Nanotechnology Applications in Forest Products: Current Trends

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Advanced Wood Processing II Session

2012 SWST/ICBR Convention

1865 THE UNIVERSITY OF MAINE

Advanced Structures & Composites Center

Overview

- What is nanotechnology?
- Brief history of nanotechnology
- Nanotechnology Research Initiatives
- Past Applications
- Current Trends
- *Low Hanging Fruit*
- Challenges!

What is Nanotechnology?

- Nanotechnology is science of
  - A nanometer (nm) is one billionth of a meter (10-9 m) about 4 times the diameter of an atom
  - Creating uniquely designed materials or systems through the control of matter on the nanometer (atomic) scale
  - The exploitation of novel properties and phenomena developed at that length scale

Nanotechnology Research Directions: IWGN Workshop Report, M.C. Roco, R.S. Williams, and P. Alivisatos, Eds., Kluwer, 2000.

Why is This Length Scale So Important?

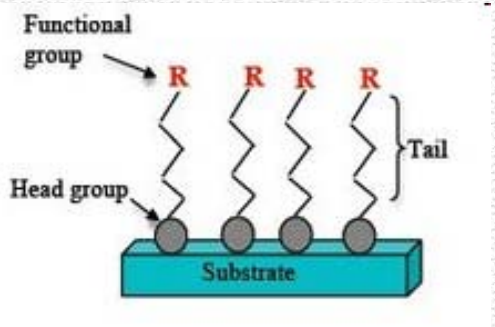
- Interactions are influenced by material variations on the nm scale
  - Control fundamental properties of materials without changing the materials' chemical composition
  - New, high-performance products and technologies that were not possible before
  - Use of nanoparticles and nanolayers with very high surface-to-volume ratios for use in polymeric materials

Brief History of Nanotechnology

Wikipedia filtered by Gardner

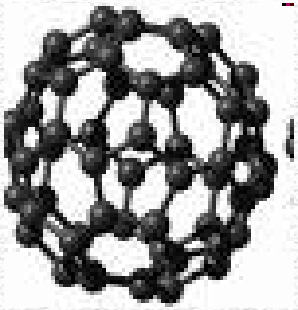
- Richard Zsigmody 1914 Gold Sols
- Interface and colloid science (20th Century)
  - "colloids, heterogeneous systems consisting of a mechanical mixture of particles between 1 nm and 1000 nm dispersed in a continuous medium."
- Langmuir-Blodgett films "monolayers"
- Richard Feynman 1959 "There's Plenty of Room at the Bottom"
- Norio Taniguchi 1974 first to coin the term "nanotechnology"

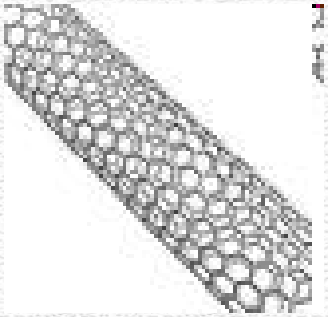
Milk is an emulsified colloid of liquid butterfat globules dispersed within a water-based liquid.



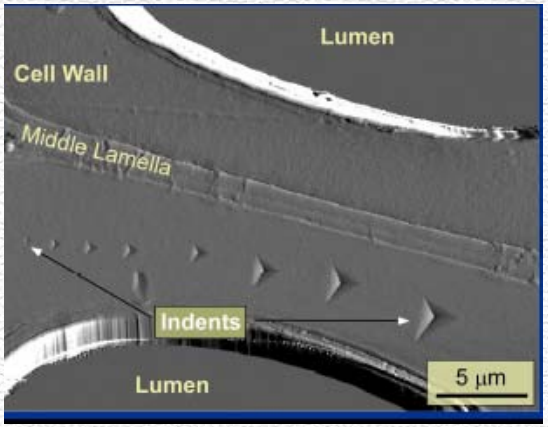
Brief History of Nanotechnology

Wikipedia filtered by Gardner



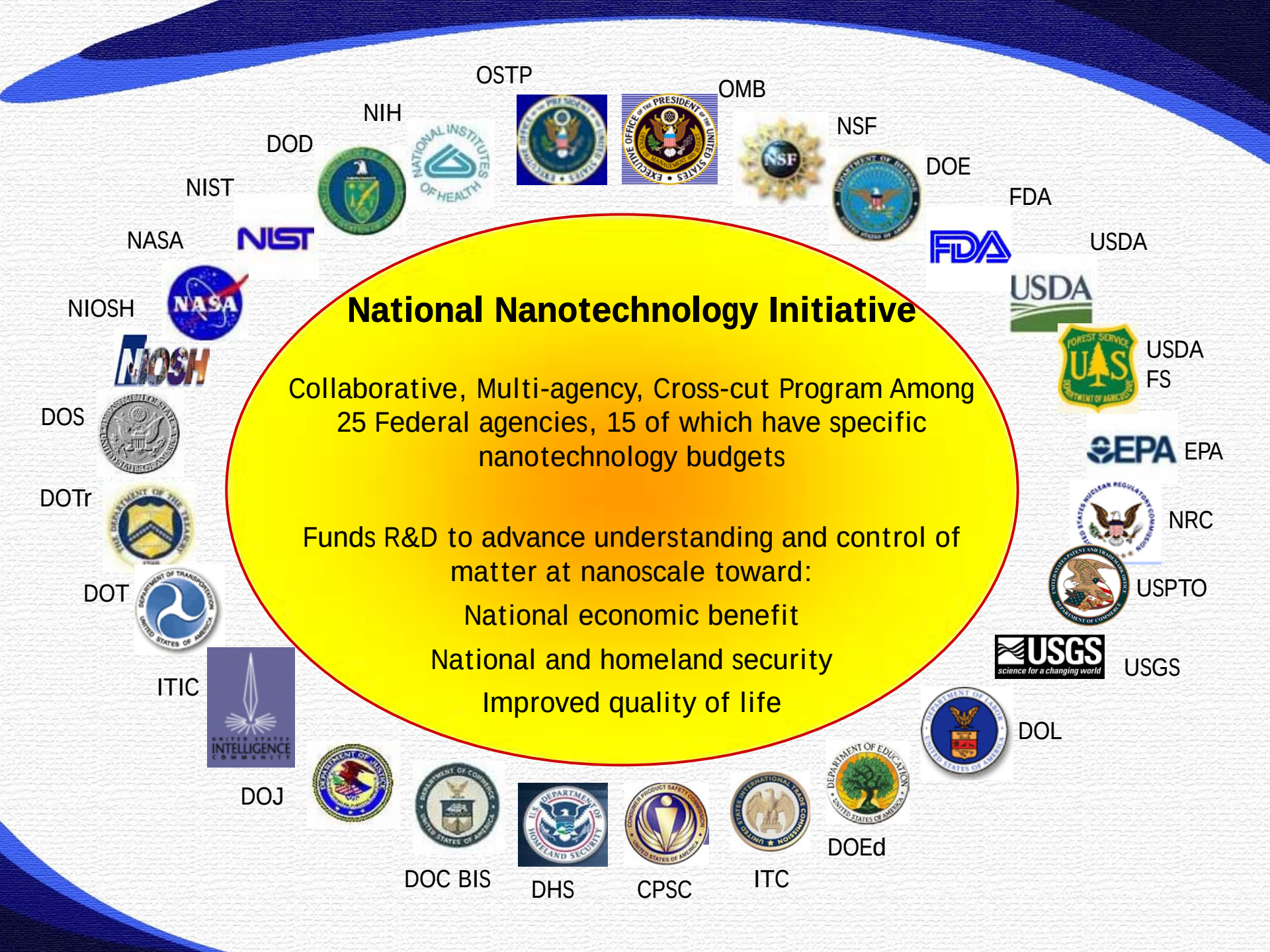


- Eric Drexler 1980s "Molecular Nanotechnology"
- Fullerenes 1985
- Carbon Nanotubes late 1980s
- Richard Jones 2004 "Biomimetic nanotechnology"
- Experimental Advancements
  - Scanning tunneling microscope (STM)
  - Atomic force microscope (AFM)
  - Nanoindentation
  - Nanolithography



Nanotechnology and Forest Products

- Apply nanotechnology to forest products
  - Coatings
  - Biocides
  - Modified resins
- Obtain nanomaterials from forest products
  - Cellulose nanofibrils
  - Lignin nanoparticles
  - Extractives


National Nanotechnology Initiative
Collaborative, Multi-agency, Cross-cut Program Among 25 Federal agencies, 15 of which have specific nanotechnology budgets
Funds R&D to advance understanding and control of matter at nanoscale toward:
National economic benefit
National and homeland security
Improved quality of life
OSTP
OMB
NIH
NSF
DOD
DOE
NIST
FDA
NASA
USDA
NIOSH
USDA FS
DOS
EPA
DOTr
NRC
USPTO
DOT
USGS
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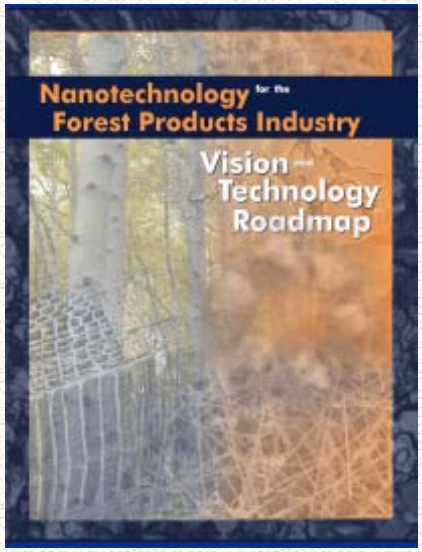
DOC BIS
DHS
CPSC
ITC

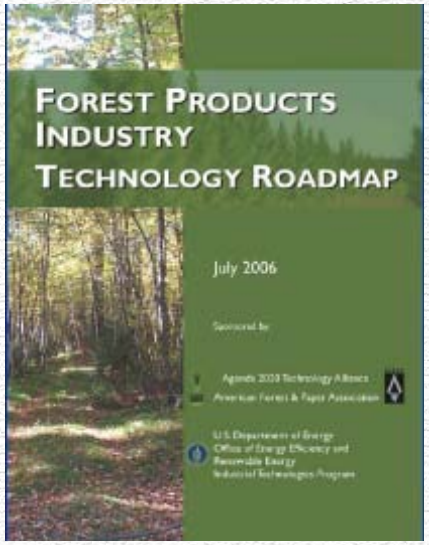
U.S. Forest Products Nanotechnology Research Roadmaps - Needs

2005



www.nanotechforest.org

2006



www.agenda2020.org

2010

NSTC Committee on Technology
Subcommittee on Nanoscale Science, Engineering, and Technology

National Nanotechnology Initiative Signature Initiative:

Sustainable Nanomanufacturing – Creating the Industries of the Future

Final Draft, July 2010

Collaborating Agencies[1]: *NIST, NSF, DOE, EPA, IC, NIH, NIOSH/OSHA, USDA, Forest Service*

National Need Addressed

This interagency initiative will establish manufacturing technologies for economical and sustainable integration of nanoscale building blocks into complex, large-scale systems.

A decade of research under the National Nanotechnology Initiative has led to remarkable discoveries of nanoscale materials with unique properties, laboratory demonstrations of a range of innovative nanoscale devices, and introduction of a limited number of nanotechnology-based products into the marketplace. For this investment to become the basis for high-value industries, methods must be established to efficiently assemble products that integrate together billions of nanoscale devices with disparate functions. Current manufacturing methods such as those used in the semiconductor industry will not be economical at these scales; radically new approaches are needed. Moreover, for such products to be ubiquitous in the nation's future economy without causing long-term negative environmental or health impacts, these new approaches and the resulting products must be inherently sustainable by design.

A long-term vision for nanomanufacturing is to create flexible, "bottom-up" or "top-down/bottom-up" continuous assembly methods that can be used to construct elaborate systems of complex nanodevices. Moreover, these systems by design will reduce the overall environmental and health impacts over their full life cycle; for example, by minimizing any release of harmful nanomaterials or substances, and reducing energy consumption. To create the foundation for achieving this vision, over the next decade this initiative will first establish sustainable industrial-scale manufacturing of functional systems with relatively limited complexity based on manufactured nanoparticles with designed properties. The organized assemblies of nanoparticles manufactured here will be designed to control and manipulate information, thermal energy, and electromagnetic radiation. The systems to be manufactured will include disruptive technologies for high-speed communication and computation, solar energy harvesting, waste heat management and recovery, and energy storage. The methods developed will be immediately extendable to more complex components and systems as future nanodevices mature.

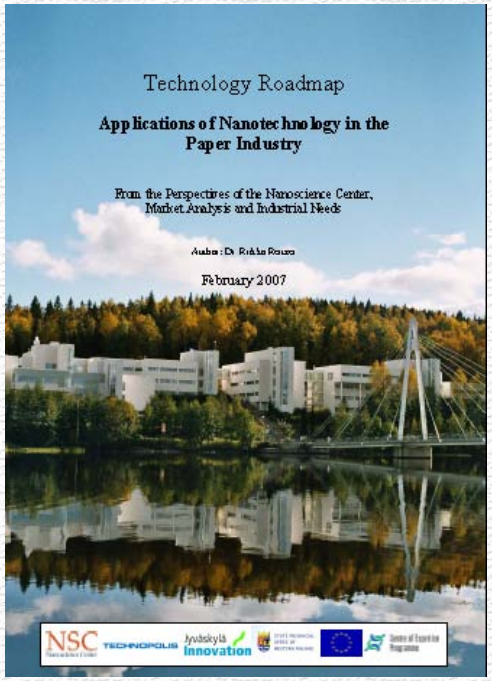
[1] Please note that "collaborating agencies" is meant in the broadest sense and does not necessarily imply that agencies provide additional funds or incur obligation to do so. Agencies leading this effort and responsible for carrying out key aspects of these initiatives are underlined.

http://www.nano.gov/html/research/NNISigInitSustainableMfrFINALJuly2010.pdf

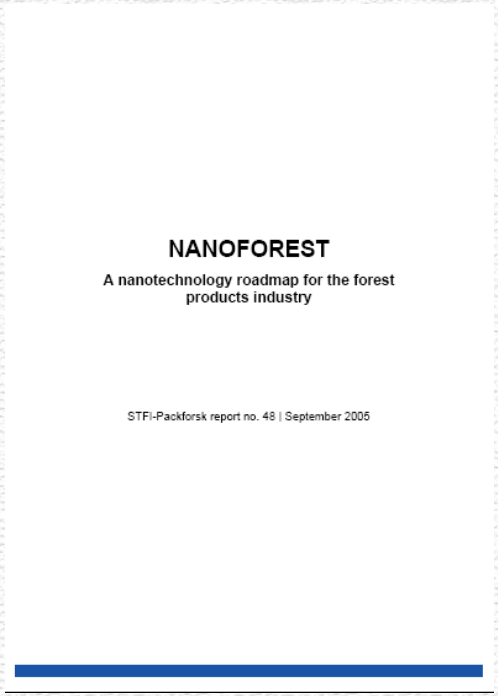
International Forest Products Nanotechnology

- FP Innovations Canada
  - Nanotech. Applications in the forest sector (McCrank 2009)
- Nanoforest – Innventia, Europe
- Japan
- New Zealand
- Etc.

2007

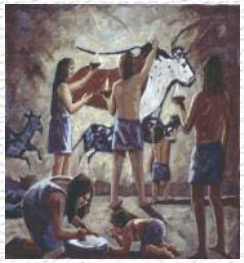


2005

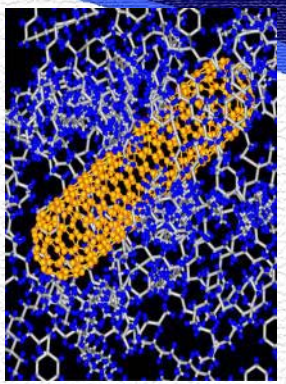


Nanotechnology for the Forest Products Industry R&D Focus Areas

- Polymer Composites and Nanoreinforced Materials
- Self-Assembly and Biomimetics
- Cell Wall Nanostructure
- Nanotechnology on Sensors, Processing and Process Control
- Analytical Methods for Nanostructure Characterization



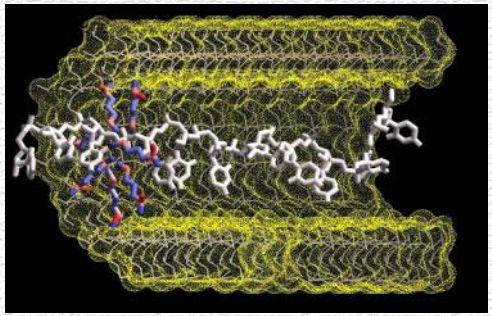




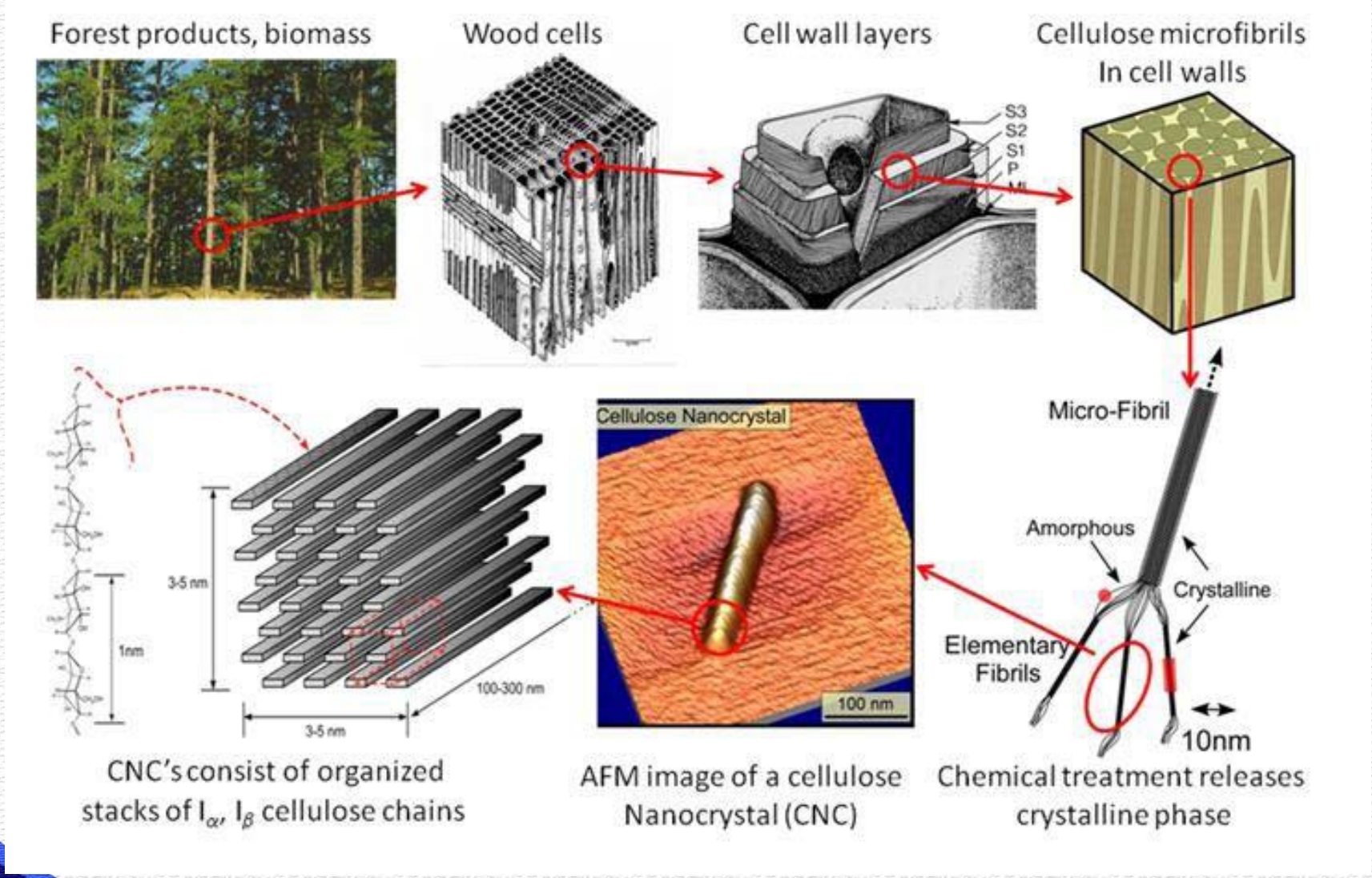
Stone Age ……. Bronze Age ……. Iron Age ……..... Nano Age?

- Nanotech is 3rd Industrial Revolution
- Renewable Forest-based Materials: Maine's Niche to Compete in Nanotech

"From the Sawmill to the Nanomill?"



Size Scale of Lignocellulosics



FRP Laminate

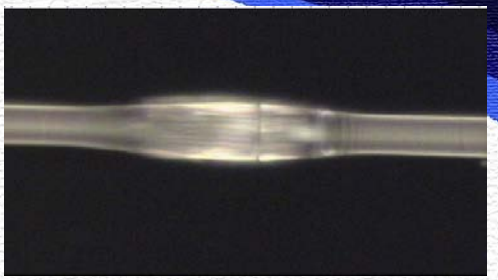
1 meter

Glulam-FRP

10 centimeters

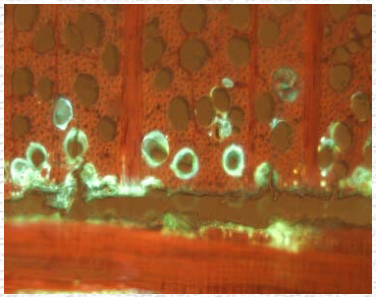
Shear specimen

1 centimeter



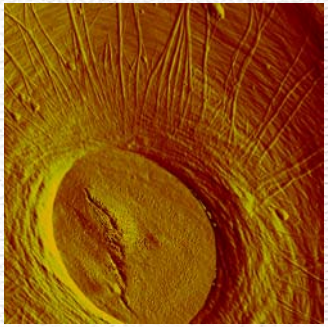
Microdroplet on

Fiber, 1 millimeter



Bond line micrograph

100 microns



Bordered Pit

10 microns

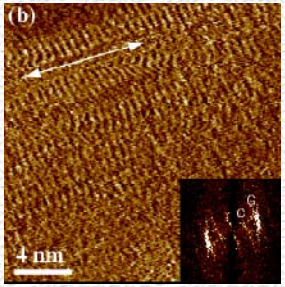
UF Resin on

loblolly fiber

(2 micron scan)

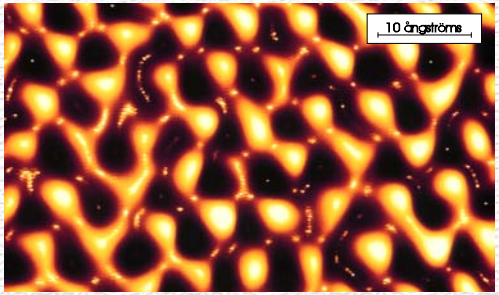
Cellulose nanocrystals

200 nm long, 10 nm wide



Valonia

10 nanometers

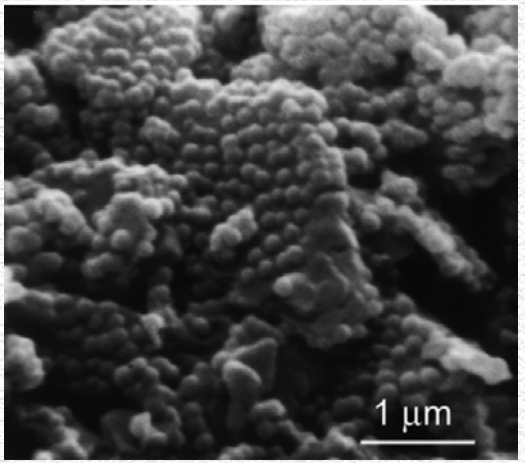


1 nanometer

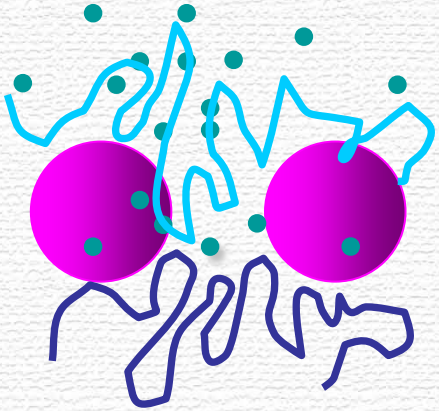
Wood-Orders of Scale (Powers of 10)

Past Applications in Forest Products

- Colloids in Paper Manufacture
  - Fines retention
  - Filler retention
  - Modifying zeta potential
  - Rosin Sizing (100 to 1000 nm particle size
- Going back more than 50 years
- "Nano" Terminology becomes important



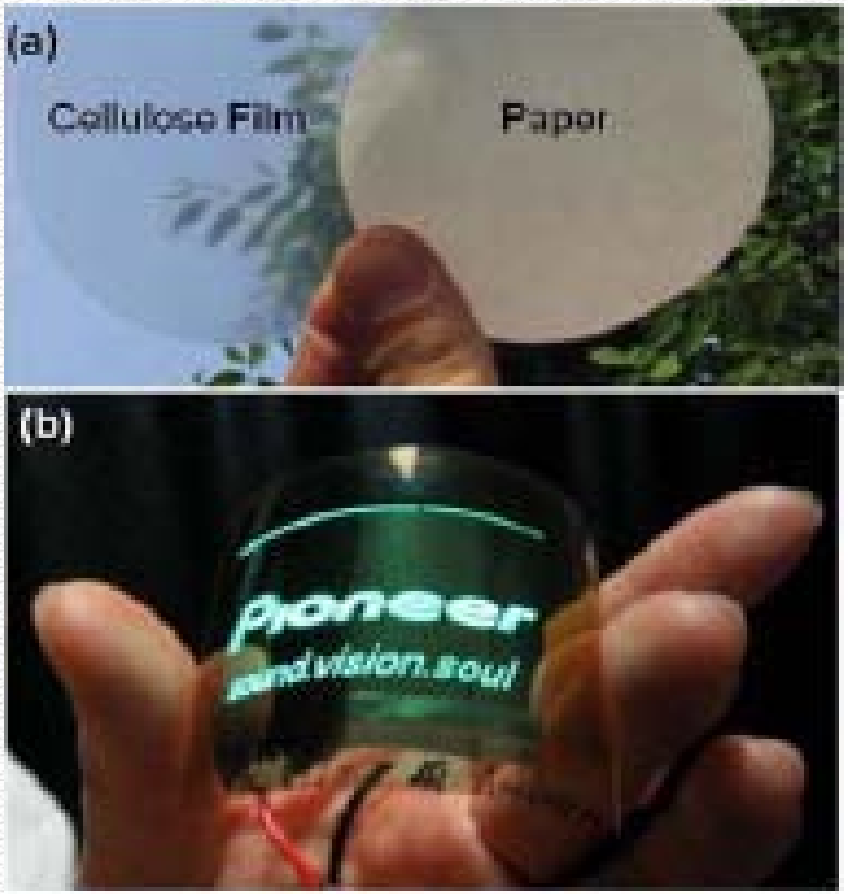
Clay coated by cationic polystyrene Latex (130 nm diameter
Source: van de Ven 2009



Nanosilicate sol as flocculants

Current Applications in Forest Products

- High Profile Nanotechnology applications in forest products
  - Optically transparent nanofiber paper
  - Optically transparent cellulose nanocomposite for flexible LED display



Yano research group (Japan 2009)

Wood Protection Applications

(Clausen 2007)

- **Nanobiocides**
  - Preservative penetration in commerical lumber species
  - Treatability of refractory species
  - Durability of engineered composites
  - Non-leachable treatments
- **Nanocarrier delivery systems**
  - Delivery and placement of biocides
  - Slow release of biocide
  - Release under specific environmental conditions
  - Protection of heat labile biocides during treatment of composite fabrication

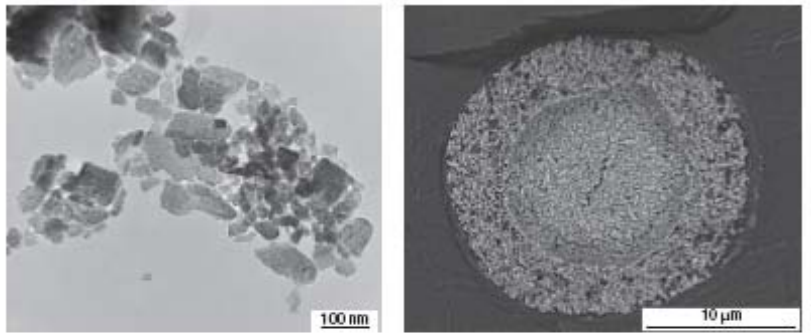


Figure 1 Copper carbonate micro- and nanoparticles in a commercially produced wood preservative (left) and accumulation of larger particles on a membrane within an opening (bordered pit) that connects fibres in treated southern pine wood (right).

Evans et al. 2008

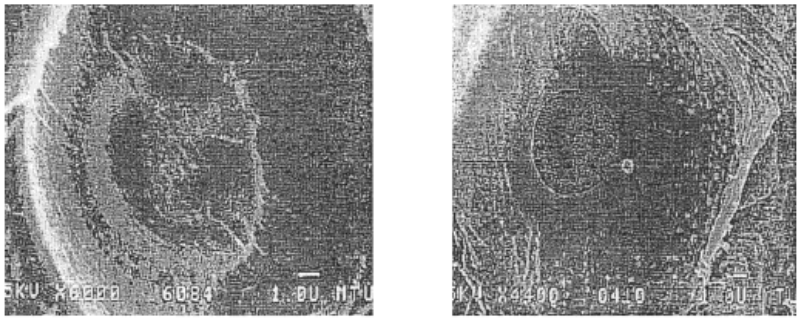


Figure 1 SEM micrograph of (a) untreated sample of southern pine, and (b) southern pine treated with tebuconazole in a PVPy matrix.

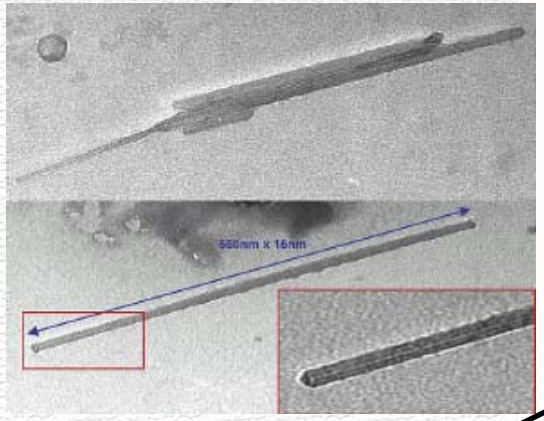
Laks and Heiden, 2001

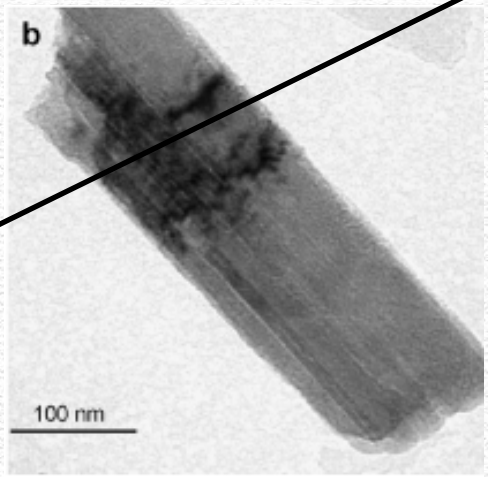
Wood Coating Applications

- Improve
  - Scratch resistance
  - Abrasion resistance
  - Gloss/matting
  - UV blocking without loss of clarity
  - Hydrophobicity
  - Oleophobicity
  - Dust free surfaces?

Carbon nanostructures formed from the wood cell wall

- Formation of unique carbon nanostructures via carbonization of wood.
- Does this provide an explanation for the quality of Damascus steel?

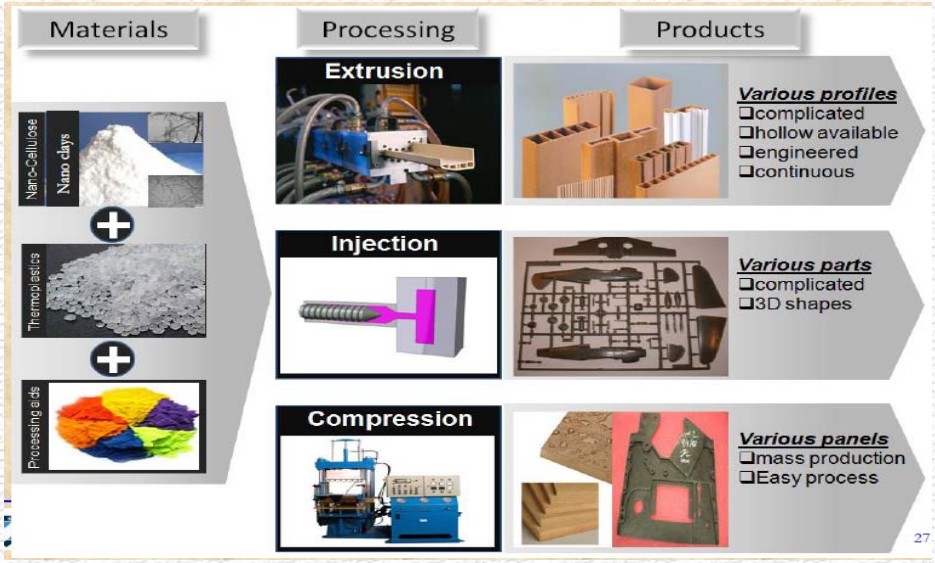


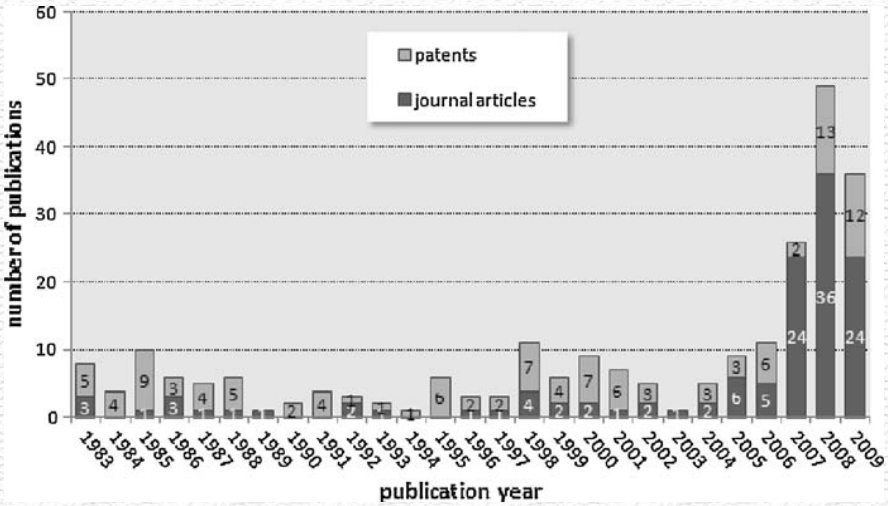


Xie et al. 2009 Int. Biodet. & Biodeg.

Cellulose Nanomaterials

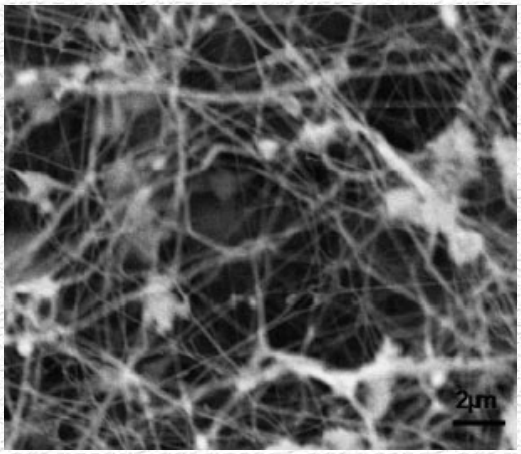
- Significant research activity in cellulose nanomaterials
- In 2010-2011, 6 comprehensive reviews
  - Cellulose
  - Journal of Materials
  - Polymers
  - Chemical Reviews
  - Chem. Soc. Rev.
  - Angewandte Chemie
- Cellulose nanomaterials NNI Signature Research Initiative (Jul 2010)



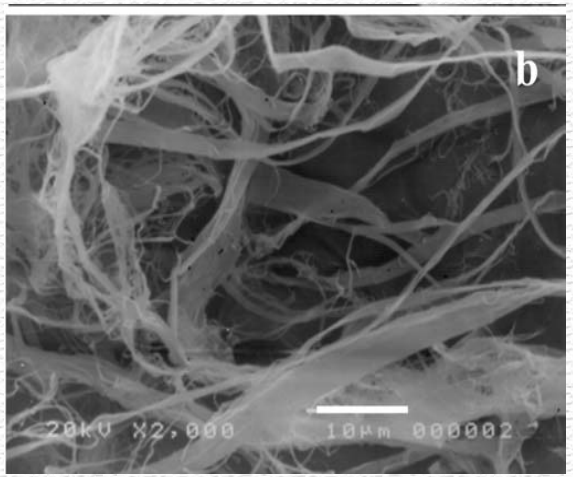


Siro and Plackett, Cellulose **17**, 459 (2010)

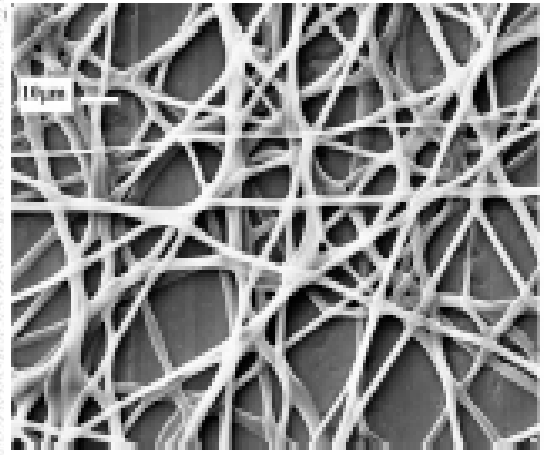
Types of Cellulose Nanofibrils (CNF)



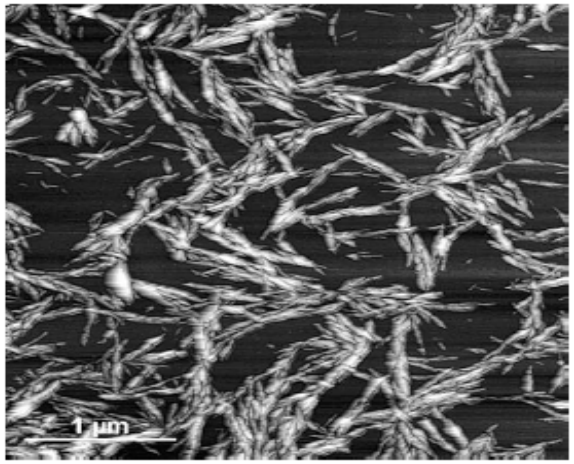
Bacterial cellulose nanofibers 5000X



Nanofibrillated cellulose



Electrospun cellulose nanofibers

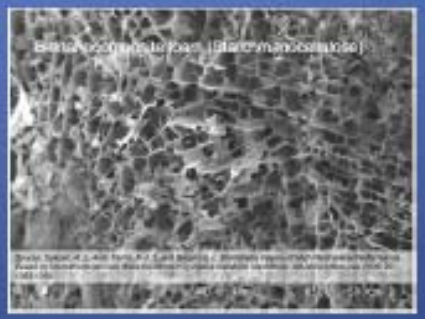


Cellulose nanocrystals (whiskers)

Applications of Cellulose nanofibrils

- Opportunities for renewable nanomaterials from wood

- Batteries
- Super-Capacitors
- Bio Plastics
- Nano Coatings
- Reinforced Polymers
- Smart Sensors
- High Efficiency Filters
- Light Weight Nano Composites
- Nano Membranes
- Photonic Devices



Can be produced in tens of millions of ton quantities

Brief history of cellulose nanofibrils

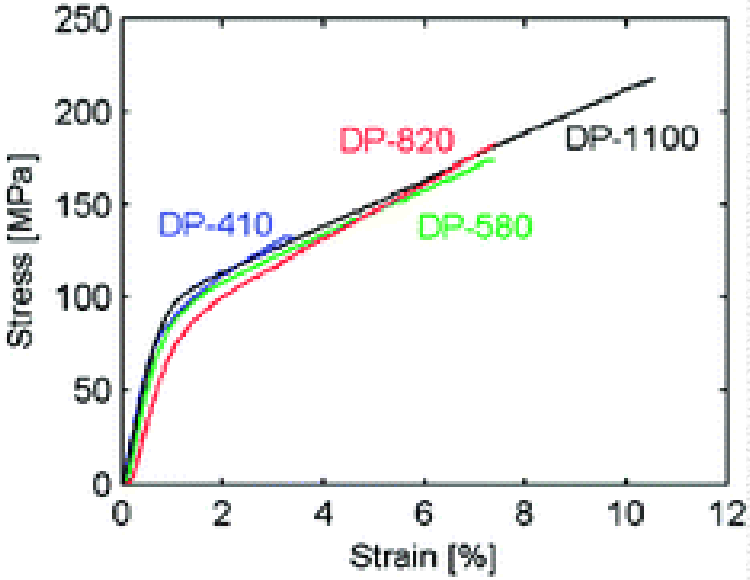
- Rånby 1951 colloidal properties of cellulose micelles
- Turbak 1983 microfibrillated cellulose
- Revol et al. 1992 self-ordering of cellulose microfibrils
- Daicel, JRS, EFTech mid to late 2000s
- Scale up in Sweden
  - Innventia 2010
- Scale up in Canada
  - 2010 Domtar $32M facility 1-tonne per day
  - 2011 Bio Vision Technology pilot plant
- Scale up in U.S.
  - FPL 2012 CNC and TEMPO
  - UMaine 2012 NFC
- Are we there yet?

Close to Commercial Applications?

1. the fruit that grows low on a tree and is therefore easy to reach
2. a course of action that can be undertaken quickly and easily as part of a wider range of changes or solutions to a problem: *first pick the low-hanging fruit*
3. a suitable product to exploit as a straightforward investment opportunity

Disclaimer: *The thoughts expressed are based on the author's world view.*

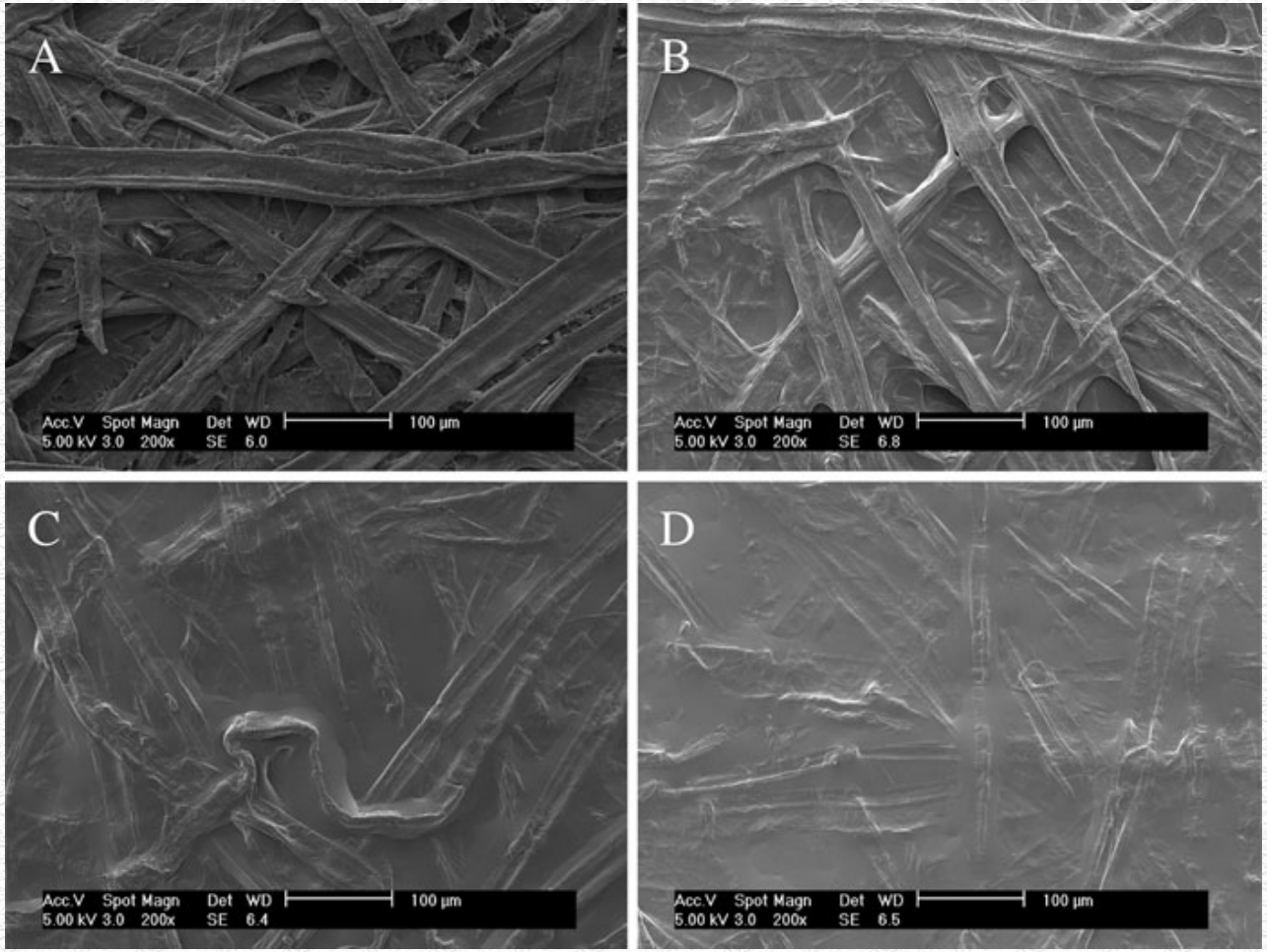
Cellulose Nanopaper



- High strength (4 times Kraft, 8 times newsprint)
- High Toughness exceeding plant fibers
- Large strain to failures

Henrikson et al. 2008 Biomacromolecules 9(6)1579-1585.

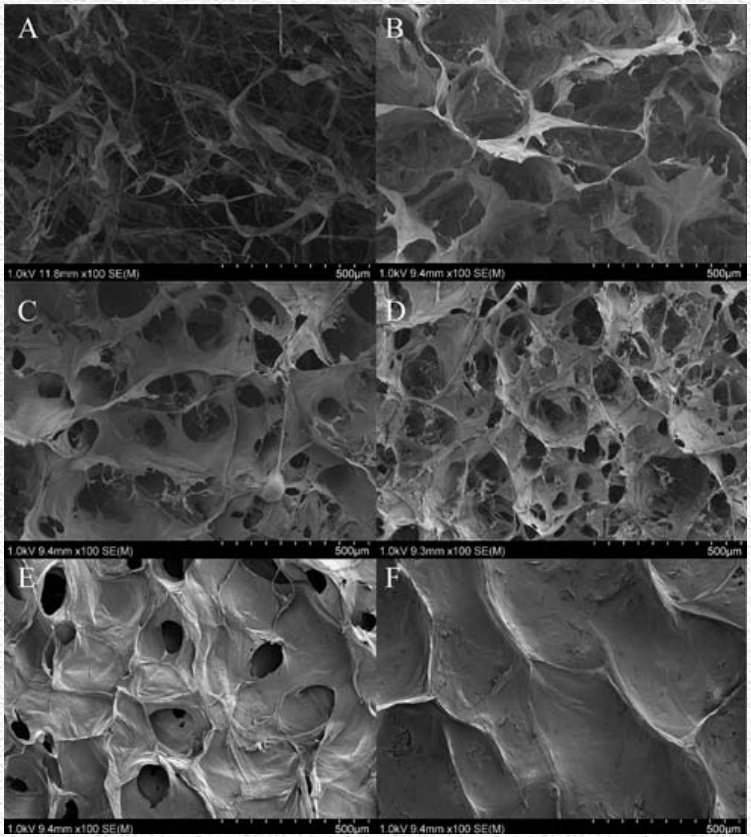
Paper or Board Coatings



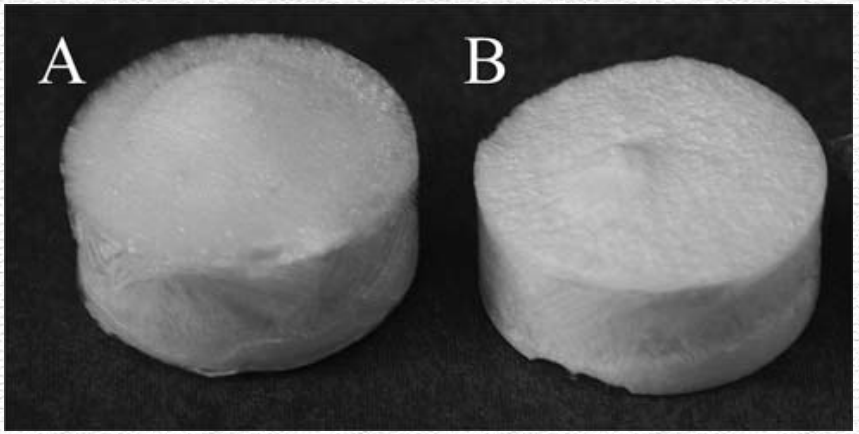
E-SEM micrographs of uncoated and NFC-coated papers Aulin et al. 2010 Cellulose 17,559-574

NFC Aerogels/Foams

Low mag. SEM micrographs



Freeze-dried NFC aerogels



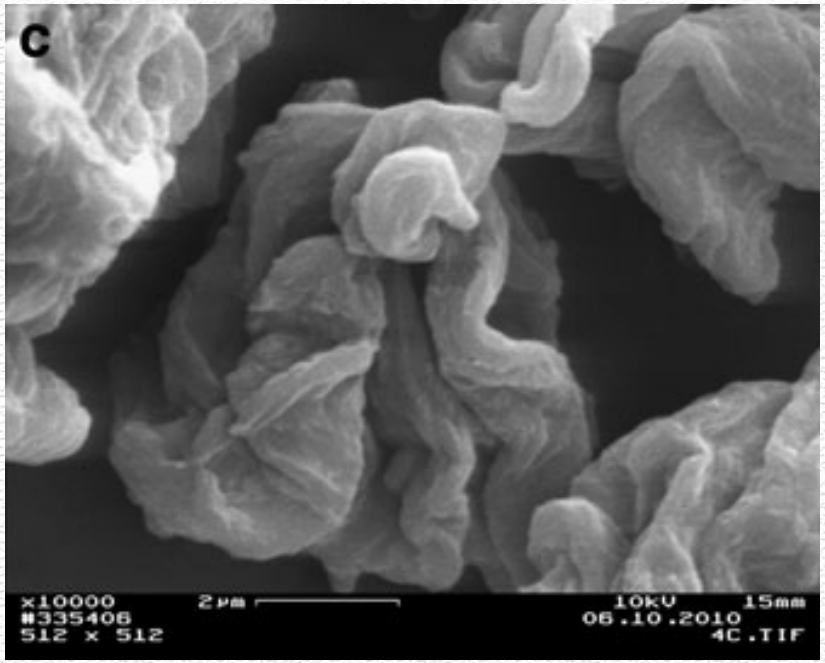
Aulin et al. Soft Matter 2010 6:3298-3305

Bacterial Cellulose Applications

- Long established food in Southeast Asia – Nata De Coco
- Clothing –Suzanne Lee, TED seminar
- Artificial veins

Spray Dried Cellulose Nanofibrils as Novel Tablet Excipient

- CNF particles less prone to permanent deformation and less ductility
- Slightly faster drug release from CNF compared to MCC
- Assuming NFC?



Kolakovic et al. 2011 AAPS PharmaSciTech 12(4):1366-1373

“Nanodiapers”

- Current disposable diapers are a composite of air-laid paper and superabsorbent polymers (hydrogels)
- Could CNF hydrogels replace “petroleum-based” acrylate hydrogels?

Country	Billion Units/Yr. Potential	Billion Units/Yr. Current
United States	22.4	21.3
China	75.7	12.1
Brazil	15.7	7.7
Mexico	10.4	6.8
Japan	5.8	5.7

Richter 2012 Nonwovens Industry

CNF Commercialization Barriers

- Only modest investment in scale up processes - development of production technology – from lab scale to pilot scale and further to mill scale
- Lack of product line growth due to “no supply” of large quantity samples
- Difficulty in cost estimation due to lack of scale up data and overly concerned for a potential initial high price
- Lack of coordinated approach between research institutes (university and research organizations) and potential customers
- Lots of uncertainties and risks (safety issues/regulations).

Mohini Sain, OECD Nanocellulose Workshop, 2009
Timo M. Koskinen, TAPPI Nanotechnology Conference, 2010

Cellulose Nanomaterial Standards

- **Standardize "Nano-cellulose" terminology**
- TAPPI and ISO Technical Committee (TC) 229
- "Nanocellulose" task group established in June 2011
- Proposed TAPPI Standard
- ***Standard Terms and Their Definition for Cellulose Nanomaterial WI 3021***

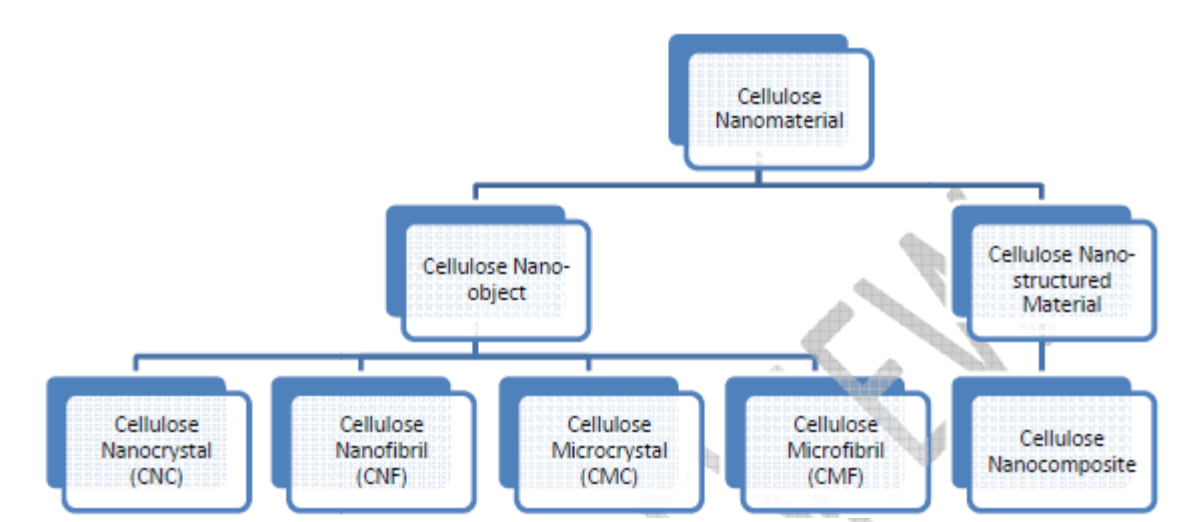


Figure 1. Standard terms for cellulose nanomateri

Future Needs of Nanotechnology in Forest Products

- Ability to have scalable nano-manufacturing
  - Adapt conventional manufacturing processes
  - Develop novel processing equipment
- "Papermaking is self assembly of wood cells at 60 mph (100 kph)"
- Novel composite manufacturing processes for ballistics, automobiles, coatings, adhesives, biomedical applications, drug delivery

Concerns, Challenges and Opportunities of Nanotechnology in Forest Products

- Consumer perception issues
  - Sustainability
  - Risks and unknowns
- Regulation issues
  - Health and Safety (Is cellulose non toxic? What about *Brown Lung*?)
  - "regulating nanotechnology will be a process not an event"
- Market opportunities
  - Improve existing products
    - Do you have nano?
    - Nano diapers?
  - Intelligent packaging

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