April 30, 2009

Critical Nanotechnology Needs in the Forest Products Industry White Paper

Executive Summary

Nanotechnology has enormous promise to bring about fundamental changes and significant benefit to the forest products industry. The U.S. forest products industry is in a unique position to tap this huge potential in two primary ways. First, by becoming a user of nanotechnology materials and components in its products and processes, it can upgrade its processes and produce new high performance consumer products from lignocellulosic-based materials in a safe and sustainable manner. Second, the industry intends to become a producer and developer of novel, sustainable nanomaterials to replace non-sustainable materials such as those from fossil-fuels. Use of nano-dimensional cellulose in nanocomposites will allow the production of much lighter weight materials to replace metals and plastics with widespread application to the forest products and other industries.

- Recognizing that he values of wood and wood-based materials at the nanoscale are virtually untapped, industry leaders developed a vision for nanotechnology and identified three priority focus areas:Improving the strength/weight performance of paper and wood-based structural materials
- Developing new value-added features for paper and forest products, and
- Creating new revenue streams based on innovative forest-derived nanomaterials

In order to understand the barriers standing in the way, industry experts next identified science and technology gaps, benefits, and research challenges for the preceding priority focus areas. This led to setting five priority nanotechnology research program areas:

- Achieving lighter weight, higher strength materials
- Production of nanocrystalline cellulose and nanofibrils from wood
- Controlling water/moisture interactions with cellulose
- Producing hyper-performance nanocomposites from nanocrystalline cellulose
- Capturing the photonic and piezo-electric properties of lignocelluloses

The need to understand and mitigate the risks to health, safety, and the environment that result from the introduction of engineered nanoscale materials, nanostructured materials, and nanotechnology-based devices was affirmed as an integral part of all research efforts.

Introduction

Global climate change and other impacts of increased human population and affluence are making the development and use of renewable materials and products, while sharply curbing CO_2 emissions, one of the central priorities of this and coming decades. Cellulose is the most abundant organic chemical on earth, with an annual production in the biosphere of about 90 billion tons. Renewable forest material is carbon-neutral. Managed forests, one of the largest sustainably-managed biomass sources in the U.S., have high potential to reduce U.S. greenhouse gas emissions and foreign fossil fuel dependency by conversion of forest materials into novel materials and products such as nanomaterials, high-performance composites, chemicals, and transportation fuels.

The US Forest Products Industry Today

The U.S. forest and paper industry is an important and vital segment of the nation's economy, representing approximately 6% of U.S. manufacturing output. The industry directly employs nearly 1.0 million people and ranks among the top ten manufacturing employers in 42 states with an estimated payroll of $50 billion/year and average employee salary of approximately $50,000 per year. Sales of the forest and paper industry products top $230 billion annually in the U.S. and export markets. The U.S. forest and paper industry is the world's largest manufacturer of forest products. The industry is a leader in biomass-derived energy, with two-thirds of its energy generated from renewable fuels. Of all biomass energy generated by industry in the U.S, 82% is produced in the forest products industry. The industry also is a leader in recovering its waste products, with 57% of paper consumed in the U.S. recovered in 2008, more than for any other commodity..

Yet this industry has encountered significant business challenges for a number of years, facing global competitors who use the latest and most efficient installed technologies, many of whom have wood, energy or labor cost advantages. The forest products industry alone has lost more than 250,000 manufacturing jobs 2006. The impact of paper mill closings is devastating in the mostly rural communities where the mill is the main employer, and the lost jobs are high paying, skilled manufacturing jobs. These direct job losses do not count the substantial multiplier effect of additional secondary and tertiary service jobs that are lost in the region as mill suppliers and contractors lose their livelihood. Despite its recent economic problems, the industry has a vital and unique role to play in the nation's efforts to develop a renewable materials base to replace fossil fuel based products and energy sources such as plastics, oil and metals. There are several compelling reasons:

- Wood and paper represent by far the largest volume of materials used in the US economy, see figures below ("Consumption of Materials in the

United States1900–1995”, Grecia Matos and Lorie Wagner, *pubs.usgs.gov/annrev/ar-23-107/aerdocnew.pdf)*.

Figure 5. Measurement (by weight) of the amount of selected materials consumed in the United States.

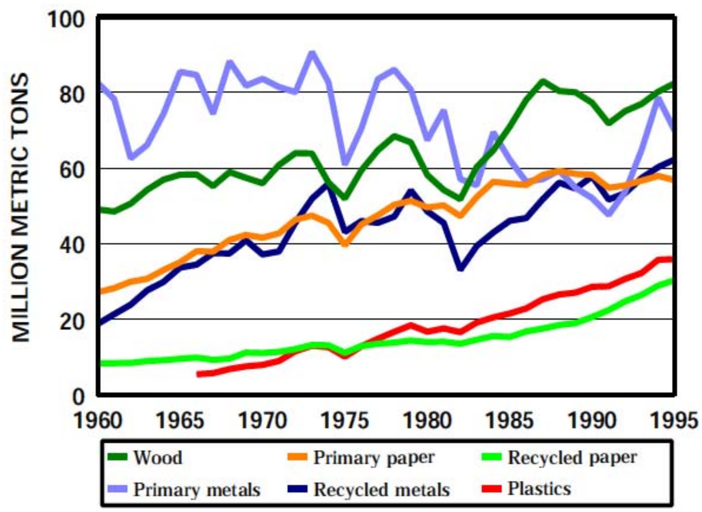
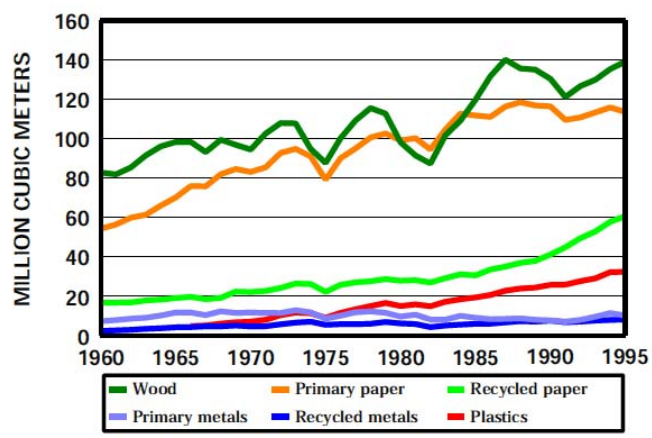


Figure 6. Measurement (by volume) of the amount of selected materials consumed in the United States.



- Wood and paper come from CO_2 sequestered by photosynthesis. Even though it takes energy to manufacture these products, their energy and environmental footprints are small compared to those of plastics and metals.
- The forest products industry sees its inherent strengths to include (1) stewardship of an abundant, renewable, and sustainable raw material base, (2) a manufacturing infrastructure that can process wood resources into a wide variety of consumer products, and (3) being uniquely positioned to move into new, growth markets centered on bio-based environmentally-preferable products. These industry goals are well aligned with society’s goals of establishing a native source of sustainable materials and products.

The Promise of Nanotechnology for the Forest Products Industry and the United States -- 21st Century Technologies for the 21st Century Economy

The United States has an immediate opportunity to build a world-leading program for the development and commercialization of nanotechnologies in the forest products industry. Wood-derived nanomaterials offer potential new revenue streams with high-value products. Applications of nanotechnology to the manufacture of forest-based products promise new value-added features, improved performance attributes, reduced energy intensity, and more efficient use of materials. These new revenue streams will create economic growth, new jobs, and new opportunities for skilled workers – using materials that can be grown, transported, and converted into value-added products in the United States more efficiently than nearly anywhere else in the world.

By becoming both a user of nanotechnology and a producer of novel nanomaterials, the forest products industry, has enormous opportunity to reinvent and reinvigorate itself in the twenty first century:

1. The industry looks forward to becoming a user of nanotechnology to solve problems and achieve optimum properties in existing products – advances that cannot be achieved with conventional technology. Nanotechnology will also enhance the industry's ability to develop new high performance products in a safe and sustainable manner.

2. The industry also looks forward to becoming a developer of novel, sustainable nanomaterials for use in the forest and other industries to replace non-sustainable and fossil-fuel-based materials. By tapping the enormous undeveloped potential of trees as photochemical "factories" that produce abundant sources of raw materials using sunlight and water, the potential benefits to society are enormous. Lignocellulosic biomass resources provide a key materials platform for the sustainable production of renewable, recyclable, and environmentally-preferable raw materials for producing goods and products to meet the needs of society in the twenty-first century. Wood, being made up of nanofibers that are extremely strong, offers ways to replace non-sustainable materials such as plastics and metals. Liberation of nano-dimensional cellulose and its use in nanocomposites will allow the production of much lighter weight materials to replace metals and plastics in all sorts of applications. The manufacturers of packaging products, for example, are seeking ways to move away from plastics, glass, and metal packaging and substitute use of paper and paperboard which are far more sustainable and "greener".

Overall Benefits to Society

Investments in nanotechnology for the forest products industry sector will have substantive, measurable, and pervasive beneficial effects for society in addition to those measured by increased Gross Domestic Product (GDP), increased employment, and creation of high paying, skilled jobs. It will usher in cost effective and affordable production of sustainable materials and products close to the point where they are used, thus greatly reducing transportation costs and energy consumption producing and transporting materials great distances as is the practice now. It will also greatly reduce the waste of materials and energy due to unnecessary over-construction of products and structures arising from our current lack of knowledge of nanoscale structures and interfaces. A nanotechnology-revitalized forest products industry will enhance forest health and condition; retard the current accelerating trends of forest fragmentation, parcelization, clearing, and conversion of forest lands to non-forest uses; increase recharge of water to aquifers as 90 per cent of the precipitation that falls on a forest is retained; and provide the full array of other forest ecosystem services to include animal habitat, clean water, clean air, carbon sequestration, recreation, etc. While the nuances of forest management practices can be debated, the fact remains that a managed forest remains a forest and provides a return on investment to the forest owner versus being sold and destroyed to make room for permanent commercial development "parks" or suburban housing tracts.

Forest Products Industry Research Priorities

Over the last five years the forest products industry has made a significant effort to develop a vision for a nanotechnology program (Appendix 1). Recently, the Chief Technology Officers (CTOs) of member companies in the Agenda 2020 Technology Alliance, a special project of the American Forest and Paper Association (AF&PA), explored the potential benefits that would accrue from a robust nanotechnology industry/government partnership. Using the outcome of the visioning efforts and their understanding of commercial market opportunities, they selected three primary focus areas for nanotechnology research and development:

- Improving the strength/weight performance of paper and wood-based structural materials
- Developing new value-added features for paper and forest products
- Creating new revenue streams based on innovative forest-derived nanomaterials

Industry matching funds are anticipated as projects move into development and demonstration stages. The CTOs of Agenda 2020 recognize the need and have confirmed that promising projects with good value potential will receive significant industry financial support.

Building off the CTOs' priorities and the *"The Forest Products Industry Technology Roadmap"* (see http://www.nanotechforest.org) a group of industry experts identified the benefits and research challenges of a program focused on the three preceding priority areas. They are summarized below for each of the focus areas:

1. **<u>Improving the strength/weight performance of paper and wood-based structural materials</u>**

Benefits to Society

If a theoretical understanding and ensuing commercially-viable approaches to achieving substantial strength/weight performance improvement can be reached, it will provide opportunities to develop new and advanced products with superior performance for existing and totally new markets that will provide significant "green benefits", such as:

- Increased efficiency of wood use and reduced volumes of materials being processed with proportional decreases in energy and environmental footprints
- Substantially reduced mass of non-recoverable paper and other products ending up in landfills
- Replacement of non-renewable materials in a wide range of markets with sustainable and renewable materials made from wood-based alternatives
- Reduced energy costs for shipping and transporting materials (e.g. structural products, packaging, mail, books, magazines, etc.)

Scientific/Technology Gaps

The strength of a cellulose fiber network in paper and board is governed by the bond strength, fiber strength, fiber size and shape, effect of any additives or fillers and uniformity of material distribution. Both nature and science have accomplished impressive results in strength development at the nanoscale level using very small amounts of materials. The overall objective is to improve strength/weight performance of paper and paperboard by at least 40 percent using one or several nanotechnology based approaches. Such improvement is not attainable with current technology and will require one or several breakthroughs in the three key areas of: (1) strength, (2) optical properties and (3) surface enhancement. Gaps include:

- Lack of a theoretical foundation for a nanotechnology-derived strength enhancement and impact on optical and other functional properties
- Lack of multi-scale models that elucidate and predict strength and other functional effects of nanoscale-level modifications to the network structure and effects of nanodimensionally-sized additives
- Lack of knowledge on how to leverage the inherent strength of cellulose nanofibrillar material (which approaches that of steel)
- Understanding of human health effects and environmental detection and analysis

2. **Developing new value-added features for paper and forest products**

   a. **<u>Controlling Water/moisture Interactions with Cellulose</u>**

Benefits to Society

Understanding and manipulating the interactions between water and wood/paper will permit huge reductions in energy and water usage in processes by which products are made. It will result in the more economical (effective and efficient) use of the raw materials in a broad base of new and existing products. It also will enable the substitution of products based on a sustainable renewable resource for some of the products derived from a more limited and less environmentally friendly material such as petroleum. It will make products more durable and resistant to mold and decay, and reduce the need for failure-related replacement of products under high moisture end use conditions.

Scientific/Technology Gaps

The response of wood's and wood-based material's lignocellulosic composite structure to moisture (both liquid and vapor) is due almost entirely to the super molecular structure of its biopolymers (i.e., cellulose, hemicelluloses and lignin), the nanoscale structures that comprise the wood fiber, and the hierarchical characteristics of these nanoscale structures in cell walls. Elementary nanofibrils, which have cross-section dimensions of about 3 – 5 nm are composed of cellulose polymer chains arranged in ordered (crystalline) and less ordered (amorphous) regions. The nature of these structures greatly influence the way in which the woody plants respond to moisture. The development of a substantial knowledge base of cellulose nanoscale/water interactions is expected to lead to the development of new and improved products as well as more efficient and effective processes. Gaps include:

- Lack of a fundamental knowledge base relating to cellulose nanoscale/water interfacial interactions at the nanoscale, including
    - Understanding of the nature of bonding within paper and wood structures at the nanoscale level
    - Knowledge of structure at the nanoscale that is relevant to moisture impact
        - Size of the nanofibrils
        - Dimensional stability of the fiber in response to moisture (the angle of orientation of the fibrillar bundles of nanofibrils relative to the long axis of the fiber plays a major role)
        - Degree of crystallinity (i.e., the ratio of the ordered regions to the amorphous regions in the microfibrils)
        - Because of inter- and intra-chain hydrogen bonding, crystalline regions are less accessible to moisture
- Lack of a model based on the above fundamental information that would enable the manipulation of the structures at the nanoscale to decrease the negative impacts of moisture (such as durability and resistance to mold) on woody materials

- Inability to modify and control mechanosorptive behavior
- Inability to provide physical/chemical barriers to prevent or control the transfer of moisture by modifying surfaces of composites based on lignocellulose using nanocoatings or nanoparticles
- Inability to modify the topography and surface chemistry to control attractive and repulsive forces between cellulosics and other materials
- A knowledge base and model which relate these interactions to more applied areas of adsorption/desorption, drying, dimensional stability strength/weight relationships, surface modification, product durability, and process improvements.
- Understanding of human health effects and environmental detection and analysis

b. Producing Hyper-Performance Nanocomposites from Nanocrystalline Cellulose

Benefits to Society

Combining wood-based with nanoscale materials has the potential to develop new or improved composite materials with unique multifunctional properties. Properties which may undergo substantial improvements include mechanical properties (e.g. strength, dimensional stability), thermal stability, chemical resistance, surface appearance, optical properties and electrical conductivity. If these improvements can be achieved, they will lead to a reduction and far more economical use of raw materials in a broad base of new and existing products such as paper products and paperboard packaging. It will also reduce or eliminate creep under load experience by composites. Higher performance, lighter weight structural materials will be much more durable and will not need to be replaced as frequently and can be tailored to meet unique end use performance requirements. This will also allow substitution of sustainable light weight materials for non-sustainable materials in a wide array of end uses.

Scientific/Technology Gaps

In addition to the wood based composites, paper and paperboard can be considered to be a form of nanocomposite as they are made up of components that are essentially nanodimensional. Most work, to date, has been the result of empirical formulation where wood or pulp fibers have been mixed together with other components to make useful functional materials. Cellulose is a material which has unique tensile properties. In its pure form it can create fibers that are as strong or stronger then Kevlar® (Cellulose = 70 to 137 GPa, Kevlar = 100 GPa). It is desired to form composites in which cellulose provides its maximum tensile strength and stiffness. Other properties of interest include formability and geometrical complexity at very small scale, unique physical properties, surface smoothness, biomedical compatibility, and ability to reinforce polymer foams.

It is also desired through the use of nanomaterials, and chemistry to either form or reform cellulose fibers in a variety of matrixes in which the cellulose can contribute its full modular strength to the matrix. It has been postulated that the structure of wood is the result of the cellulose nanofibrils forming liquid crystal arrays under the influence of the hemicellulose. This represents a form of self-assembly that could be used to produce new materials with high strength and lightweight. The interactions are typically non-covalent, such as hydrogen bonding and Van der Waals forces, but because of the extremely small size the interactions add up to provide a high degree of strength. Use of cellulose in a variety of different matrixes will be dependent on the interactivity of the matrix material with cellulose and lignocellulose surface chemistry. Wetting and surface area play key roles in the formation of high strength interfaces between the matrix, matrix components, and cellulose. Nanomaterials can provide unique levels of surface area for the formation of chemical bridges between the cellulose, the matrix, and other fillers used. The strength of cellulose composites is influenced by the chemical interface and cellulose particle geometry. Interfacial interactions are governed by adhesion, water sorption, durability, and processing of the material. Cellulose derivatives can also be combined with nanomaterials and used in conjunction with cellulose fibers, or other fibers to form nanocomposites. Gaps include:

- Understanding the self-assembly process and non-covalent interactions leading to the structure of wood, including
    - How to modify the side chains of inorganic compounds, such as siloxanes, silanes, or sodium silicates to link the cellulose fibers through Si-OH bonds forming an organic/inorganic matrix
    - How to grow the cellulose from bacteria; or an enzyme engine such that the cellulose forms in a matrix
    - How to use a nanostructure template and nano-catalysts to help structure the matrix and increase the rate of formation of the cellulose fibers within the structured matrix
    - How to use enzymes/chemistries to separate cellulose from lignin without mechanical action
    - How to develop systems that simulate the growth of cellulose in trees or plants on a industrial scale
    - How to achieve dissolution of cellulose into ionic liquids with precipitation of cellulose into a continuous fiber or incorporation of threads or honeycomb weaves of cellulose into a variety of different material matrixes
    - How to react wood pulp fibers in a solvent medium that does not fully penetrate the fibers followed by hot-pressing the partially modified pulp fibers at elevated temperature to form

    - a semi-transparent polymer sheet that is a nanocomposite of cellulose esters and unmodified cellulose
    - How to use cellulose nanocrystals for reinforcement of other matrix materials
    - How to modify the side chains of cellulose to further enhance self assembly.

- The lack of characterization techniques needed to accomplish the above including:
    - Understanding cell wall formation in tree and plants
    - Knowledge of the inorganic chemistry for linking cellulose
    - Understanding of cellulose chemistry and the sheet layering of cellulose to establish pathways by which cellulose could be modified to enhance self assembly
    - Understanding and modeling the formation of cellulose from glucose or other simple sugars by bacteria
    - Understanding of the effect of a variety of enzymes on the structure and tensile strength of cellulose
    - Understanding of the chemistry of cellulose and manipulation of its precipitation based on its solubility in various liquids and subsequent processing
    - Effects of enzymes and extreme refining conditions on cellulose and cellulose composites
- Understanding of human health effects and environmental detection and analysis
- Understanding on how to use cellulose from wood to strengthen plastics, providing a biodegradable lightweight component.

c. Capturing the Photonic and Piezo-electric Properties of Lignocelluloses

Benefits to Society

Many grades of paper require using higher grammage (basis weights) than needed, not because of strength property end use requirements but because of the need to achieve sufficient opacity. While it is desirable to achieve costs and materials savings by reducing the amount of raw material for a given unit of functionality in both fiber and coating, optical performance of the paper cannot be compromised. More efficient optical performance with minimal weight will benefit all grade levels but especially the ultra-lightweight grades where opacity decreases rapidly with weight. Benefits include significant reduction in materials, processing and distribution costs.

Scientific/Technology Gaps

Currently the Kubelka-Munk approach of deriving apparent light scatter and absorption coefficients is useful for characterizing materials. In addition, Mie theory uses fundamental Maxwell equations to describe the way light is scattered from particles and is useful for predictions of optimal sizes for light scattering units. Regular arrangement of these units can give rise to reinforcement of light interactions and is called a “Photonic Effect”. For example, photonic band-gaps are structures that prevent the passage of light. Photonic properties have been shown to be possible using “standard” materials and producing structures with regularities that provide photonic effects. Natural materials such as butterfly wings, seashells (abalone) and insect cuticles demonstrate effective optical barriers with minimal materials. These are effects different from those described by Kubelka-Munk, Mie or Raleigh scattering. Gaps include:

- Lack of knowledge on how to make a photonic structure with a range of sizes that has an effect over a very broad bandwidth and therefore, appears white and exhibits high (close to 100 percent) opacity.
- Lack of knowledge on how white species in nature achieve scattering structures that are optimized for performance against weight (bio-mimetic studies)
- Lack of knowledge on how to achieve the potential of cellulose as smart lightweight material that can be used as a sensor and an actuator
- The fundamental knowledge to enable the development of process, material and coating technologies capable of supporting device operation in the 1-50 MHz and 50-500 MHz range.
- Understanding of human health effects and environmental detection and analysis

.

3. Creating new revenue streams based on innovative forest-derived nanomaterials

<u>Production of Nanocrystalline Cellulose and Nanofibrils from Wood</u>

Benefits to Society

The objectives in this area are the liberation and use of nanocrystalline cellulose and nanofibrils (also called nano-whiskers) derived from lignocellulosic feedstock. Success in this area will allow the forest products industry to become a major supplier of nanoparticles for a wide-range of industries. Because of the tonnages of wood available for processing, commercial production would be both sustainable and renewable as well as create an industrially significant supply. Nanocrystalline cellulose and nanofibrils could be extracted from currently under-utilized feedstocks, such as forest residuals and sorted wood wastes. Incorporation of the nano-dimensional materials in products would decrease materials usage, lead to new generations of light-weight and high performance composite products for a wide array of end uses, and greatly reduce energy consumption in both producing and shipping materials and products.

Scientific/Technology Gaps

- Commercially attractive methods, including non-covalent disassembly and reassembly to liberate nanodimensional materials.
- Understanding of the entropic effects in the assembly and disassembly of forest nanomaterials.
- Ability to impart multi-functional properties and characteristics to nanocrystalline cellulose and nanofibrils.
- Adequate separations, characterization and stabilization methods.
- Cost effective methodologies to liberate, fractionate, and separate cellulosic nanomaterials into uniform, reproducible cohorts that can be easily dispersed for fabrication of macroscale products.
- Predictive models of nanomaterials behavior to correlate nanomaterials' properties and end-use performance requirements.
- Understanding of the effects of species, age, growth conditions, juvenile wood, mature wood, reaction wood, etc, on nanocrystalline cellulose/nanofibril properties and morphology
- Identification of the commercially viable nanomaterials present in biomass.
- The availability of metrologies for nanomaterials derived from biological materials.
- Understanding of human health effects and environmental detection and analysis

APPENDIX 1

Industry Efforts to Develop Vision for Nanotechnology Program

The vision for nanotechnology in the forest products industry is to **"*sustainably meet the needs of present and future generations for wood-based materials and products by applying nanotechnology science and engineering to efficiently and effectively capture the entire range of values that wood-based lignocellulosic materials are capable of providing*"**.

Determining technology needs:

- Forest products Nanotechnology Roadmap – 2005
- Forest products Technology Roadmap – All Platforms – 2006
- Forest products nanotechnology needs and priorities – 2006
- Short list of nanotechnology priorities from Agenda 2020 Chief Technology Officers – March 2008
- Strategic Issues Workshop for the Forest Products Industry, December, 2008

Building relationships with federal agencies and the National Nanotechnology Initiative (NNI):

- Federal Department and Agency participation on the Agenda 2020 CTO Committee and Task Groups - U.S. Forest Service, USDA Cooperative State Research, Education and Extension Service, Department of Energy (DOE) – Ongoing
- National Science Foundation (NSF) Nanoscale Science & Engineering Grantees Conference – 2006, 2007
- NNI Forest Products Industry CBAN (Consultative Board for Advancing Nanotechnology) – Established 2007 through a Memorandum of Understanding
- DOE Workshop – Nanotechnology for Energy Reduction – June 2007
- NSF Workshop – Predictive Modeling for Nanomaterials – October 2007
- Department of Defense (DOD) Nanomaterials for Defense Conference – April 2008
- National Institute for Standards and Technology (NIST) Cross-Industry Issues in Nanomanufacturing – May 2008 (co-sponsored by Agenda 2020)
- Co-sponsorship of the International Conference on Nanotechnology for the Forest Products Industry – 2006, 2007, 2008 – U.S. Forest Service, NSF

Communicating the vision:

- Meeting with Dr. John Marburger, President's Science Advisor – January 2008
- Meeting with U.S. Forest Service Chief Gail Kimbell – January 2008
- Meeting with USDA Undersecretary Mark Rey – January 2008
- Meeting with Doug Kaempf, Department of Energy – April 2008