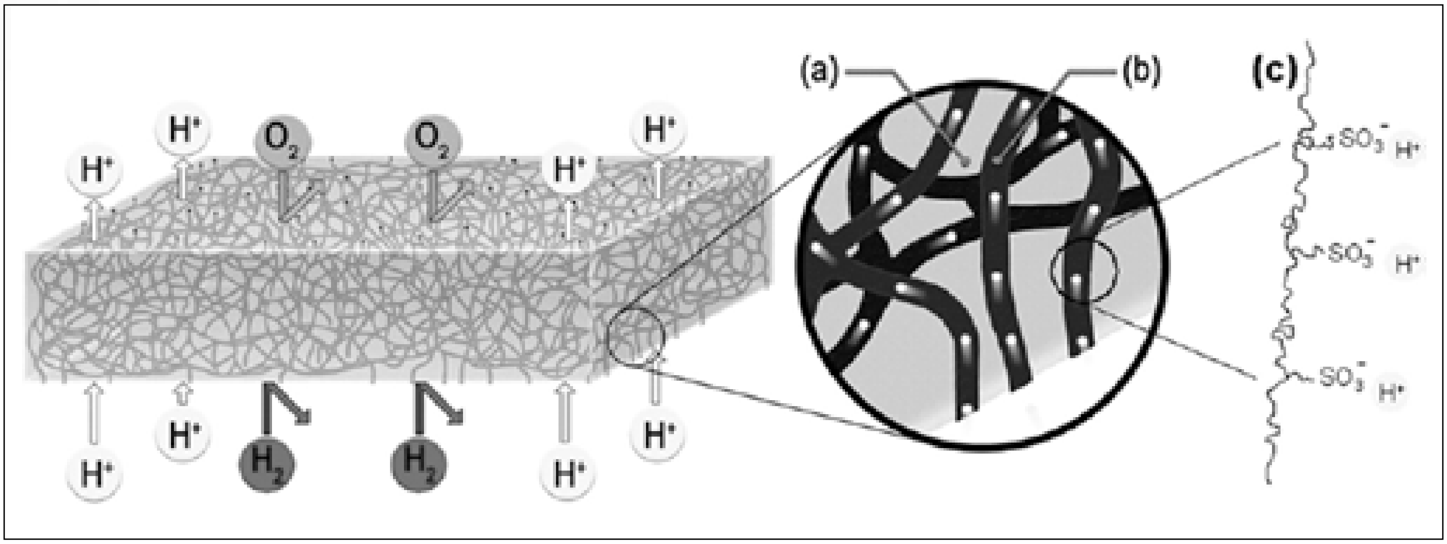


Figure 2. Example of an electrospun composite membrane morphology. The uncharged polymer matrix (a) restricts swelling and imparts mechanical strength to the membrane, while the water-swollen fiber network (b) composed of an ionomer with sulfonic acid fixed charge groups (c) provides pathways for proton transport. [2] (Reprinted with permission. Copyright 2008 American Chemical Society/Released)

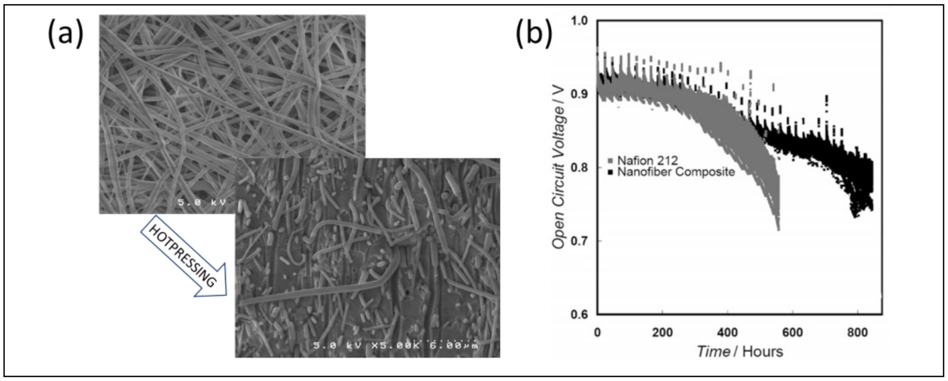


Figure 3. (a) SEM micrographs of an electrospun Nafion/PPSU dual fiber mat surface and the dense composite membrane cross-section after mat hot-pressing and annealing, and (b) the results of a fuel cell open circuit voltage wet/dry cycling accelerated durability tests. The PPSU nanofiber reinforced Nafion composite membrane had 65 vol. % Nafion, with a dry film thickness of 31 µm. (Adapted with permission from [3] J. B. Ballengee and P. N. Pintauro, Macromolecules, 44, 7307 (2011). Copyright 2011 American Chemical Society/Released)

The resulting membrane morphology is shown in Figure 2. Alternatively, an uncharged polymer was first electrospun followed by ionomer impregnation into the nanofiber mat. One or more post-electrospinning processing steps were usually required to convert an electrospun mat into a dense defect-free fuel cell membrane (e.g., mat compression, ionomer annealing and rinsing in acid and water). These steps were dependent on the particular choice of charged and uncharged polymer. One can easily change the type of ionomer and uncharged polymer and the relative amounts of each, to change membrane properties (e.g., conductivity, swelling or mechanical strength).

Dual-fiber electrospinning was later introduced by Ballengee and Pintauro as an alternative to a separate pore-filling impregnation step for the fabrication of composite fuel cell membranes. [3] Here, both polymer components (ionomer and uncharged polymer) are simultaneously electrospun as separate fibers onto a common collector surface to create a mixed fiber mat. Subsequent processing induces flow of one of the polymer components into the interfiber void space between fibers of the second polymer (after processing the nanofiber morphology of the second polymer is retained).

For example, a PFSA polymer (e.g., Nafion) was simultaneously electrospun with poly(phenyl sulfone) to create a dual fiber mat, which was then processed into a dense membrane with either one of the following structures: (i) an interconnected network of Nafion nanofibers encapsulated by PPSU or (ii) a Nafion film reinforced by PPSU fibers.

Figure 3a shows scanning electron microscope images of the as spun dual-nanofiber mat and the cross-section of a final, dense membrane obtained after hot-pressing and annealing the mat. Excellent pore closure, with the retention of the reinforcing PPSU fibers is evident.

Ballengee and Pintauro showed that the combination of high proton conductivity, good mechanical properties and low water swelling of the electrospun composites resulted in excellent membrane performance and improved membrane durability in a H_2/air fuel cell. [3] As shown in Figure 3b, a Nafion/PPSU nanofiber composite membrane exhibited 54 percent longer lifetime in an accelerated fuel cell open circuit voltage humidity cycling test, as compared to a commercial Nafion 212 film.

Very recently, in cooperation with the University of Kansas and Lawrence Berkeley National Laboratory, Pintauro and coworkers fabricated and tested nanofiber composite membranes for hydrogen/bromine (H_2/Br_2) and hydrogen/vanadium redox flow batteries. [7,8,9,10]. These flow batteries are used in grid-scale load leveling applications and for coupling energy-storage with intermittent renewable energy sources like wind and solar radiation. [11,12,13]

During charge of a H_2/Br_2 RFB, Br- in a liquid HBr electrolyte is oxidized to Br_2, while H+ is reduced to H_2. Both the oxidant and the fuel are stored externally during the charging process. During discharge, H_2 and a Br_2/Br_3- complex are pumped from the external tanks into the battery and spontaneously react to generate HBr and electricity. The key role of membrane in this device is to allow for facile H+ migration while minimizing unwanted Br_2 and Br_3- crossover (these species degrade the Pt catalyst at the hydrogen electrode and decrease the device's coulombic efficiency).

For an H_2/Br_2 RFB, nanofiber composite membranes were fabricated from electrospun Nafion/ poly(vinylidene fluoride), or PVDF, dual-fiber mats, where the Nafion volume fraction in the final membrane ranged from 0.30 - 0.65. [7] Two general structures were investigated: (1) an interconnecting network of Nafion nanofibers embedded in an uncharged PVDF matrix, denoted as N(fibers)/PVDF membrane and (2) a PVDF fiber mat embedded in a continuous Nafion matrix, denoted N/PVDF(-fibers) membrane. Both membrane types showed reduced bromine species permeability with excellent mechanical strength and good proton conductivity.

For example, an N(fibers)/PVDF membrane with 40 vol.% Nafion had a reduced ion conductivity (36 percent that of Nafion) but excellent bromine barrier properties (8.3 times lower than that of Nafion 115). Expressing the results in more practical parameters, it

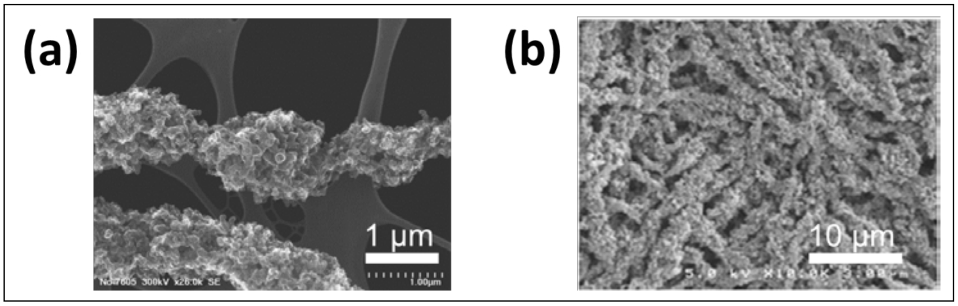


Figure 4. SEM micrographs of: (a) a single Pt/C/Nafion/PAA electrospun fiber (courtesy of Karren More at Oak Ridge National Laboratory) and (b) a top-down view of an electrospun nanofiber cathode mat. (Released)

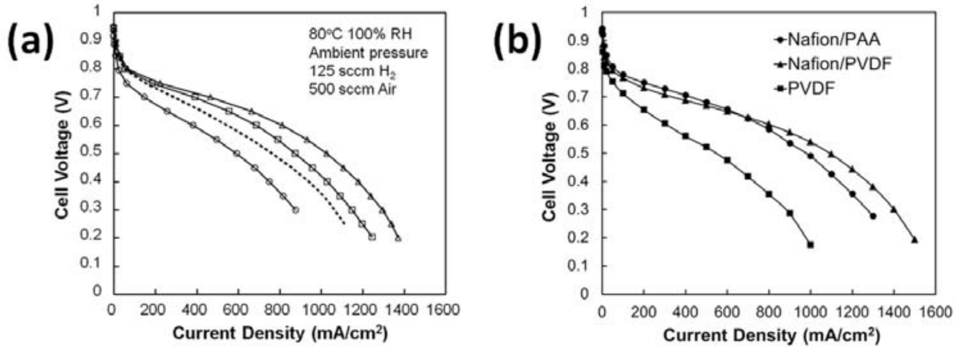


Figure 5. (a) Polarization curves for 5 cm2 MEAs with a Nafion 212 membrane and electrospun HiSpec™ 4000 cathodes and anodes. The Pt/C:Nafion:PAA weight ratio was fixed at 64:24:12. The anode Pt loading was 0.10 mg/cm2. The cathode Pt loading was: (Δ) 0.107 mg/cm2 (□), 0.065 mg/cm2, and (○) 0.029 mg/cm2. Performance of a decal MEA with cathode and anode Pt loadings of 0.104 mg/cm2 and 0.40 mg/cm2, respectively is also shown (---); (b) Beginning-of-life polarization curves for 5 cm2 MEAs with a Nafion 211 membrane, a 0.10 mgPt/cm2 electrospun cathode and a 0.10 mgPt/cm2 electrospun anode. The cathode binder (w/w) was: (●) Nafion/PAA (67/33), (▲) Nafion/PVDF (80/20), or (■) PVDF. Figure (a) Adapted with permission from [15] J. Electrochem. Soc., 160, F744 (2013), Copyright 2013, The Electrochemical Society. Figure (b) Reproduced with permission from [16] J. Electrochem. Soc., 163, F401 (2016). Copyright 2016, The Electrochemical Society.

can be concluded that a nanofiber composite film with a thickness of 48 μm had an area-specific-resistance equal to that of Nafion 115 (0.13 Ωcm2) but its Br_2/Br_3- crossover flux (4.28 × 10-9 mol/s/cm2) was 3.0 times lower than that for Nafion 115.

As an alternative to dual fiber electrospinning, a new concept of single blended fiber electrospun membranes was recently introduced by Pintauro and associates [9] where Nafion and PVDF were mixed in a common solvent and then electrospun to obtain a blended single fiber mat. Hot-pressing of the resulting fiber network removed all voids and produced a dense film with excellent properties for a redox flow battery. The method requires some level of compatibility of the two polymers, but it appears that shear forces at the spinneret tip, strong extensional forces of the fiber jet, and rapid solvent evaporation from the fiber during electrospinning can augment blend compatibility and produce a nanomorphology within the fibers that is much different from the phase-separated structure of a solution-cast polymer blend membrane. A single fiber membrane from Nafion and PVDF was tested in a H_2/Br_2 RFB with 2 M HBr/0.9 M Br_2 electrolyte. After 100 charge/discharge cycles at 400 mA/cm^2 with cutoff voltages of 0.5/1.15 V, the electrospun blended single fiber membrane performed well and the RFB exhibited an average coulombic efficiency of 95 percent. [10]

Electrospun Fuel-Cell Electrodes

There is a critical need to lower the Pt loading of the electrodes (especially the cathode) in a H_2/air PEM fuel cell while maintaining high power output, with minimal electrode degradation (i.e., resistance to carbon corrosion and Pt dissolution) during long-term use. Electrospinning is well suited for the preparation of nanofibrous fuel cell electrodes with low Pt content, and Pintauro's group has demonstrated excellent performance of nanofiber mat electrodes, where the fibers were electrospun from a suspension of Pt/C catalyst particles in a solution of Nafion, poly(acrylic acid), and alcohol solvent. [14]

Exceptionally high power densities and high platinum mass activities were achieved when electrospun cathode mats were incorporated into membrane-electrode-assemblies for H_2/air fuel cells. The nanofiber cathodes also exhibited outstanding chemical stability in accelerated voltage cycling durability tests. These beneficial characteristic were associated with a uniform nanoparticle/binder distribution in the nanofibers, generated by mixing at the spinneret tip, high extensional forces and ultra-fast solvent evaporation during electrospinning. Scanning electron microscope images of a single electrospun fiber and a fiber mat

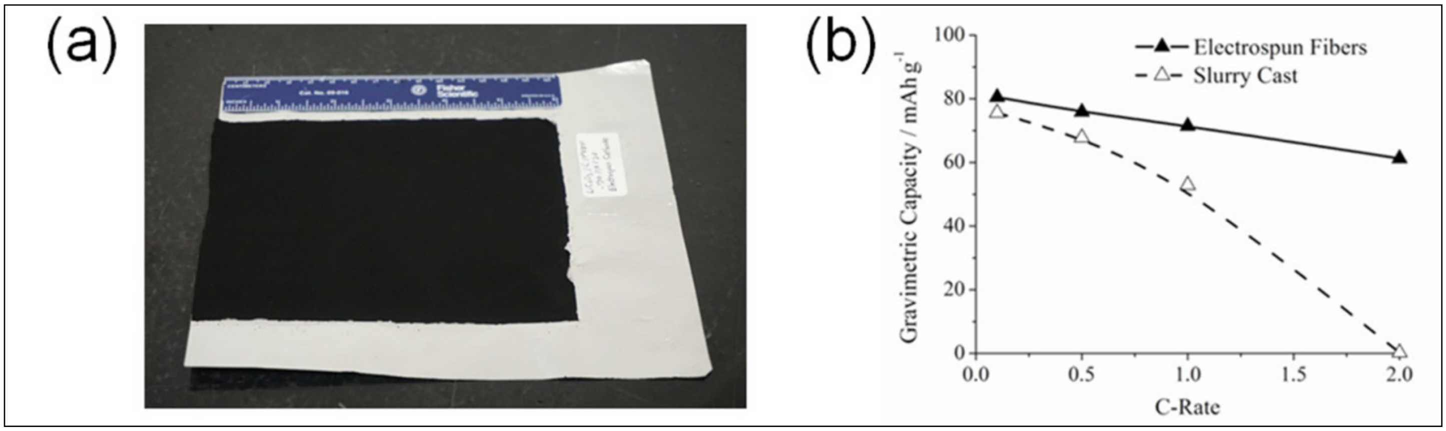


Figure 6. (a) As-electrospun nanofiber mat cathode composed of LiCoO2/C/PVDF and (b) Gravimetric capacity vs. C-rate for the nanofiber vs. slurry cast cathode in a half cell configuration. (Released)

cathode are shown in Figure 4. The fibers contain 65 wt% Pt/C catalyst particles, with a mean fiber diameter of 600 nm. There is some internal porosity within a fiber, with Nafion/PAA binder uniformly distributed on all catalyst particles.

Hydrogen/air fuel cell polarization data were collected with electrospun fiber mat electrode MEAs at 80^{o}C, 100 percent relative humidity and ambient pressure (See Figure 5a), where the anode Pt loading was fixed at 0.1 mg/cm^2 and the cathode Pt loading was either 0.107, 0.065 or 0.029 mg/cm^2. [15] The performance of the 0.065 mgPt/cm^2 nanofiber cathode was superior to that of a decal cathode at a Pt loading of 0.104 mg/cm^2. Also, there as only a modest drop in power output when the cathode loading was reduced from 0.107 to 0.065 mg/cm2 (i.e., the maximum power density decreased only 15 percent, from 513 to 437 mW/cm^2 when the Pt loading was reduced by about 40 percent).

The effect of binder on the initial performance and durability of nanofiber mat electrodes was also investigated. [16] Nanofiber cathodes were fabricated by electrospinning particle/polymer mixtures containing commercial Pt/C catalyst and a binder of either Nafion/PAA, Nafion/PVDF (with different Nafion/PVDF wt. ratios) or neat PVDF. Hydrogen/air fuel cell polarization curves for MEAs with cathodes containing 80/20 Nafion/PVDF and neat PVDF binders at a cathode Pt loading of 0.10 mg/cm^2 are shown in Figure 5b. For comparison, data are also presented for a 0.10 mg/cm^2 nanofiber cathode with a binder of Nafion/PAA where the fiber composition is 64 wt.% Pt/C, 24 wt.% Nafion, and 12 wt.% PAA. Data were collected at 80°C with air and hydrogen at ambient pressure and 100 percent relative humidity.

The Nafion/PVDF and Nafion/PAA cathode MEAs generated similar polarization curves, with the Nafion/PVDF cathode MEA having slightly higher current densities at voltages less than 0.65 V and slightly smaller current densities at voltages greater than 0.65 V. The neat PVDF cathode MEA produced low power, but it worked better than expected (a maximum current density greater than 1 A/cm^2), considering the fact that there was no proton conducting ionomer in the cathode. It was also found that increasing the hydrophobicity of the cathode binder by replacing PAA with PVDF and decreasing the Nafion/PVDF ratio slowed catalyst carbon support corrosion in the cathode, presumably by reducing the amount of water near the catalyst surface. [16]

Electrospun Li-ion Battery Electrodes

Lithium-ion batteries convert chemical energy into electrical energy through reversible redox reactions involving Li storage in the anode and cathode. A LIB is constructed from two or more cells connected in series and/or parallel, where each cell contains three components: an anode (typically graphite), a cathode (often LiMO2, where M = Co, Mn or Ni) and an ionically conductive liquid electrolyte embedded in a porous polyolefin separator.

LIB electrodes are typically prepared by slurry casting a solution containing active material, conductive carbon (when needed) and polymer binder onto an electronically conductive current collector. While these slurry cast electrodes are used in all of today's commercial batteries, such electrodes suffer from slow recharge rates due to Li+ transport limitations. The drawback of slurry casting is its inability to provide internal porosity for electrolyte penetration in an easily controlled manner. New electrode manufacturing strategies would allow for the intelligent arrangement of LIB nanomaterials at the micron-scale, where particle/particle contacts and electrode porosity are optimized for high capacities and fast recharge rates.

Driven by successes with the electrospun fuel cell electrodes, Pintauro's group has fabricated and tested a number of electrospun particle/binder anodes and cathodes for Li-ion batteries, including: (i) anodes containing titania nanoparticles, carbon powder and poly(acrylic acid); [17] (ii) anodes containing carbon powder and PVDF; [18] and (iii) cathodes containing $LiCoO_2$ nanoparticles, carbon powder and PVDF (See Figure 6a). [19]

Nanofiber electrode performance in coin cells was exceptional, with higher capacities at fast charge/discharge rates, as compared to conventional electrodes. Figure 6b shows excellent rate capabilities for an electrospun $LiCoO_2$-C/PVDF cell, where the gravimetric capacity at 2C (61 mAh g-1) is much greater than that of a slurry cast cathode of the same composition (0.25 mAh g-1). Similar results were obtained for capacities normalized with respect to electrode footprint and volume (i.e., areal and volumetric capacities) which are important for practical battery applications. The excellent performance of the electrospun electrodes is attributed to the unique fiber mat morphology which provides: (i) a large electrode/electrolyte interfacial area; (ii) good electrolyte infiltration throughout the intra- and interfiber void space of the fiber mat; and (iii) short Li+ transport pathways between the electrolyte and active material in the radial fiber direction.

Ongoing work is focused on high capacity silicon anodes for next-generation Li-ion batteries. Si undergoes large volumetric changes during charging (e.g., a 300 vol.% change during the lithiation of Si); such extreme volume changes could be accommodated by the interfiber void space in a properly designed nanofiber mat anode. [20,21]

Summary and Future Prospects

In this paper, representative examples and lab data are given to demonstrate the practicality and wide-ranging applicability of electrospinning for the fabrication of fuel cell and Li-ion battery components. The excellent performance of electrospun electrodes and membranes is a consequence of their unique multi-scale morphology and the ability to control this morphology via adjustment of electrospinning parameters and post-electrospinning processing steps. The nano-level structure is a consequence of the electrospinning process itself, where there is shear mixing at the spinneret tip augmented by the high extensional forces and rapid solvent evaporation of the fiber jet. Micron-level structure (e.g., the porosity, thickness, and distribution of reinforcing fibers in a dense membrane or the fiber volume fraction in a Li-ion battery cathode) is controlled by nanofiber mat processing after electrospinning. The applications of electrospinning are practically unlimited and extend well beyond energy conversion and storage devices. For example, Pintauro's group showed that an electrospun fiber mat of zirconium hydroxide nanoparticle in a polyvinyl butyral binder was a highly effective sorptive/reactive media for the removal of toxic chemicals from air, [22] where such mats could be used in clothing and gas masks for military personnel. Clearly, more research and development is needed to fully exploit this transformative technology. ■

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Nanotechnology and the Human Body

Imaging Techniques

Nanocarrier-based molecular imaging systems [1]

- "Electrical, optical, and magnetic properties" of nanoparticles can be tailored for special imaging use.
- "Multicomponent nature of nanoparticles provides a... platform for... multiple imaging modalities." [1]

Contact Lenses

Photochromic soft contact lenses fabricated from Nanoemulsion polymers [5]

- Transparent under visible light.
- Reduces glare by darkening, blocking UV radiation.

Nanotattoos

Temporary tattoos that use tattoo film with printed electrodes

Nanosensors

Measuring humidity and human biological features

- Novel dry electrodes, exhibiting outstanding electromyography recording and excellent user comfort. [2]
- Battery-free, stretchable optoelectronic systems for wireless optical characterization of the skin. [3]

Second Skin

Breathable carbon nanotube pores that form a protective membrane [4]

- Carbon nanotubes allow selective fluid transfer, allowing skin to sweat and breath while simultaneously keeping out hazardous agents.
- Protects against biological, chemical and pharmaceutical components.

- Sensitive electrochemical sensor monitors and measures chemical processes in the body. [6]
- TiO_2 nanoparticles used to manufacture ultra-sensitive humidity sensor. [7]

Clothing

Simultaneously harvesting solar and mechanical energy

- Solar ribbons developed for synchronous energy harvesting and storage. [8]
- Harvesting both solar and mechanical energy, smart fabric can be incorporated into various fabric mediums from curtains to clothing, powering wearable electronics. [9]

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National Securi

“It is a staggeringly small world that is below. In t
wonder why it was not until the year 1960 that anyb

By: Matthew Hull, Ph.D.

Introduction

It is only fitting that an article relating nanotechnology and national security begin with a quote from a figure central to both – Richard Feynman. After all, it was Feynman who helped launch both the atomic age and the modern nanotechnology revolution. It is also fitting that the 2016 Nobel Prizes for chemistry and physics recognized breakthroughs in molecular machines and exotic materials, both of which reflect strongly upon progress made in nanoscale science and engineering over the half century since Feynman's famed “There's Plenty of Room at the Bottom” address to the American Physical Society.

Advances in nanoscale science and engineering promise to reshape how we think about national security. Nano-enabled devices and materials offer both enhanced and, in some cases, completely new defense systems. In the words of one author, “Perhaps no other emerging technology will prove as disruptive in the future as nanotechnology.” [2] Conversely, these same advances force us to consider how we protect national interests against sophisticated, nano-enabled threats that are evolving at an accelerating and unpredictable pace.

Convergence of nano-enabled technologies with other domains like biotechnology, autonomy, artificial intelligence and informatics adds additional layers of com-

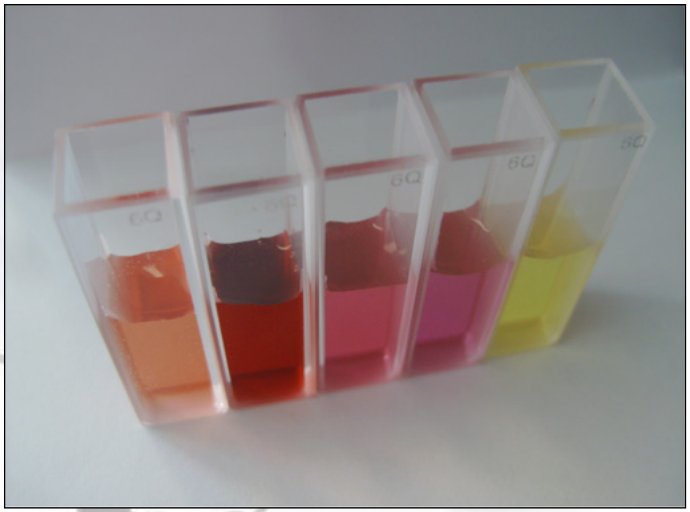

Figure 1. From right to left: Silver nanoparticles along with gold nanoparticles of decreasing particle size. (Released)

ity and the Nano Factor

he year 2000, when they look back at this age, they will
ody began seriously to move in this direction." [1]

-Richard
Feynman
Dec. 1959

plexity and unpredictability. [3] Beyond the extraordinary applications and defense-related implications of nano-enabled technologies, there are also unintended human and environmental health and safety issues associated with their development, production, use and decontamination/decommissioning.

The Nano Factor:
More than Just Size

Much emphasis has been placed on defining a specific size range to encompass what is and is not nanoscale science and engineering. However, what excites us most about nano-enabled technologies really has more to do with the point where unique material properties begin to emerge.

While the emergence of these properties is primarily related to size, it can also be driven by shape and many other factors. So, when we talk about the "nano" factor, we are actually referring to no less than three features whose complex interactions can cause a particular material property to diverge from its expected behavior at the bulk-scale.

Those three features are: 1) the particular material property of interest (e.g., mechanical or thermal behavior that is being observed); 2) the type of matter possessing that property (i.e., the elemental composition); and 3) the physical structure of that matter (i.e., the arrangement of atoms into a structure of varying size and shape, for example).

A classic example of the nano factor is observed with gold nanoparticles. At the bulk scale, gold looks and behaves just as expected – lustrous gold-like color, chemical inertness and malleability. At the nanoscale, somewhere around 200 nm and below, its properties change dramatically – to the point where it causes us to question everything we know about what has defined gold as gold. The classical gold color gives way to a deep ruby red; it becomes catalytic; and it displays unique and tunable optical properties that have inspired entirely new fields like plasmonics. [4]

Nanoscale silver particles take on a bright yellow/gold color that looks more like what we would expect to see from gold nanoparticles (See Figure 1). And those are just two elements – we have an entire periodic table of elements that, when arranged into structures of varying shape and size, can display behaviors dramatically different from their bulk forms. Even highly stable carbon-based materials display unique electronic, thermal and mechanical behaviors at the nanoscale. [5]

Along with the changes in behavior that occur at the nanoscale come very important physical consequences. Nanoscale particles present new challenges to protective barriers such as filters, seals and joints; protective clothing; and even biological barriers like skin and membranes.

For example, research initiated by the National Institute for Occupational Safety and Health found that while respirators were generally very efficient at removing nanoscale particles from air, the most penetrating particle size for common filter media was between 30 and 100 nm. NIOSH also reported that the size of leaks between respirators and the faces of test manikins had the greatest impact on particle leakage into the respirate facepiece, with nanoparticles being more likely than larger particles to penetrate small leaks. [6]

Small size also means vastly increased surface area as well as surfaces that are potentially more reactive due, in part, to the increased fraction of atoms on the corners and edges of particles (See Figure 2). Gold, for example, which is usually considered an

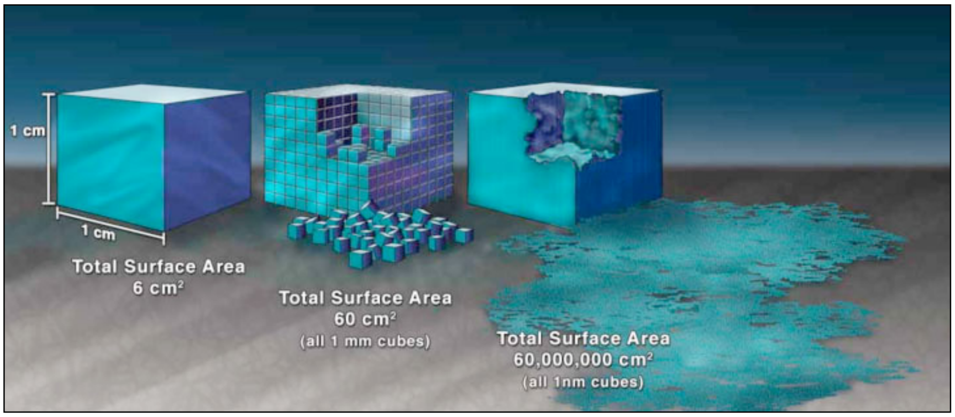

Figure 2. Illustration demonstrating the effect of the increased surface area provided by nanostructured materials. [19] (Nano.gov/ Released)

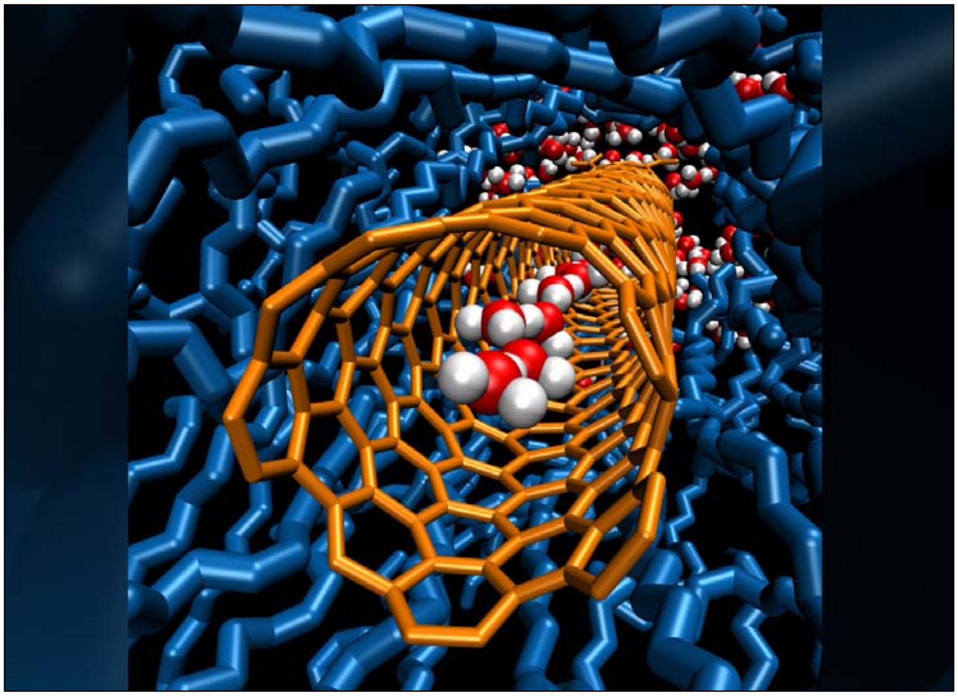

Figure 3. "A single chain of water molecules lines the cavity inside a carbon nanotube porin, which is embedded in a lipid bilayer." [20] (Image by Y.Zhang and Alex Noy, Lawrence Livermore National Laboratory/Released)

inert metal, can catalyze multiple chemical reactions when present as nanoparticles of less than 3-5 nm in diameter. [7] Some of these surfaces can provide suitable scaffolds for conjugation of chemical and biological entities, and thus enable certain types of nanostructures to act as highly-mobile nano carriers or "Trojan Horses."

For example, see work by Park et al. [8] In some instances, nanoscale materials can be made highly dispersible, enabling them to be broadly disseminated in various types of fluid and semi-porous media. As they move through these media, they can acquire and transport toxicants. For example, the Hochella group at Virginia Tech has reported that naturally occurring nanoparticles of 5-10 nm in diameter played important roles in transporting heavy metals like lead and arsenic in riverine systems. [9]

Many overviews probe the spectrum and origins of nanoscale phenomena much more thoroughly than can be accomplished here. For additional information on this topic, refer to the recent review by Yan et al on the importance of nano in catalysis. [10] However, the central point of this article is that nano changes what we know about the physical and chemical world around us. From the way we interact with materials and what we can do with them to the way we perceive the physical world – all of that changes at the nanoscale. Ultimately, these changes have significant impacts on global and national security.

National Security and Defense Applications of Nanotechnology

Some of the most exciting aspects of nanotechnology over the last decade have been the seemingly limitless defense and security related applications they offer. The number and diversity of these applications have even inspired their own conference – NT4D or Nanotechnology for Defense. [11] According to the federal budget, U.S. Department of Defense spending on nanoscale science and engineering will top $130 million in 2017. [12]

Applications of nanotechnology in security and defense systems have included advanced chemical and biological detection systems; advanced imaging systems; next generation energetic materials: next-generation camouflage; high-strength/lightweight armor; medicine and human performance enhancement (wound healing, drug delivery, etc.); and advanced weapons systems.

The sections that follow briefly describe a few important and diverse ways that nano is impacting national security and defense.

Nano-bio Interface and Human Performance Enhancement

Nanotechnology has enabled science and engineering to progress at the scale of natural biological machinery, and this capability has led to important breakthroughs in areas like targeted delivery of nanomedicines, disease diagnostics/therapeutics, 3D-printed biomaterials and a growing list of wearable and implantable devices that offer biological feedback and intervention capabilities. Professor John Rogers, for example, who leads the Center for Bio-Integrated Electronics at Northwestern's Simpson Querrey Institute for BioNanotechnology, pioneered the development of soft, flexible, skin-mounted bio-electronic devices that exploit novel nanoscale material properties to perform a variety of functions from monitoring ultraviolet exposure to mapping electrophysiology in the heart and brain.

Some have observed that advances in nano-bio devices could, for example, help enhance human performance by detecting changes in neurological behavior or fine motor coordination signaling fatigue, stress, inattention and other behavioral changes that could impact the safety and effectiveness of military personnel. [13] Recognizing the critical advances underway at the nano-bio interface, the Nano-Bio Manufacturing Consortium was established in 2013 to help mature nano-bio manufacturing technologies with an initial focus on physiological readiness and human performance monitoring priorities set forth by the U.S. Air Force Research Laboratory, the DoD and other partners. [14]

The Rise of Molecular Machines and Exotic Materials

The awarding of the 2016 Nobel Prizes for physics and chemistry highlighted important examples of advances in nanoscale science and engineering that have important national security implications. While nano has been discussed, hyped and under-/over-hyped for more than a decade now, many nanoscientists recognize that in some ways we have really only just begun to explore the nano realm through our studies of basic nano characterization and fabrication tools and the most fundamental nano-enabled building blocks. Much like children tinkering with Legos for the first time, we are just now exploring how to hold and manipulate them, how to assemble them in meaningful ways, how to integrate mechanical functions that allow the systems to do work, and how to translate those functions to accomplish missions and enhance performance.

As this article goes to print, the news is filled with reports of the awarding of the Nobel Prize in chemistry to Jean-Pierre Sauvage, J. Fraser Stoddart and Ben L. Feringa, "for the design and synthesis of molecular machines." Upon addition of energy in the form of, for example, changing pH gradients, light or heat, these single-molecule machines can perform simple tasks like rotate around an axis or move up and down in a controllable manner. [15] Similarly, the 2016 Nobel Prize for Physics was awarded to J. Michael Kosterlitz, Duncan Haldane and David J. Thouless, "for theoretical discoveries of topological phase transitions and topological phases of matter" that could lead to practical applications in new materials, electronics, and quantum computing.

Finding Nano: Nano Tracking and Forensics and Their Importance to National Security

One of the greatest security challenges of a nano-enabled future is the difficulty involved in locating and characterizing nano-scale systems once released into human and environmental systems. How would a faulty nano-biomedical implant device be found and retrieved from the body? How would a nano-scale weapon, or even a swarm of nano-scale weapons for that matter, be distinguished from naturally occurring aerosols and dust particles and eliminated on a future battlefield?

For answers to these types of questions we can learn from interdisciplinary fields like environmental nanotechnology that offer tools and techniques to discriminate signals attributable to nanoscale contaminants from vast amounts of biological and environmental "noise." Trying to detect engineered nanoparticles in complex environments is a daunting task. The minuscule scale at which nanoparticles exist relative to the scale of human and environmental systems makes searching for a needle in a haystack seem remarkably simple.

For perspective, the task of searching for a single 50 nm nanoparticle contaminant in your morning cup of coffee would be equivalent to searching for a needle in a haystack large enough to fill the Grand Canyon more than 30 times (See Figure 4)!

To complicate matters further, the chemical composition of many nanoparticles, carbon nanotubes and fullerenes for example, is virtually indistinguishable from materials like soil and plant matter that co-occur in natural environments.

Practical Nano Security Scenarios

As best we can tell, current to near-term nano security scenarios are much more limited and manageable than those that can be imagined based on the trajectories of nano- as well as other emerging and converging technologies. But it is a waiting game, and the gap between science fiction and reality has shrunk rapidly over the last decade. The tangible progress in molecular machines noted earlier is proof enough of that. For the most part though, current embodiments of nanoscale materials appear more like building blocks for increasingly sophisticated material and devices of the future, and less like the "grey goo" they were once feared to be. [16] Nevertheless, present day nano security concerns do exist, and we consider three of these below:

- Nano-enhanced delivery of chemical and biological agents: Chemical and biological agent attacks remain a very real threat to global and national security. The potential for nanoscale agents to be deployed to enhance the efficacy of such attacks is one practical and near-term concern. As noted earlier, researchers have already demonstrated that nanoscale particles can act as ubiquitous carriers of toxic chemicals. A NATO report on the security implications of nanotechnology noted that:

"The potential for [nanotechnology] innovations in chemical and biological weapons is particularly disquieting, as NT can considerably enhance the delivery mechanisms of agents or toxic substances. The ability of nanoparticles to penetrate the human body and its cells could make biological and chemical warfare much more feasible, easier to manage and to direct against specific groups or individuals. Dr. Sean Howard, in his work on NT security implications, has even called the threat of chemical and biological warfare a 'real nano goo.'" [17]

- Limited nano detection/forensic capa-

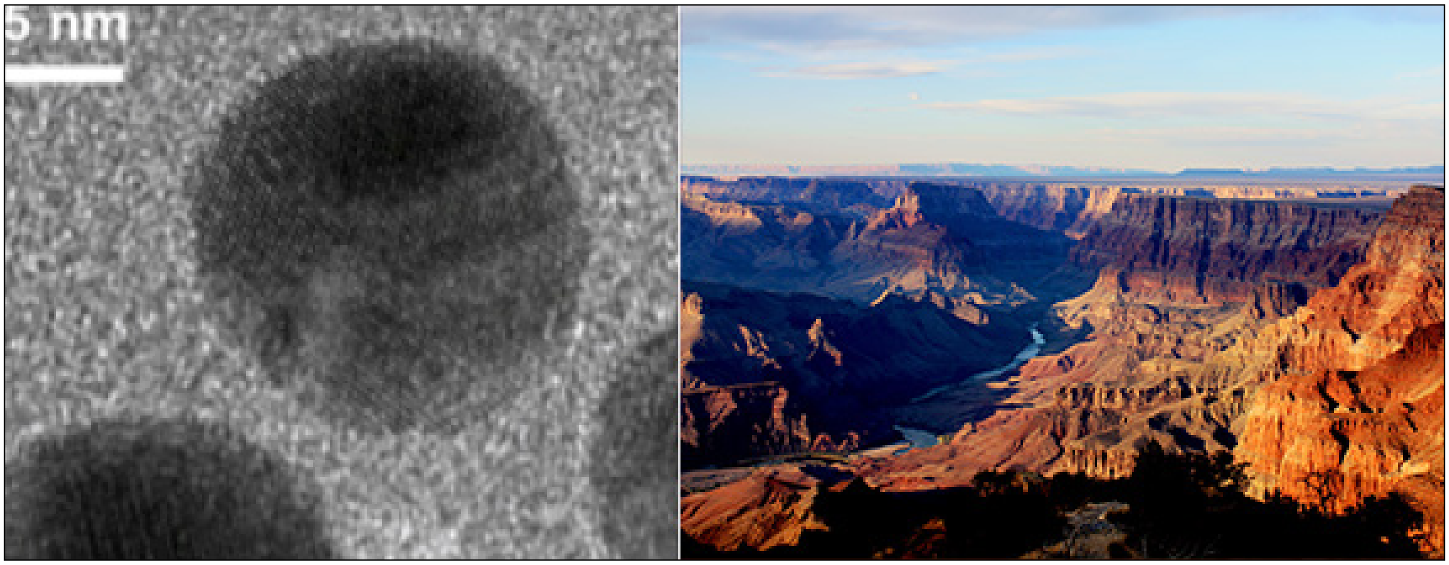

Figure 4. Searching for a 50 nm nanoparticle in your morning cup of coffee? Good luck, that task would be equivalent (by volume) to searching for a needle in a haystack large enough to fill the Grand Canyon—more than 30 times! (Released)

bilities: A major security concern and unmet need lies in our limited ability to determine forensically, whether and to what extent a particular nano threat may have been deployed. Additionally, there exists a clear lack of field deployable and scalable tools capable of detecting and monitoring nanoscale threats beyond laboratories and clean-rooms. Scientific and engineering-based approaches can be taken to address these gaps. For now, capabilities suitable for enhanced detection/mitigation of nanoscale tracking devices or nano-enabled “Trojan Horse” delivery threats, for example, remain limited.

- Complacency amidst a silent arms race: The number of state-sponsored nanotechnology initiatives globally signifies a clear arms race to assume a dominant position in nano-enabled science and technology. While not as visible as the nuclear threat, this race is every bit as important to national and global security. A major threat to U.S. national security on this front is the potential to become complacent and to prematurely reduce federal investments into nano and convergent technologies. The United States has established itself as a global leader in nanoscale science and engineering research, scholarship and commercialization. Nevertheless, failure to maintain strategic, long-term investments in these areas, particularly rapidly evolving infrastructure and human capital, could severely impact U.S. innovation in nano-enabled industries and many other emerging technology fields that are simultaneously enhanced by progress in nanotechnology. Attrition of U.S. intellectual and infrastructural capabilities across nanotechnology-related programs would weaken U.S. defense and security interests in the future, when strategic nanoscale science and engineering investments are expected to yield their greatest payoffs.

Off Buttons and Erasers:
Integrating Security Features into Nano-enabled Technologies

A critical security feature of any technology is the ability to turn it off, undo it, deactivate it or otherwise separate the harm it might cause from those it might harm. Even the humble pencil has evolved to include an eraser for undoing its mistakes. But, mankind has endured a host of challenges that arise when new technologies yield unintended consequences – the persistence of consumer plastic goods has left debris scattered across the Earth’s oceans; the use of nuclear weapons and runaway reactor cores have rendered cities uninhabitable for thousands of years; and the use of CFCs in coolant systems migrated unabated to the stratosphere where they’ve depleted the earth’s ozone layer.

The recent Galaxy Note 7 battery fire controversy coupled with growing use of lithium ion batteries in mobile devices underscores the importance of technology that can be turned off. At present, it is unclear how persistent nanostructures and the unique behaviors that may accompany them will be in biological and environmental systems, and that should be alarming.

An unprecedented dialogue around responsible nanotechnology has yielded progress, but feasible safeguards have been limited at best. Researchers have called for more green chemistry/nanotechnology approaches to help address some of these issues, [18] but those are likely to be effective only in situations where they clearly do not compromise performance of nano-enabled materials and devices.

Nano and National Security:
Key Considerations for the Future

Looking ahead, nanoscale science and engineering will continue to impact security both nationally and globally in significant and far-reaching ways. The following list summarizes some key opportunities for the nano defense and security community:

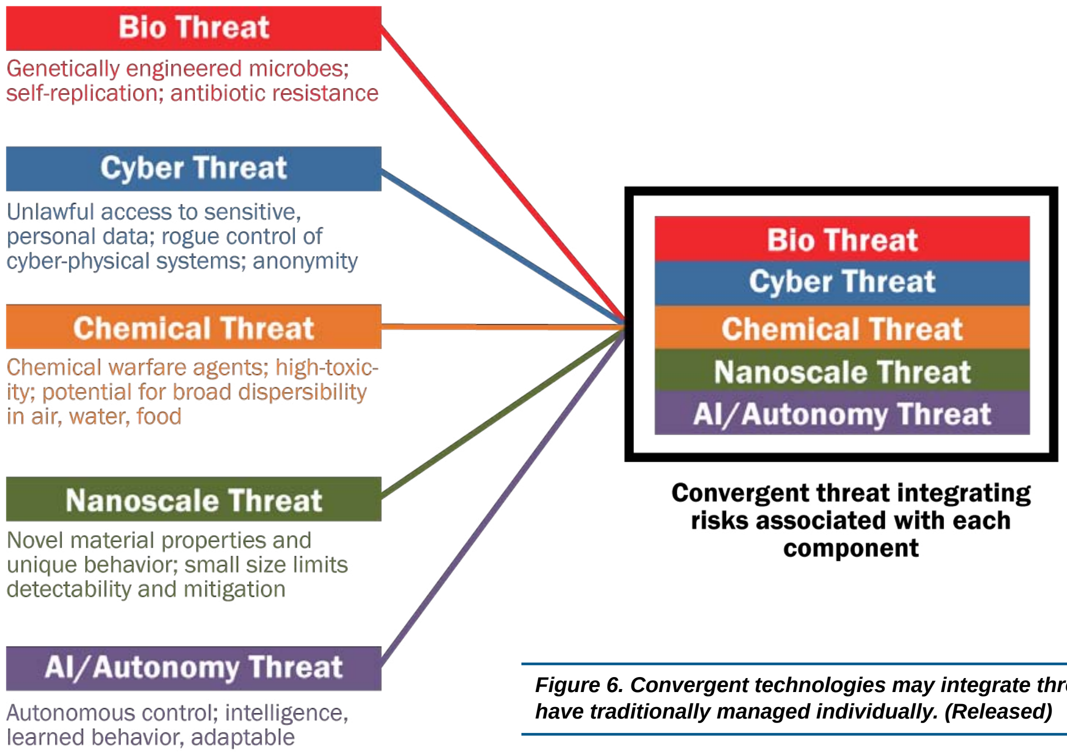

Figure 6. Convergent technologies may integrate threats that we have traditionally managed individually. (Released)

- Translate nano properties to human scale devices and systems. Much of the hype surrounding nanotechnology has been muted by a lack of real-world examples demonstrating how unique nanoscale material properties can be translated into materials and devices with performance capabilities that are vastly enhanced relative to their bulk counterparts.

- Perfect nanoscale power systems. Realization of some of the most exciting security and defense applications of nanotechnology requires innovative strategies to power and mobilize nano devices against ambient molecular forces that are far greater at the nanoscale than they are at the human scale. To nanomachines, molecules of air, water and biological fluids appear as impenetrable walls of infinite thickness.

- Enhance nano forensic capabilities. Analytical capabilities, particularly in the field, have not kept pace with nanoscale innovations. As researchers continue to perfect and advance nano-enabled systems, those systems will possess capabilities to perform increasingly sophisticated functions – delivery, communications, listening, imaging and others. As these functions are acquired, the need for national security and law enforcement personnel to have readily available nano forensic tools and procedures will become more vital to ensure justice, public safety, and security.

- Convergence complicates future threat assessment and mitigation. As multiple technology domains converge into more sophisticated systems, they link not only the benefits of those disparate technologies but also their risks. Consequently, threat assessment must stay ahead of convergence through interdisciplinary programs linking nano to other emerging technology domains like bio, big data, artificial intelligence, and autonomy (See Figure 6).

- Prepare for every eventuality. Robust emergency preparedness and response planning and procedures are needed. While much progress has been made to better understand the risks of emerging technologies, translation of this knowledge into coordinated emergency response procedures has been lacking. The absence of dialogue between researchers investigating the hazards posed by new technologies and emergency managers is alarming, and poses risks to numerous stakeholders (e.g., students, research professionals, first responders, the general public) and national security. ■

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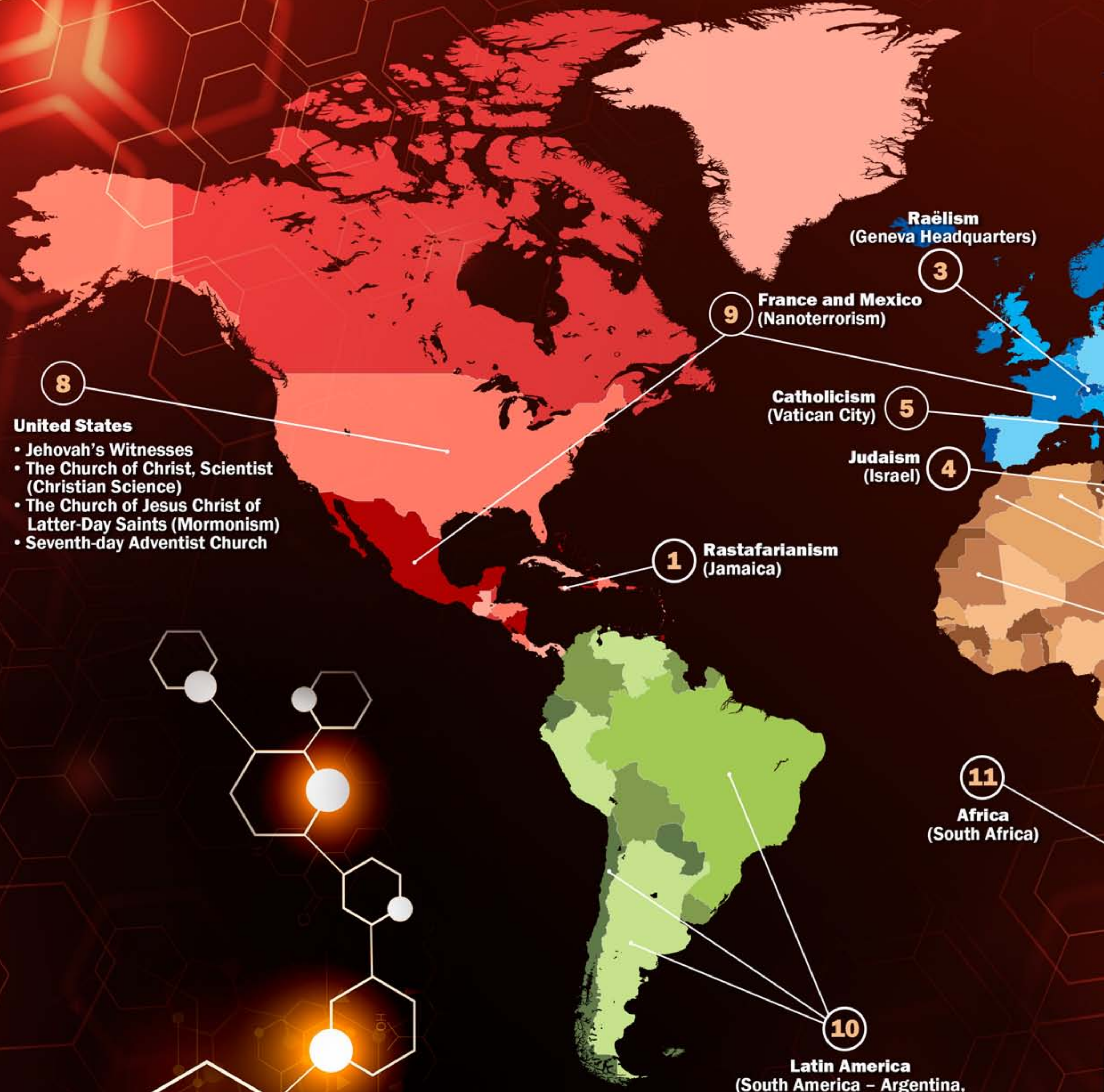
The Impact of Culture & Religion



Raëlism
(Geneva Headquarters)
3

9
France and Mexico
(Nanoterrorism)

8
United States
- Jehovah's Witnesses
- The Church of Christ, Scientist (Christian Science)
- The Church of Jesus Christ of Latter-Day Saints (Mormonism)
- Seventh-day Adventist Church

Catholicism
(Vatican City)
5

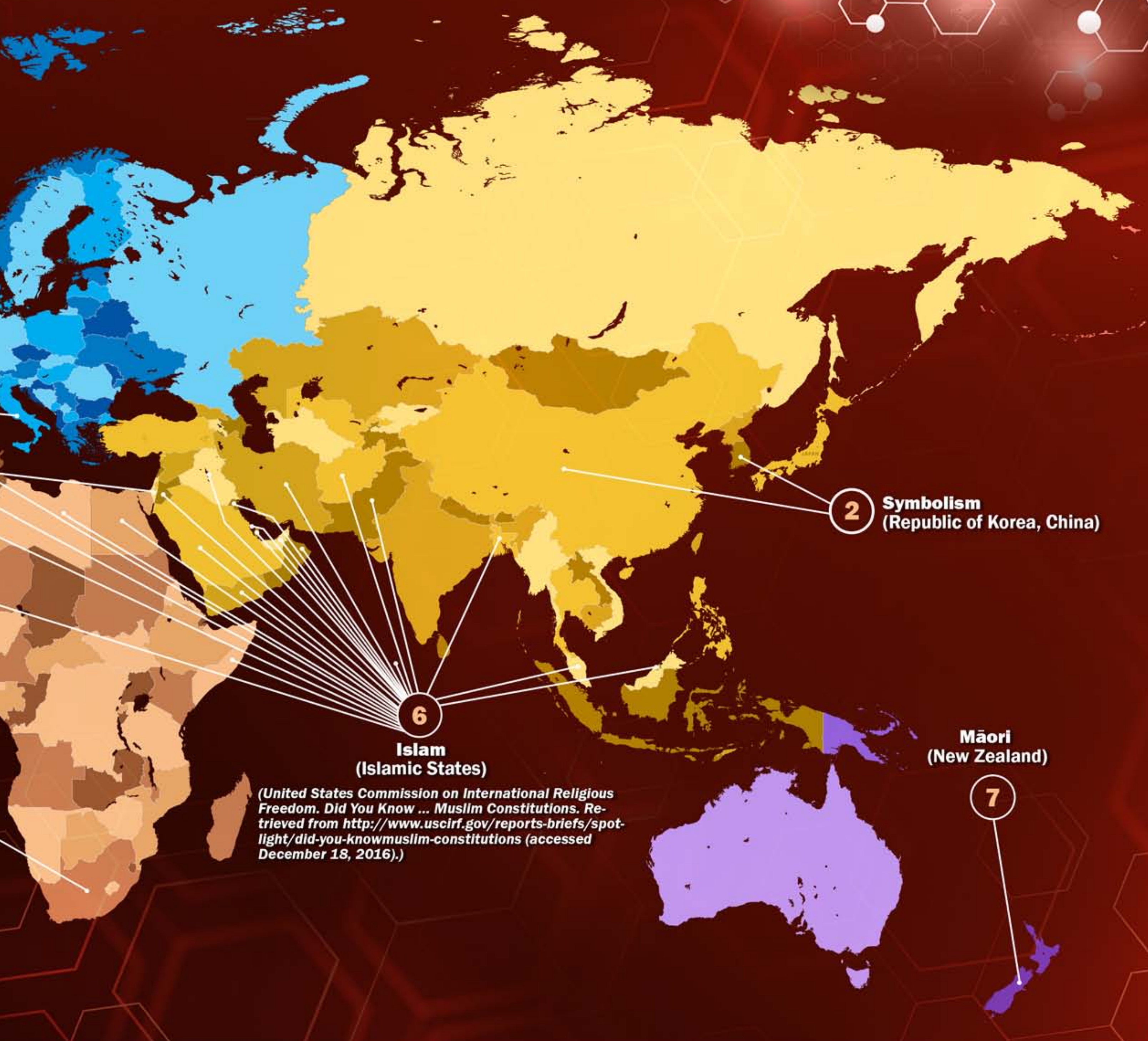
Judaism
(Israel)
4

1
Rastafarianism
(Jamaica)

11
Africa
(South Africa)

10
Latin America
(South America – Argentina, Brazil and Chile)

on Nanotechnology



(United States Commission on International Religious Freedom. Did You Know ... Muslim Constitutions. Retrieved from http://www.uscirf.gov/reports-briefs/spotlight/did-you-knowmuslim-constitutions (accessed December 18, 2016).)

The field of nanotechnology is becoming more widely used in both military and medical applications. As the Department of Defense employs a diverse workforce, an understanding of the cultural, religious, and ethical implications of nanotechnology remains critical to ensure that nano-based technologies do not disrupt operations due to cultural or ideological objections by service members.

The Impact of Culture & Religion on Nanotechnology

1 Rastafarianism (Jamaica)

Rastafarians oppose the consumption of non-pure, modified foods, which may include nanoparticles used in food additives, such as Titanium Dioxide used to increase a food's shelf life. [1,2]

2 Symbolism (Republic of Korea, China)

Cultures that symbolically associate chrysanthemums with death may express reservations to the use of Zinc oxide nanoflowers, which strongly resemble chrysanthemums, as an antimicrobial. [3,4,5]

3 Raëlism (Geneva Headquarters)

Raëlians view nanotechnology capable of mitigating health concerns, including the use of carbon nanotubes to trap harmful gases or pollution, as beneficial in extending the human life span. [6,7]

4 Judaeism (Israel

Certain uses of nanotechnology, such as in the creation of synthetic biology, echoes the Jewish story of the Golem, which portrays ethical issues concerning the creation of artificial life. [8,9]

5 Catholicism (Vatican City)

The use of nanotechology to develop more effective fetal diagnostics may correlate to a rise in abortions, which the Catholic Church historically opposes, with the increased discovery of fetal abnormalities. [10,11]

6 Islam (Islamic States)

The future use of nanotechnology to potentially produce artificial meat, naturally comprised of nanofibers, may generate ethical questions as artificial meat was never part of an animal and therefore could not undergo the Halal preparations required. [12,13]

7 **Māori (New Zealand)**

The potential impact of nanotechnology as a pollutant on the environment remains one of the larger concerns posed by indigenous groups such as the Māori that maintain a close relationship with the environment and nature. [14]

8 United States

- ***Jehovah's Witnesses***

  Jehovah's Witnesses do not believe in receiving blood products through blood transfusions due to a passage in the Old Testament of the Bible; however, the convergence of nanotechnology with biotechnology, polymer chemistry and molecular biology has allowed for the creation of artificial blood substitutes, which may provide a reasonable alternative for this group. [15,16]

- ***The Church of Christ, Scientist (Christian Science)***

  Christian Scientists believe that God is the only reality leading to their conclusion that matter is an illusion. This belief also leads many Christian Scientists to choose handling health issues with prayer rather than relying on conventional medical treatments. Apart for the obvious rejection of any medical applications created by nanotechnology, Christian Scientists believe that sickness and death are consequences of a reliance on matter, and thus would not necessarily be interested in the advances of manipulating matter through nanotechnology. [17,18]

- ***The Church of Jesus Christ of Latter-Day Saints (Mormonism)***

  Mormon scripture holds that power is derived through persuasion and not through force, and that this limitation even applies to God. Some believe that leveraging the natural tendencies of atoms and molecules to achieve new forms and functions plays into the grander scheme of natural persuasion; however, the limits would be set at utilizing nanotechnology to create brain-machine interfaces that stimulate artificial emotional experiences. [19,20]

- ***Seventh-day Adventist Church***

  Seventh-day Adventists follow strict guidelines in regards to their health. There are many proscriptions on diet, including adherence to a well-balanced vegetarian diet and the avoidance of particular foods such as highly refined foods. In addition, Seventh-day Adventists refrain from consuming any mind-altering or harmful substances, such as tobacco and alcohol, in order to keep their minds clear. Engineered nanomaterials are used in many foods for coloring and as preservatives and in food packaging. It is not necessarily clear how these food-grade nanomaterials would affect the choice of Seventh-day Adventists; however, the prohibition of highly processed foods may apply in some of these instances. [21,18]

9 France and Mexico (Nanoterrorism)

Nanotechnology has been embraced by most, but some countries have faced more resistance to the technology than others. From October 2009 through February 2010, five public events in a series of 17 planned town halls sponsored by the French Government regarding nanotechnology were disrupted by protesters. A series of explosions, thwarted attacks, and bomb threats spanned a two-year period from 2010-2012 and targeted facilities engaged in nanotechnology across 10 cities in Mexico. The attacks were planned and carried out by an eco-anarchist group identified as Individuals Tending Towards Savagery. [22,23]

10 Latin America (South America – Argentina, Brazil and Chile)

Nanotechnology has generally been embraced as a positive advancement throughout Latin America, but primarily in South America as a way to remain competitive with other parts of the world, particularly the United States and Europe. Research and development efforts in nanotechnology are especially dominant in Brazil, Argentina, and Mexico. However, the level of resources committed to assessing the societal impact of nanotechnology remains far lower among Latin American countries compared with developed nations. [24,25]

11 Africa (South Africa)

Nanotechnology development in Africa is primarily aimed at improving sustainability and meeting UN Millennial Development Goals. Advances include improving the clean water supply and minimizing the spread of disease. Most nanotechnology research efforts in Africa occur in South Africa, where there is a well-coordinated effort through organizations such as the South African Nanotechnology Initiative. South Africa is often considered the most technologically advanced nation in Africa, which often shifts the focus of science and technology efforts away from nations along the North African cost and traditional Sub-Saharan African nations. [26,27,28,29]

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Soft Micro-Robots for Military Medicine

By: Hen-Wei Huang,
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&
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Military medicine spans the gamut from emergency field care to rehabilitation. Across this spectrum technologies that are robust, portable and adaptive are critical for the patient's recovery. Traditionally, medical robotics is associated with intricate, bulky and specialized equipment, which is deployed in major hospitals but is not relevant in the field. Micro-robotics, by contrast, advertises treatment delivery capabilities that are portable, robust and targeted. Recent progress in smart materials and fabrication techniques enables medical robots to be smaller, softer, smarter and safer than ever before. [1] Soft micro-robotics provides a tactical advantage for precision medical treatment in austere environments. Furthermore, the use of soft and smart polymers, such as hydrogels, eliminates many safety issues concerning humans and robots.

Smart Materials Used in Soft Micro-robots

Hydrogels are hydrophilic, biocompatible and bioerodible. These characteristics are exploited in areas ranging from tissue engineering and cell scaffolding, to wound dressing and therapeutic cargo delivery. [2] By cross-linking different polymers, hydrogels can be engineered to be simultaneously highly deformable and tough, [3] which are generally considered incompatible requirements for other materials. To make micro-robots smarter, intelligence is embedded in the materials. By combining hydrogels with stimuli-responsive components, hydrogels can be designed to adapt to their environment; regulate the transport of ions and molecules; alter their adhesion with other materials; or transform chemical and biochemical signals into optical, electrical, thermal or mechanical signals, and vice versa. [4]

The embedded intelligence in smart materials facilitates remote monitoring of patients through personal smartphones. Stimuli-responsive hydrogels coupled with a high-sensitivity inductive wireless sensor enables wireless chemical monitoring, a kind of wireless sensor network. WSNs are widely used in monitoring personal health conditions through near-field communications connecting sensors and smartphones. [5] Different types of chemical sensors have been developed to fulfill real-time monitoring for personal daily life, such as blood oxygen, blood pressure, glucose, etc. Wireless communication bridges the gap between hospitals and patients. Information on the patients' health condition is transferred and recorded at the health center. Therefore, patients can be remotely diagnosed by doc-

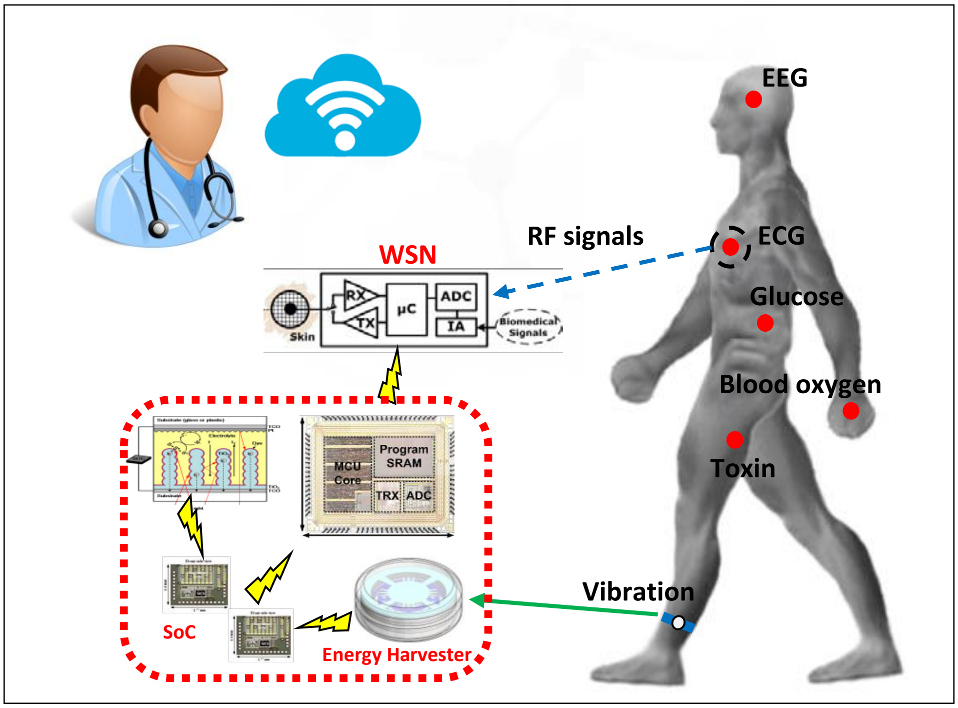

Figure 1. The concept of a wireless body sensor network.

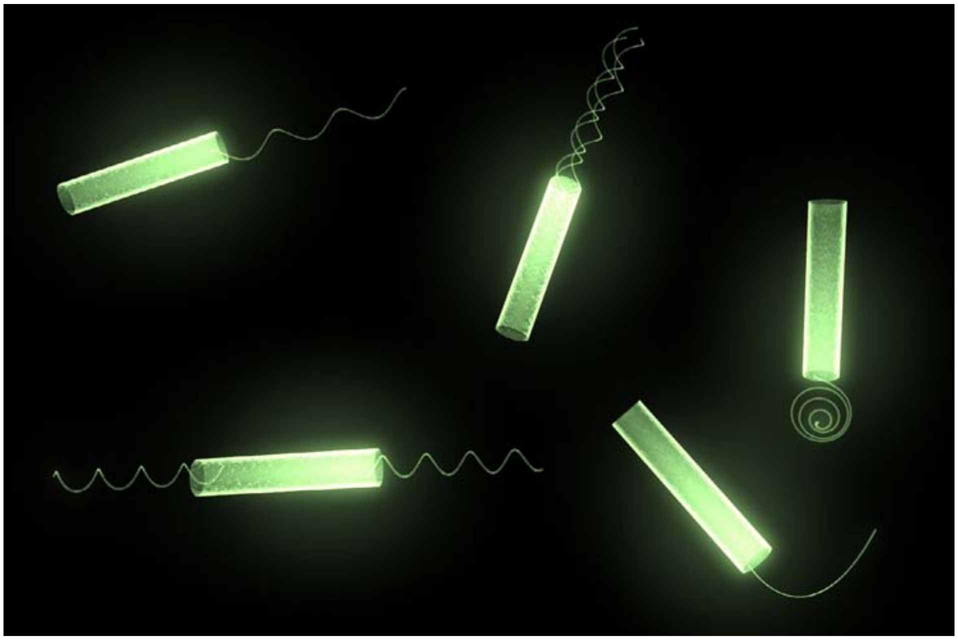

Figure 2. Bacteria inspired micro-robots are composed of a tubular body and various types of flagella.

tors (See Figure 1).

To achieve faster diagnoses, smart materials can be equipped with more than one responsive group to attain multi-stimuli responsive properties and the detection of various physiological conditions. [6] For instance, soft micro-robots with the ability to detect autoantibodies can target specific tissues and cells and are being developed to diagnose and treat early-stage cancer. [7] Smart hydrogels are also capable of rapid self-repair, allowing robots to recover from damage in aqueous environments. [8]

Building Soft Micro-Robots for Therapeutic Delivery

One major advantage of forming soft micro-robots from smart materials is that such a micro-robot could automatically deliver therapy to damaged areas. This requires coordination between the embedded sensors and actuators in the devices. This level of sophistication is exhibited at this size scale by leukocytes cells, which are able to find and target pathogens. In a similar manner, smart materials can sense variations in the environment and then respond with a programmed action. For example, a micro-gripper can be programmed to open and deliver its payload only when it senses the target. [9,10] There are many emerging technologies developed for creating 3D micro/nano mobile machines employed in minimally invasive therapies, such as 3D printing [11] and self-folding. [12] Among them, origami folding based on photolithography are the most promising for generating complex shapes and high throughput production. [13,14] Developments in foldable printed circuit boards, [15] rolled-up supercapacitors for electrostatic energy storage [16] and biodegradable circuit boards [17] will equip future soft micro-robots with sophisticated programming akin to their macro-scale counterparts.

Self-folding is achieved by coupling two materials that swell differently when hydrated. For example, a spiral tube provides both a large volume for carrying therapeutic agents and a large surface area, when uncoiled, to disperse the agent. The reversible stimuli-responsive property of hydrogels enables self-folded micro-robots to change their shapes on demand to deliver an agent. [9,18,19,20] These tiny machines are small enough to be directly injected into the human body by a syringe to perform minimally invasive therapies. The micro-robots can either be manipulated remotely by external user control or navigate passively through blood flow. Hydrogel based micro-robots, with intrinsically soft and flexible properties, are able to access mechanical constrictions, such as narrowed and obstructed vessels. The remote control of micro-robots can be achieved by embedding magnetic nanoparticles into polymer-based actuators. The layout of the embedded particles determines the mobility of the magnetically guided micro-robots. Alternative actuating methods, such as near-infrared light, [12] electrical fields [21] and chemical sources [22], can be realized by embedding different types of micro/nanoparticles. Advanced mobility of self-folded micro-robots has been achieved by mimicking the morphology, locomotion, and morphological adaptation of natural microorganisms [13] (See Figure 2). Microorganisms are usually composed of a large cell body attached to tiny flagella. A synergetic motion between cell body and flagella enables exceptional motility. [23,24]

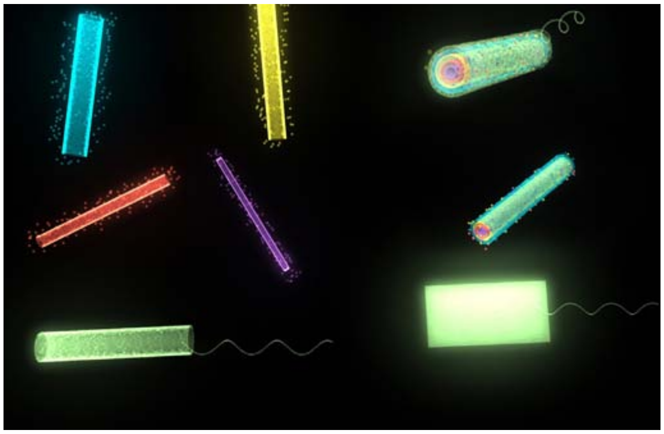

Figure 3. Matryoshka inspired micro-robots for extendable drug delivery. (a) Folded tubes loaded with different drugs. (b) Multiple folded tubes are assembled together for more efficient propulsion. (c) Chronological delivery of the therapeutic tubes by sequentially unfolding the tubes.

One major disadvantage of using hydrogel-based devices as drug carriers is the leakage of drug during transportation. Soft micro-robots with multiple shape transformations can be used to reduce pharmaceutical leakage before reaching targeted areas by refolding a self-folded tube to shield the drug loaded layer from the surroundings. [25] Moreover, the foldable micro-robots enable several devices to be assembled together to achieve more efficient propulsion or multiple functionalities (See Figure 3). The release of multiple assembled tubes can be also used in extendable release. For example, some treatments require multiple doses periodically or a controlled long-term sustainable release. Nested micro-robots can achieve sequential releases of multiple drugs or varying dosages. In this way, soft-micro robots can deliver target and tailored therapies in a robust and portable package. ■

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