Highlights from the Sustainable Nanomanufacturing: Creating the Industries of the Future (*Nanomanufacturing*) NSI

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Manufacturing is an essential element in the commercialization of any technology. The development of reliable and repeatable, cost-effective, safe, and environmentally responsible methods for the scaled production of engineered nanomaterials and their incorporation into nanotechnology-enabled products is a critical need in moving nanotechnology discoveries from lab to market. Recognizing this need, Federal agencies participating in the National Nanotechnology Initiative launched the Nanomanufacturing Nanotechnology Signature Initiative (NSI) in 2010 to accelerate the development of industrial-scale methods for manufacturing engineered nanomaterials, functional nanoscale devices, and nanotechnology-enabled systems. The Nanomanufacturing NSI white paper[1] describes two thrust areas that focus the efforts of the eleven participating agencies[2] on cooperative, interdependent research and development (R&D):

1. Design of scalable and sustainable nanomaterials, components, devices, and processes.
2. Nanomanufacturing measurement technologies.

Federal agencies participating in the Nanomanufacturing NSI have focused their activities on the production-worthy scaling of two classes of sustainable materials—high-performance carbon-based nanomaterials and cellulosic nanomaterials—that have the potential to affect multiple industry sectors with significant economic impact. Key features of this NSI include productive industry, government, and university partnerships to develop methods to reliably produce these materials, including high-throughput in-line metrology, and to demonstrate those methods in high-payoff applications.

This report highlights examples of individual and collaborative accomplishments of the Federal agencies participating in the Nanomanufacturing NSI.

Thrust 1: Design of Scalable and Sustainable Nanomaterials, Components, Devices, and Processes

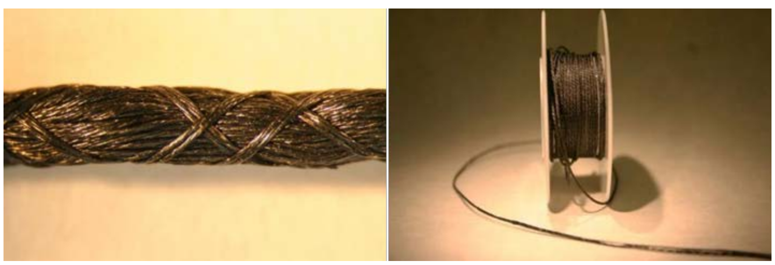

Figure 1. A 16-gauge wire (*left*), approximately 1.3 millimeters in diameter, made from carbon nanotubes that were spun into thread; the same wire on a 150-ply spool (*right*). (Source: Nanocomp Technologies, Inc.)

Due to their high tensile strength and modulus as well as their outstanding electrical and thermal conductivity, **carbon nanotubes** have received a significant amount of interest for use in such applications as ultra-lightweight, high-strength composites and multifunctional materials. While carbon nanotubes have found use in conductive inks, transparent conductive coatings, displays, and sensors, their broader use in high-performance applications has been hampered, in part, by the lack of robust methods to reliably produce them at a scale and in forms that are more readily incorporated into materials and devices. Since the launch of the Nanomanufacturing NSI, significant collaborative efforts have aimed at advancing carbon nanotube (CNT) manufacturing, and partnerships have been formed to coordinate research on manufacturing methods

[1] www.nano.gov/NSINanomanufacturing

[2] National Institute of Standards and Technology, Department of Defense, Department of Energy, National Institutes of Health, National Institute for Occupational Safety and Health, Occupational Safety and Health Administration, Environmental Protection Agency, Intelligence Community, National Aeronautics and Space Administration, National Science Foundation, and U.S. Department of Agriculture/Forest Service.

and metrology for high-performance CNT-based materials and to demonstrate their use in various applications.

To develop a trusted domestic source of bulk CNT material systems and processes for nanomanufacturing roll-to-roll bulk CNT yarns, sheets, and tapes (Figure 1), a Government-led CNT manufacturing partnership was founded. This partnership has involved seven companies in the aerospace and defense industry, five companies in the materials industry, four companies in the wire and cable manufacturing industry, a bulk CNT manufacturer, four universities, and the federally funded research and development center Aerospace Corporation. Federal partners include the Department of Defense (DOD) under the Defense Production Act (DPA) Title III, the Air Force Space and Missile Systems Center (AFSMC), the Army Engineer Research and Development Center, the National Aeronautics and Space Administration (NASA), and the National Institute of Standards and Technology (NIST). This partnership expanded the domestic capability to provide, for the first time, tonnage quantities of advanced CNT bulk materials sufficient for qualification and initial insertion into programs for aerospace, ballistics protection, and aircraft. This activity met the four-year goal set out in the Nanomanufacturing NSI white paper of demonstrating material systems and processes for nanomanufacturing that are scalable, sustainable, efficient, and safe as well as the eight-year goal (ahead of schedule) of engaging with industrial partners for the identification of materials and processes appropriate for production, followed by technology transfer and/or technology adoption by U.S. manufacturers. Under the Nanotechnology Project supported by the Space Technology Mission Directorate's Game Changing Development program, NASA has built upon the capabilities developed under the DPA Title III investments to improve the structural properties of CNT yarns and utilize them as reinforcements in ultralight-weight, high-strength composites. These materials were demonstrated in a CNT-reinforced composite overwrap pressure vessel (Figure 2) that was successfully flight-tested on May 15, 2017.[3]

Figure 2. CNT-reinforced composite overwrap pressure vessel. (Source: NASA)

In an effort to build industry, academic, and government collaboration, the technical interchange meeting, *Realizing the Promise of Carbon Nanotubes: Challenges, Opportunities, and the Pathway to Commercialization* was held in 2014.[4] The goals of this meeting were to identify, discuss, and report on technical barriers to the production of CNT-based bulk and composite materials with electrical and mechanical properties approaching values of individual CNTs, and to explore ways to overcome these challenges. The meeting gathered some of the Nation's leading experts in CNT R&D as well as executives and experts from the Federal Government, academia, and the private sector. A number of common themes and potential future R&D priorities emerged, including efforts devoted to improving quality control and scale-up, improving the mechanical and electrical properties of CNT-based bulk materials, effective use of simulation and modeling to provide insight into CNT growth process, and the use of public–private partnerships or other collaboration vehicles to leverage resources and expertise to solve these technical challenges and accelerate commercialization. NNI agencies continue to address these challenges through a combination of intramural and extramural research programs, interagency collaborations, and collaborations with industry and academia. One outcome was the establishment of the Institute for Ultra-strong Composites by

[3] https://www.nasa.gov/feature/nanotechnology-flight-test-material-impact-on-the-future

[4] www.nano.gov/2014CNTReport

Computational Design by NASA in 2017. The focus of this institute is to develop and deploy nanotube-based structural materials.[5]

Cellulosic nanomaterials, primarily isolated from trees or other plant sources, offer great promise for commercial applications due to their high strength, electrical conductivity, and optical transparency. Since the inception of the NNI, significant advancements have been achieved in the manufacturing of these materials at pilot scale. A public–private partnership between the U.S. Department of Agriculture (USDA) and the U.S. Endowment for Forestry and Communities (see below) was established in 2013 to accelerate the commercialization of cellulose nanomaterials, and pilot plants are now producing these materials in quantities much beyond laboratory-scale production.

Figure 3. Forest Products Laboratory nanocellulose pilot plant. (Source: Forest Service)

Since 2012, the Forest Products Laboratory (FPL) has commissioned pilot plants for the production of cellulose nanocrystals (CNCs)[6] and cellulose nanofibrils (CNFs) at its facility in Madison, WI (Figure 3) and at the University of Maine. These pilot plants now produce sufficient quantities of CNC and CNF for government, academic, and industrial research while providing scientists with an opportunity to identify knowledge gaps manufacturing cellulose nanomaterial at a commercially-viable scale. The FPL has been working in partnership with the forest products industry's Agenda 2020 Technology Alliance[7] and universities to advance a common vision for developing the precompetitive science and technology critical to the commercial production and application of cellulose nanomaterials for new generations of products. Universities involved in this collaborative effort include Georgia Institute of Technology, North Carolina State University, Oregon State University, Pennsylvania State University, Purdue University, University of Maine–Orono, Mississippi State University, and University of Tennessee–Knoxville. Ten high-priority research projects were initiated in 2011 involving this group of partners. The Federal Government and industry have identified several research opportunities to develop and commercialize cellulose nanomaterials. In 2010, the Agenda 2020 Technology Alliance, the American Forest and Paper Association, the Institute of Paper Science and Technology, and the Department of Energy (DOE) Industrial Technologies Program (now known as Advanced Manufacturing Office) sponsored a workshop that created an updated roadmap for the forest products industry entitled *The Forest Products Industry Technology Roadmap*.[8] This workshop identified the creation of new bio-based nanomaterials and the preservation of biomass nanoscale properties as research priorities for engineering new products and applications. In June 2012, research needs for cellulose nanomaterials were further defined in the DOE Advanced Manufacturing Office *Sustainable Nanomaterials Workshop*.[9] As of 2016, a technology roadmap to help facilitate rapid commercialization of cellulosic nanomaterials has been published by the Agenda 2020 program.[10]

[5] https://www.nasa.gov/press-release/nasa-selects-proposals-for-first-ever-space-technology-research-institutes
[6] www.fpl.fs.fed.us/research/facilities/nanocellulose_pilot-plant.php
[7] www.agenda2020.org/
[8] www.agenda2020.org/uploads/1/1/4/1/11419121/fpi_roadmap_2010.pdf
[9] www.energy.gov/eere/amo/downloads/sustainable-nanomaterials-workshop
[10] http://www.agenda2020.org/technology-roadmaps.html

More recent efforts from USDA have targeted the organization of consortia on commercializing cellulose nanomaterial technologies. In 2013, USDA Secretary Thomas Vilsack announced the formation of a public–private partnership called P^{3}Nano between USDA/Forest Service (FS) and the U.S. Endowment for Forestry and Communities to rapidly advance the commercialization of cellulose nanomaterials.[11] The $4 million partnership focuses on removing barriers to commercializing cellulose nanomaterials and on engaging in activities to sustain the cellulose nanomaterials R&D conducted by the partnership. In addition, USDA/FS, in collaboration with the National Nanotechnology Initiative, organized a workshop in 2014 entitled *Cellulose Nanomaterials—A Path Towards Commercialization*.[12] The primary goal of the meeting was to identify the critical information gaps and technical barriers in the commercialization of cellulose nanomaterials, with expert input from user communities. The event brought together high-level executives from government and multiple industrial sectors to define pathways for the commercialization of cellulose nanomaterials. The workshop was very successful in identifying major technical hurdles in characterization standards, processing, and dewatering of cellulosic nanomaterials which limited further development. Since this workshop was convened, many of the technical challenges identified have been successfully addressed by private companies in collaboration with programs like Agenda 2020 and P^{3}Nano. Another major hurdle identified was improving awareness about what cellulose nanomaterials are, how they may be used, and the benefits they can provide. These efforts are ongoing.

The NSF Scalable Nanomanufacturing (SNM) Solicitation was announced in 2011 as a response to the Signature Initiative, and has received between 80 and 100 proposals each year since its establishment. The annual budget has varied between $8M and $12M, and the program has focused on novel scalable processes and methods for large-area or continuous manufacturing of nano-scale structures, their integration into higher order systems, and fundamental research into technical areas that are critical to overcoming barriers to scale-up. The SNM solicitation has successfully led to scalable continuous production of aligned carbon nanotubes, development of inkjet-based roll-to-roll processing and patterning of thin film photovoltaic devices, and scalable nanomanufacturing for 3D functional biomedical devices, among many others.

Environmental, health, and safety (EHS) issues remain an important consideration for the large scale production of nanomaterials. The National Institute for Occupational Safety and Health (NIOSH), Consumer Products Safety Commission, and other NNI participating agencies are working to assess these risks and make sure that nanomanufacturing and nanotechnology-enabled products are safe in the workplace and in the home. In 2013, NIOSH released Current Intelligence Bulletin 65 on *Occupational Exposure to Carbon Nanotubes and Nanofibers.*[13] This document includes a quantitative risk assessment, a recommended exposure limit, risk management recommendations for safe handling and use of carbon nanotubes and nanofibers, and a discussion of research needed to close knowledge gaps. A critical focus for NIOSH is the development and implementation of engineering control strategies and solutions that mitigate process releases and worker exposures in two areas: (1) providing guidance to nanomanufacturers using established materials such as CNTs or carbon nanofibers; and (2) developing prospective guidance for emerging materials, such as graphene, by conducting hazard assessment employing *in vitro* and *in vivo* models of exposure and response. NIOSH also collaborates with the National Toxicology Program[14] to investigate potential hazards associated with exposure to cellulose nanomaterials. NIOSH's focused field research effort has led to the publication of two basic guidance documents on engineering controls and work practices: *General Safe Practices for Working with Engineered Nanomaterials in Research Laboratories*[15] and *Current Strategies for Engineering Controls in Nanomaterial Production and Downstream Handling Processes*.[16] NIOSH efforts aimed at providing information to industry to facilitate

[11] www.usda.gov/wps/portal/usda/usdamediafb?contentid=2013/12/0235.xml&printable=true&contentidonly=true
[12] www.fpl.fs.fed.us/documnts/pdf2014/usforestservice_nih_2014_cellulose_nano_workshop_report.pdf
[13] www.cdc.gov/niosh/docs/2013-145/pdfs/2013-145.pdf
[14] ntp.niehs.nih.gov/
[15] www.cdc.gov/niosh/docs/2012-147/pdfs/2012-147.pdf
[16] www.cdc.gov/niosh/docs/2014-102/pdfs/2014-102.pdf

effective risk management processes have helped address the four-year goal of demonstrating material systems and processes for nanomanufacturing that are safe. Partnerships with private nanomanufacturing companies will be expanded in 2016 to include extension of effective risk management practices into elements of the national advanced manufacturing priorities by working directly with the manufacturing institutes. U.S.-based entities are working collaboratively with researchers around the world to leverage knowledge about the potential environmental, health, and safety implications of novel nanomaterials and nanotechnology-enabled systems. Mechanisms such as the U.S.-EU Communities and Research (CORs)[17] and the Organization for Economic Co-operation and Development's Working Party on Manufacturing Nanomaterials facilitate international cooperation on nanosafety reserach.

Thrust 2: Nanomanufacturing Measurement Technologies

Since this signature initiative began in 2010, measurement technologies have advanced, enabling information about nanoscale material composition and behavior to be obtained at high speed. NIST is at the hub of the effort addressing this thrust area and has extensively supported collaborative endeavors with industry, academia, and other participating agencies. Ongoing investigations include the development of smart manufacturing through advanced nanopositioning, robotic metrology, sensing, and controls needed to improve nanoscale product quality and yield. NIST is using nanotechnology to improve the safety of industrial robots and to create nanometrology sensors and devices for next-generation robotics and automation. To support large-scale production of nanotechnology-based products, new methods are being developed to characterize nanomanufacturing processes. In the area of carbonaceous nanomaterials, NIST has developed high-throughput microwave-based measurement methods to characterize the nanostructure of carbon nanocomposites. This technology has been transferred via a Small Business Innovation Research award to PaneraTech, a small U.S. company. NIST is performing cooperative research and development with the Massachusetts Institute of Technology (MIT) and the University of Delaware using advanced nanoscale tomography methods to evaluate the effects of varying synthesis conditions on the morphology and structure of CNT composites. Advances in micro- and nanoscale *in situ* experiments and computational techniques are shedding light on the delicate structure–property relationships found in biomaterials. The results of this research demonstrate the potential benefits of an integrated computational-experimental approach to materials development also consistent with the goals of the Materials Genome Initiative. Access to high-performance computing resources extends the size and complexity of problems that can be solved with the aid of modeling and simulation, enabling optimized material design, manufacturing processes, and component design at the pre-fabrication stage. These activities help address the two-year NSI goal of forming industry-academic-government consortia focused on metrology for high-throughput roll-to-roll nanomanufacturing, the four-year goal of demonstrating robust measurement systems which can operate in real-time, and the eight-year goal of developing benchmarking and measurement systems for industrial partners.

The Impact of the Sustainable Nanomanufacturing NSI

The activities that have taken place in support of this NSI have met or exceeded the goals established under the 2010 white paper and have significantly advanced the scientific understanding and physical infrastructure necessary for the ongoing lab-to-market transition of carbon nanotube bulk materials and cellulosic nanomaterials. These efforts have established a national capability to produce commercially important engineered nanomaterials at pilot plant or greater scales and have enabled a number of demonstrations in several high-end applications. Investments by NNI agencies have developed a globally unique capability to produce carbon nanotube bulk materials (sheets, yarns and composites) and cellulosic nanomaterials on a pilot plant scale. Workshops organized and sponsored by agencies participating in this NSI have identified the technical challenges, suggested potential mechanisms to further advance and commercialize carbon-based and cellulosic nanomaterials, and seen many of those mechanisms come to fruition. The launch of multiple Manufacturing USA institutes that are focused all or in part on advanced

[17] http://us-eu.org/

materials presents additional opportunities to leverage the investments and resulting innovations in nanomaterial manufacturing under this NSI. The properties of carbon-based and cellulosic nanomaterials offer unique and powerful benefits in the areas of material lightweighting, advanced composites, flexible electronics, and advanced textiles, each of which has a dedicated manufacturing. Taken together, the continued success of sustainable manufacturing offers enormous potential benefits to the future of American manufacturing.