Cellulose Nanomaterials
– Technical State of Art –

Industry
Sean Ireland, Phil Jones

Academia
Robert J Moon

Government
Robert J Moon, Ted Wegner, World Neih

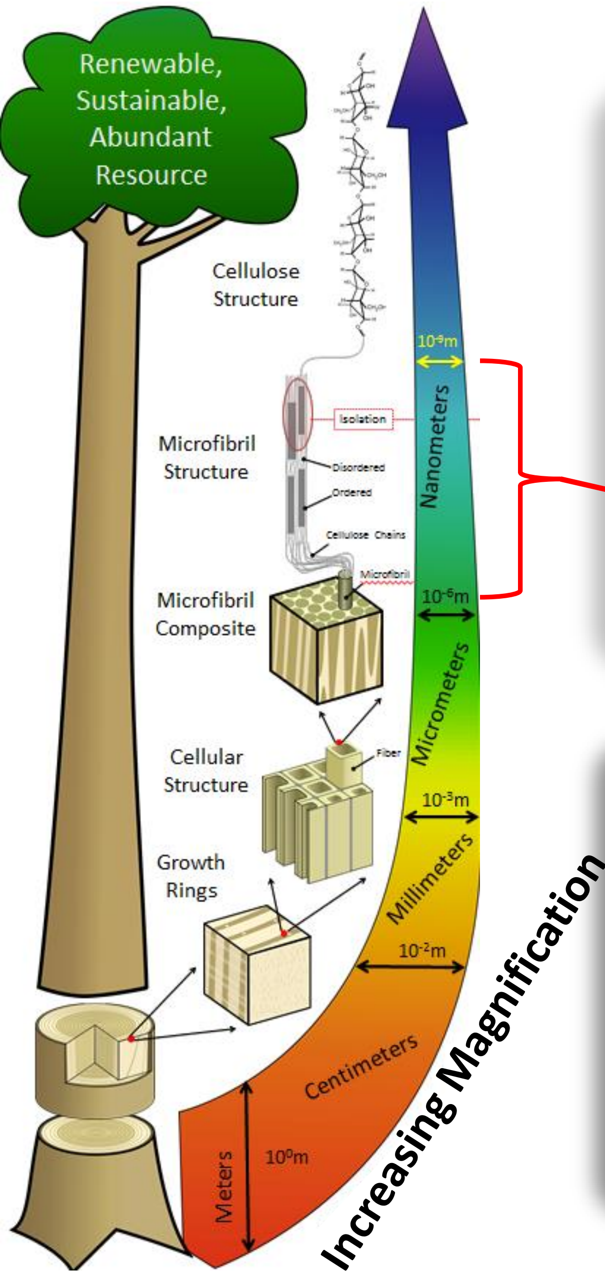
NNI and USDA-Forest Service Workshop on
Cellulose Nanomaterials – A Path Towards Commercialization
Washington DC, 20-21 May, 2014

200nm

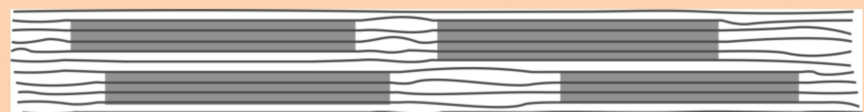
Outline of Talk

- What are Cellulose Nanomaterials
- Why Cellulose Nanomaterials
- Nano vs Bulk Properties
- Current State of the Art
- Moving Forward: Gaps/Needs

What are Cellulose Nanomaterials (CNs)



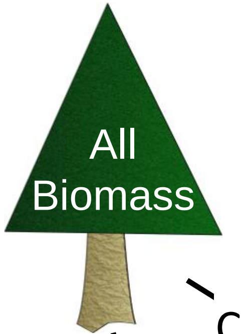
- Nano-sized particles isolated from:
  - trees, plants, algae
- Highly ordered cellulose chains:
  - fibril structure
  - crystalline domains



Strong Foundation in Biomass Industry

- Abundance of biomass (trees, plants, algae)
- Harvesting infrastructure in place
- Engineered products
  - New Properties
  - Billion $$ industries

Many “Flavors” of CNs

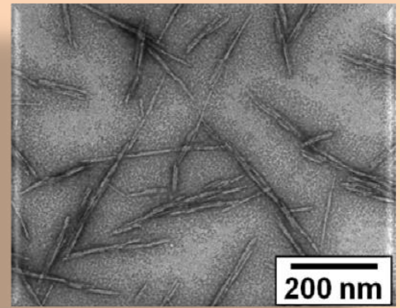


Acid Hydrolysis

Chem/Mech

Mechanical

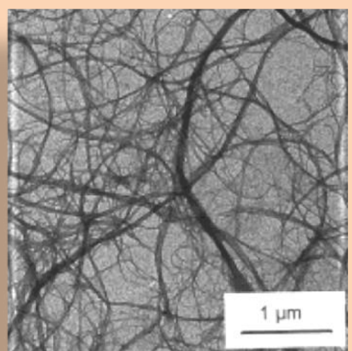
Cellulose Nanocrystals (CNC)



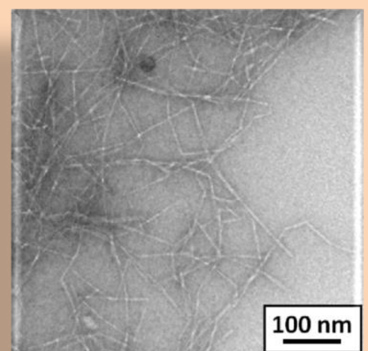
Rod-like

Particles:
- Source
- Method

Cellulose Nanofibrils (CNF)



Dufresne et al., J. App. Poly. Sci., 1997



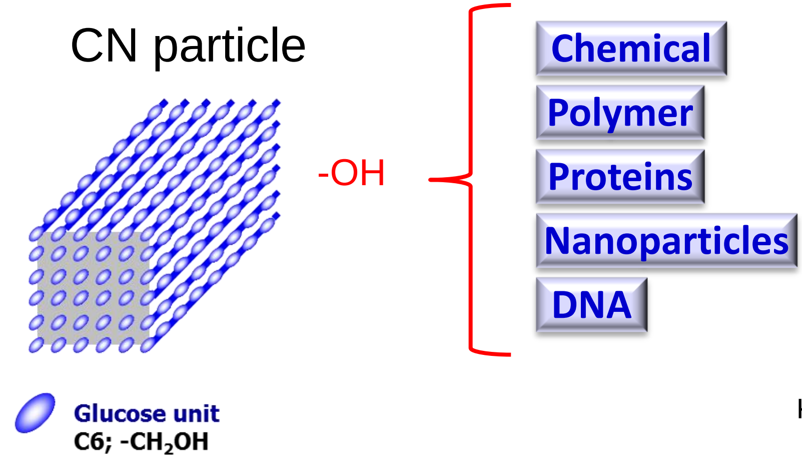
Fibril-like:

Properties:
- Length
- Aspect Ratio
- Branching
- Crystallinity

Many “Sprinkles” of Surface Modification

New Functionality

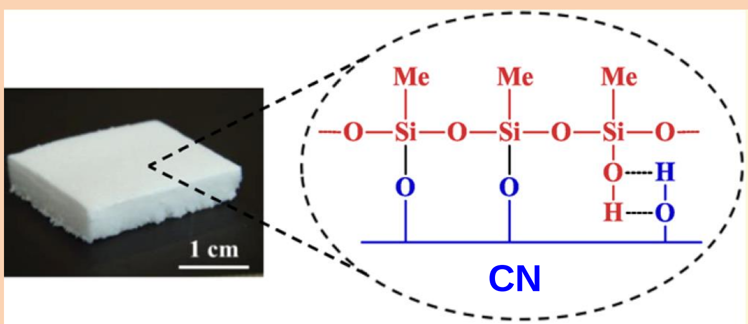
- Reactive Surface: -OH
- Simple Chemistry
- Alter Properties:
  - Interfaces: CN-CN, CN-Matrix
  - Self Assembly
  - Function: e⁻, antimicrobial,



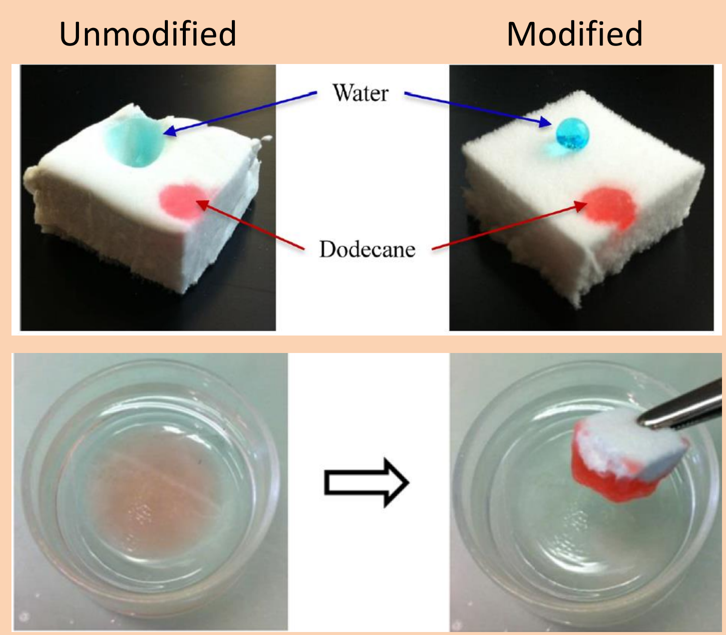
Koga et al.

CN Sponges: Remove Oil from Water

- New chemistry alters behavior



Zhang, Zheng, et al. "Ultralightweight and Flexible Silylated Nanocellulose Sponges for the Selective Removal of Oil from Water." *Chemistry of Materials* (2014).



Why Cellulose Nanomaterials?

What can CNs do that no other nanoparticle can do?

- Light/Stiff/Strong
- Optical
- Surface Chemistry

It is not one specific property that sets Nanocellulose apart from the rest, rather the unique combination of relevant characteristics that gives these materials utility

- High Production Potential
- Low Cost Potential
- US Source → Local Jobs

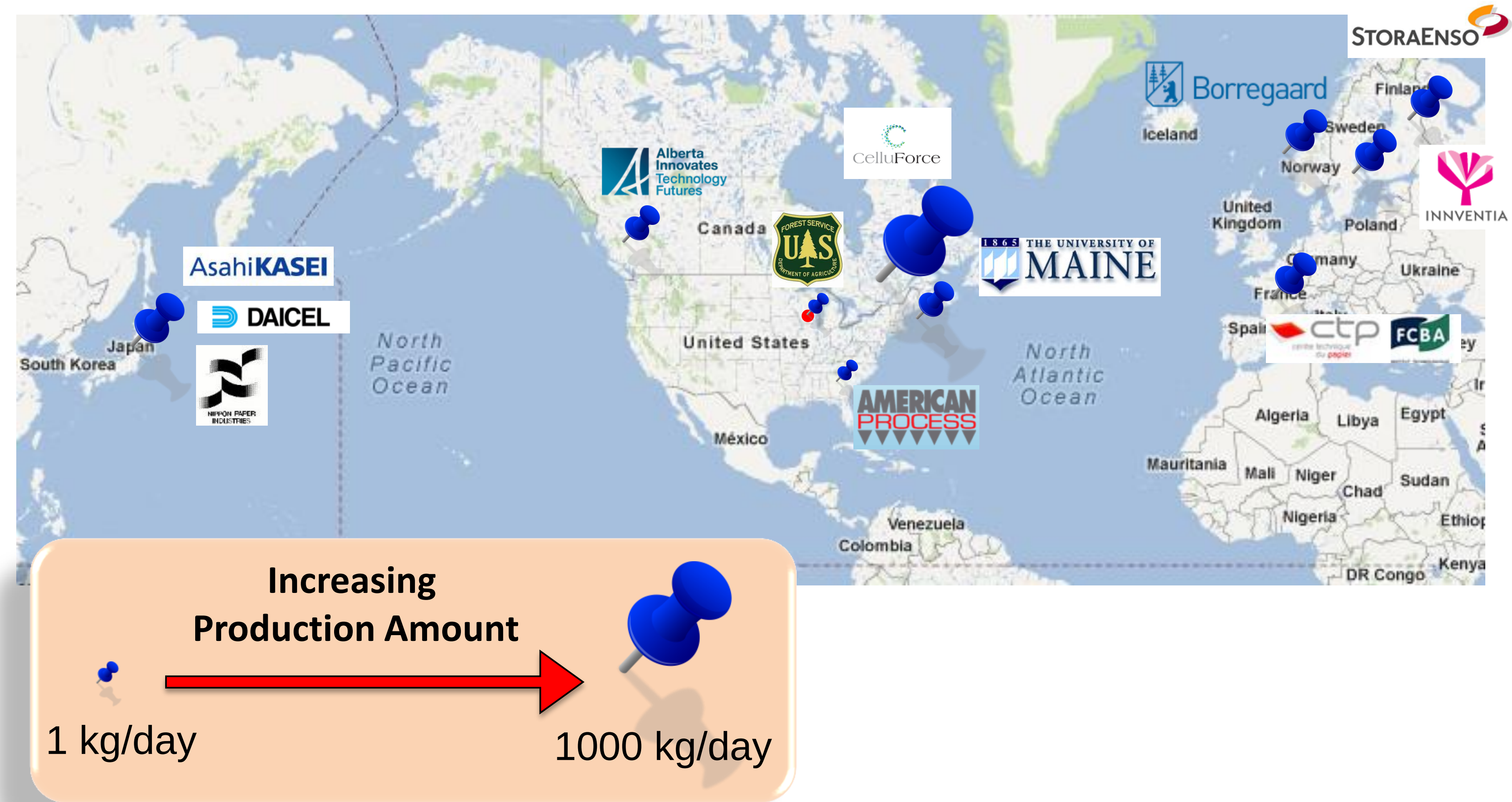
Societal Needs

Profit

- Few EHS Concerns
- Renewable
- Sustainable
- Biodegradable

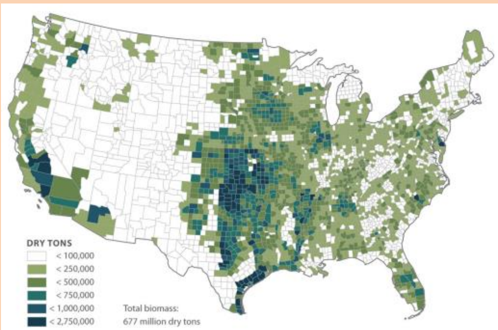

Part of a IBM computer at a Chinese e-waste scrap yard.

World Production of Nanocellulose



$$ Billions of Infrastructure in Place

Sustainable Biomass Management



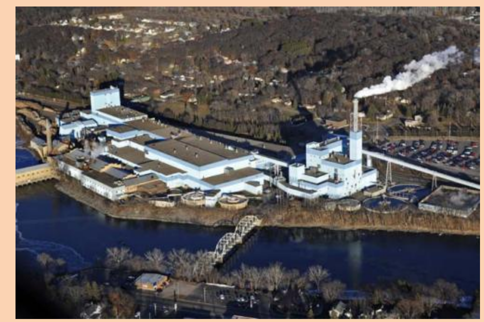
- Forestry
- Agriculture
- Biomass for Fuel

Harvesting

Distribution

Refining: Trees to Particles

- Pulp fiber
- Water, Energy
- Waste Streams



Key infrastructure is in place for LARGE scale production of cellulose nanomaterials

Environmental Protections in Place

Disposal/Recycle

Opportunity for Mass Production

Material		Production US	Production World	Cost
Pulp Demand		60 M ton/yr	175M ton/yr	~$0.75-1.0 / kg
Wood Demand		~187 M ton/yr	????	
Wood capacity		~405 M ton/yr	????	
CNF current capacity		7.5 ton/yr (est)	50 ton/yr (est)	$4-40 /kg
CNC current capacity		1.25 ton/yr (est)	30 ton/yr (est)	$2-15 /kg
Other Nanomaterials				
CNT (multiwalled) 2011		?	2000 ton/yr	~$100/kg

In Addition…

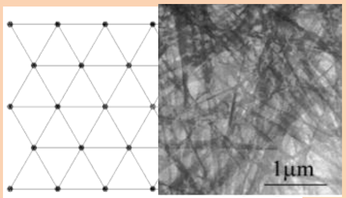
***2Billion tons** of*

Beetle killed wood looking for a use

- M.F.L. De Volder et al., Carbon Nanotubes: Present and Future Commercial Applications, Science 339, 535 (2013).
- P-C Ma et al., Dispersion and Functionalization of carbon nanotubes for polymer-based nanocomposites: A Review, Composites: Part A 41: 1345-1367 (2010)

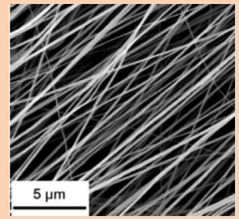
Industrially Relevant Structures from Cellulose Nanomaterials

Self-Assembly



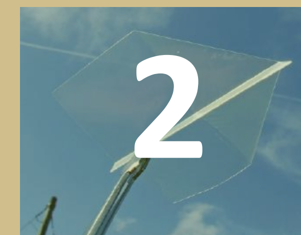
Noichiki et al., J. Appl. Poly. Sci., 2002, 86, 3425-3429

Continuous Fibers



Dong et al., Carb. Poly., 2012, 87, 2488-2495

Films



Nogi et al., Adv. Mater, 2009

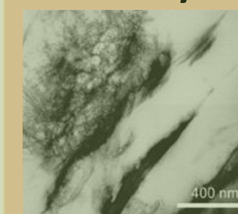
Foams/Aerogels

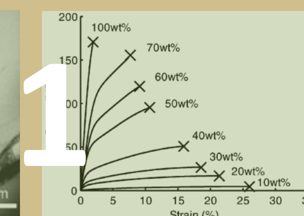
Paakko et al., Soft Matter, 2008, 4, 2492-2499

Hydrogels

Abe et al., Carb. Poly., 2011, 85, 733-737

Polymer Fillers



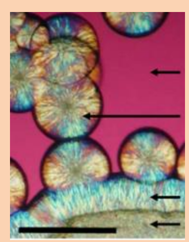


Bondeson et al., Comp. Inter., 2007, 14, 617-630
Svagan et al., Biomacromolecules,2007

Rheology Modifier

T Lindström/STFI

Nucleation Agent



Gray, Cellulose, 2008, 15, 297-301

Reaction Pathway

cement

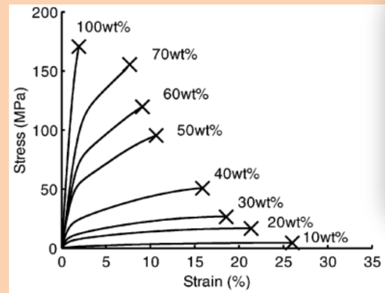
Cao et al.

Example I: Expand Materials Applications

Augment Properties of Existing Polymer Platforms

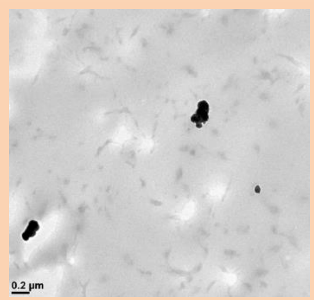
Cellulose Nanomaterials:
- behaves predictably
- like other nanomaterials
- combination of properties

- Mechanical Properties
  - Strength
  - Stiffness
  - Elongation



Svagan et al., Biomacromolecules,2007

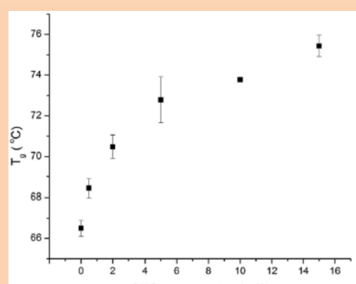
- Barrier Properties
  - Oxygen, water
  - Chemicals

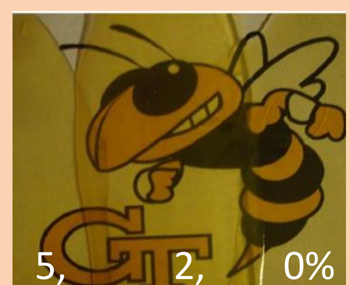


Samples	OTR * *e* (cm^3 * mm * m^{-2} * day^{-1})	Reduction in OTR (%)	Water vapour permeability * 10^{14} (kg m/s m^2 Pa)	Reduction in WVP (%)
PLA	30.5 ± 1.0		1.04 ± 0.18	
PLA/1Ag	23.9 ± 1.0	22	1.00 ± 0.03	4
PLA/1CNC/1Ag	16.5 ± 1.6	46	0.66 ± 0.10	46

Fortunati et al., J Food Eng,2013

- Thermal Properties
- Optical Properties
- Rheological Properties



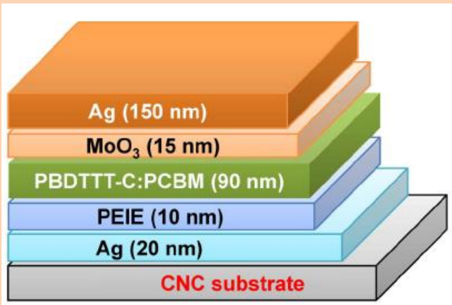


CNC-Epoxy: 5, 2, 0%

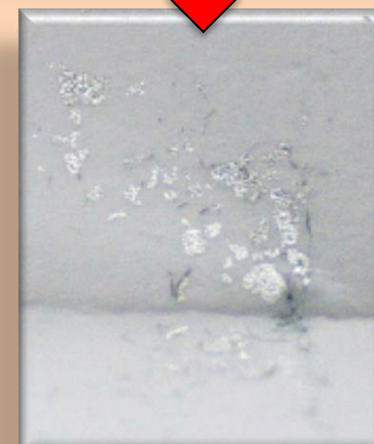
Fortunati et al., J Food Eng,2013

Example II: Enabling Technology

Solar Device: Reduce Environmental Footprint!!



Substrate material facilitates recovery of device components



Key Features:

- Smooth substrate
- Thermal properties
- Mechanical properties
- *Disintegrate in water*

Zhou, Y.H. et al. ,. Sci. Rep. 3, 1536; DOI:10.1038/srep01536 (2013).

Example III: Better Properties & Safer

CNC Additions to Cement

- 20-30% Increase in Flexural Strength
  - @ 0.2wt% CNC additions
- Modified Cement Reaction
  - Increased Degree of Hydration
  - Altered Microstructure

Win-Win: *More durable cement while maintaining Low Environmental Impact*

Gap for CN:

Cellulose Nanomaterials in Cement

CN additions to materials would likely ***not*** *increase the toxicity of the dust/debris produced from day-to-day: fabrication, machining, wear, damage, etc*

Nano to Bulk Reality

The Nano Potential

- Lighter/Stiffer/Stronger
- Near theoretical limits
- Full of potential

Realities of Manufacturing

The Bulk Reality

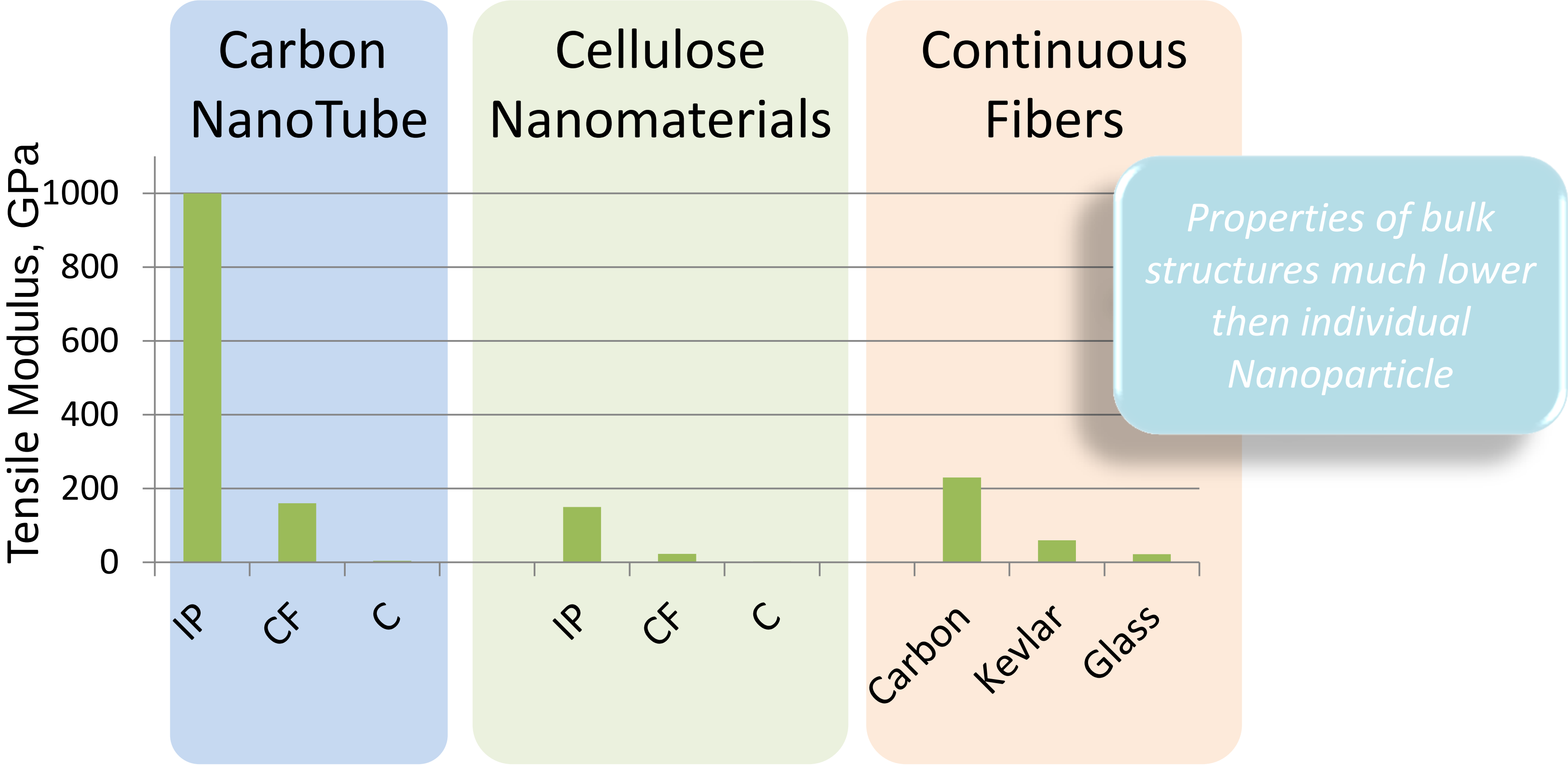
Hulk Hogan

The "Character" of bulk structures are much lower then that of individual Nanoparticle

- Improved performance
- Rough around the edges
  - Defects
  - poor dispersion
  - Interfaces
- Not reaching potential

Gap for CN:

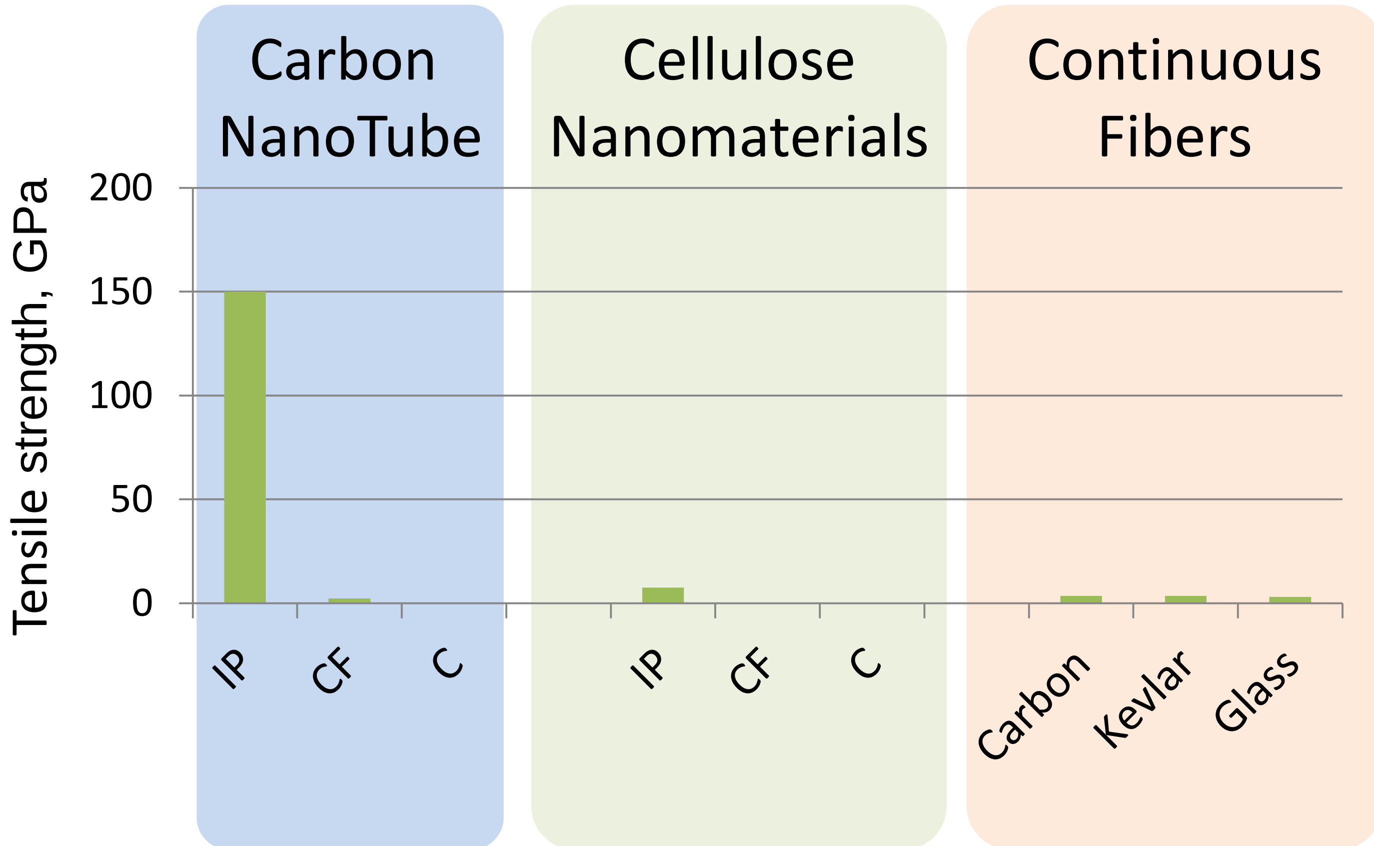
Example I: Nano > Bulk Properties



IP	Individual Particle
CF	Continuous Fiber
C	Composite -5% nanoparticles

- M.F.L. De Volder et al., Science 339, 535 (2013).
- P-C Ma et al., Composites: Part A 41: 1345-1367 (2010)
- International assessment of research and Development of carbon nanotube manufacturing And applications, World Technical Evaluation Center report , P Eklund, P Ajayan, R Blackmon, A.J. Hart, J Kong, B Pradhan, A Rao, A Rinzler. (2007)

Example II: Nano > Bulk Properties



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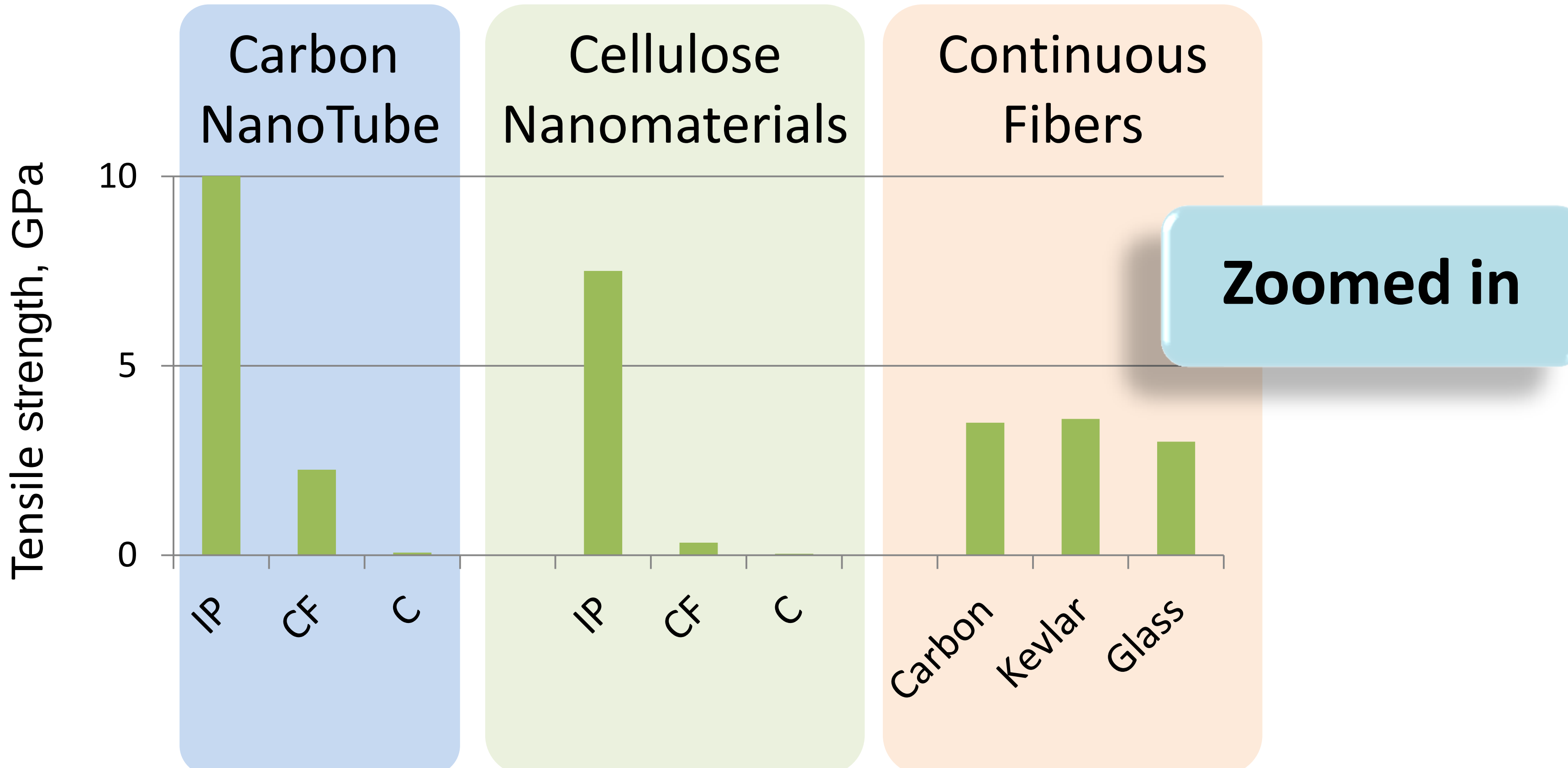
Example II: Nano > Bulk Properties



IP	Individual Particle
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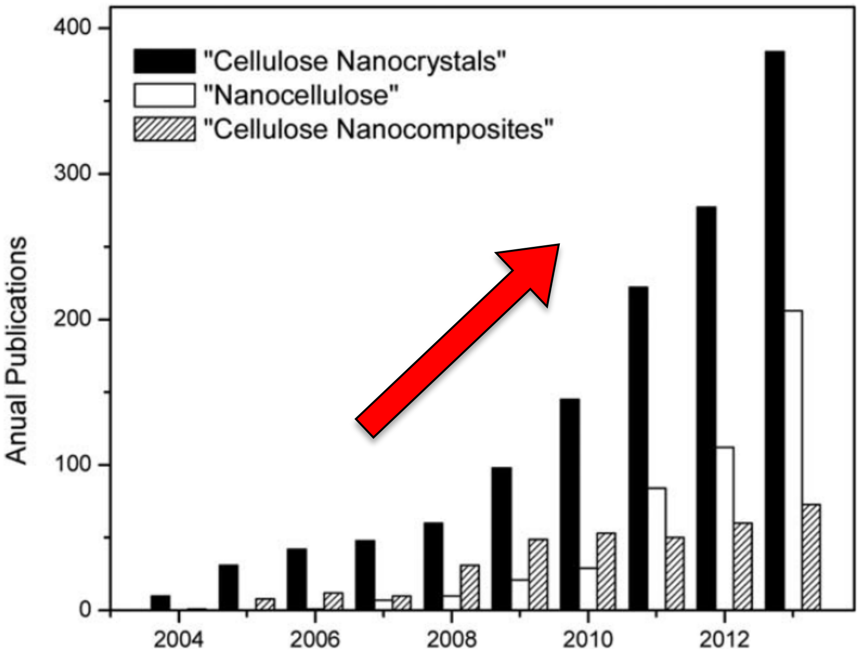
Current state of the art

Wide spread investment in Cellulose Nanomaterials, but…..
this effort is not focused nor coordinated towards commercialization



Mariano et al., J Poly Sci. poly physics,2014

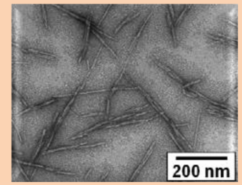
Academic/Fed Lab Research Areas

Production

- Sources
- Yields
- New methods
- Freeze drying
- …

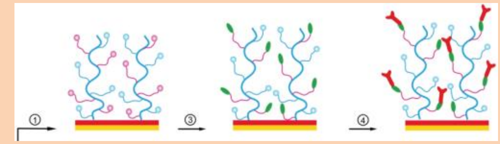
Characterization

- Particles & Comps
- Properties
- Distribution
- Interfaces



Functionalization

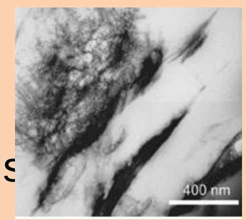
- Uniform coverage
- New Chemistries



Rojas et al.

Composites

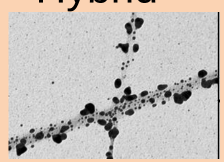
- Dispersion
- Interface
- Durability
- New systems
- Structures

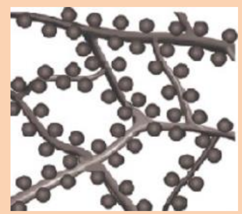


Bondeson et al., Comp. Inter., 2007, 14, 617-630

Template Structures

- Sacrificial
- Hybrid

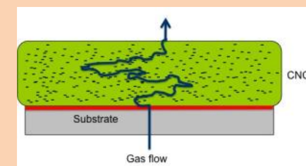




Padalkar et al.

Separators/Barrier

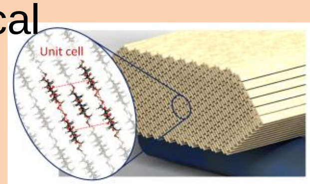
- Oxygen
- Moisture
- Chemical
- …



Herrera et al.

Predictive Modeling

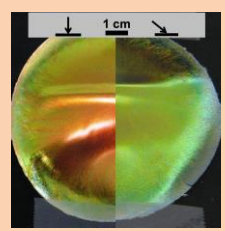
- Hierarchical
- Mechanical
- Thermal
- Interface
- …



Dri et al.

Optical

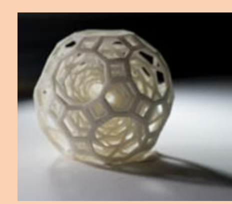
- Transparent
- Colors
- …



Beck et al.

Manufacturing

- 3-D Printing
- Roll-to-Roll
- Fibers
- Foams
- …



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Character

- Particles & C
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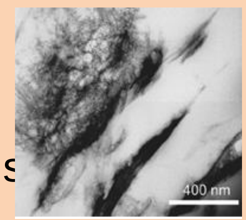
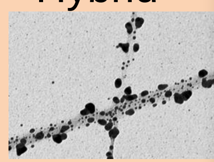


Bondeson et al., Comp. Inter., 2007, 14, 617-630

Template S

- Sacrificial
- Hybrid



Predictive Modeling

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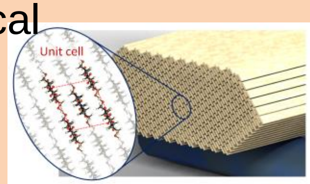

Dri et al.

Opti

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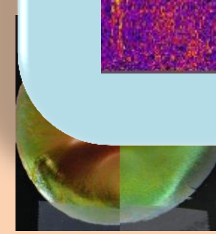
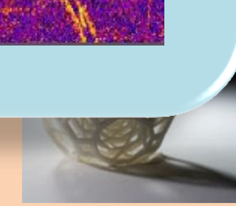
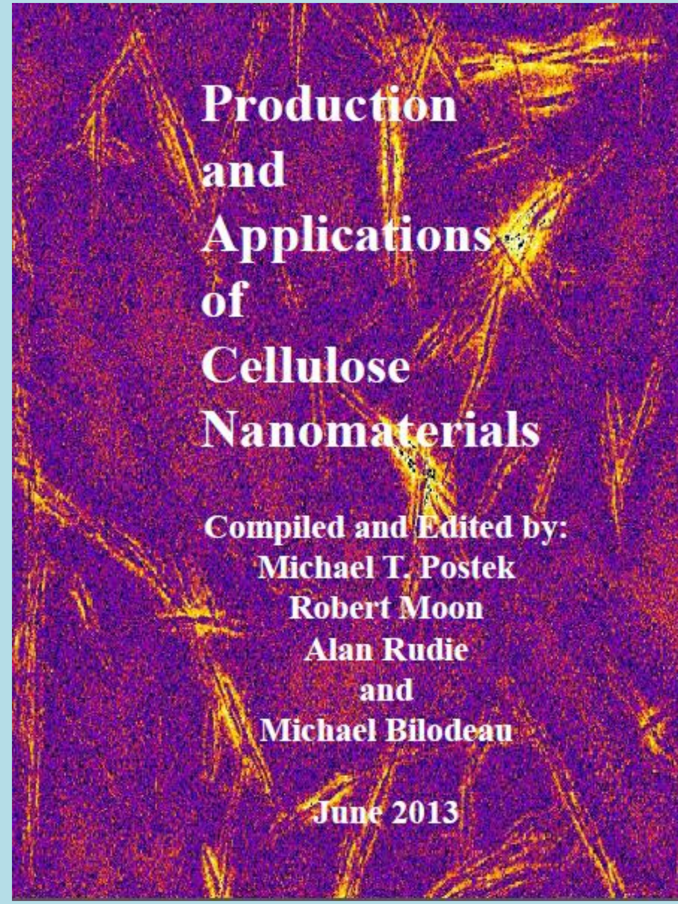


Beck et al.

- Fibers
- Foams
- …



Summarized in:



Commercial Application Areas

Production

- Yields
- Process
- Costs

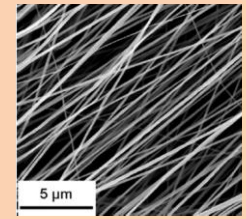
Foams

- Acoustic
- Structural
- Thermal
- …

Paakko et al., Soft Matter, 2008

Continuous Fibers

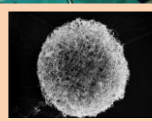
- Reinforcement
- Textiles
- Woven
- …



Dong et al., 2012

Tissue Engineering

- Scaffolds
- Bandages
- Ligament
- Blood Vessels
- Drug Delivery



Deng et al.

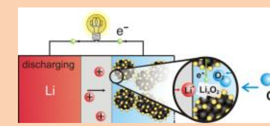
Flexible Electronics

- Self Powered
- Display
- Solar
- LED
- …

Yano et al.

Separators/Barrier

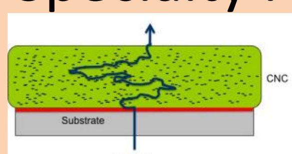
- Filtration
- Batteries
- Pumps
- …



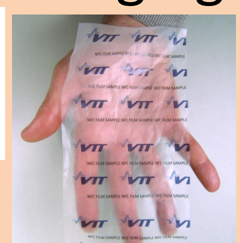
Rheology Modifier

- Paints
- Cosmetics
- Food

Specialty Packaging



Herrera et al.



Vartiainen et al.

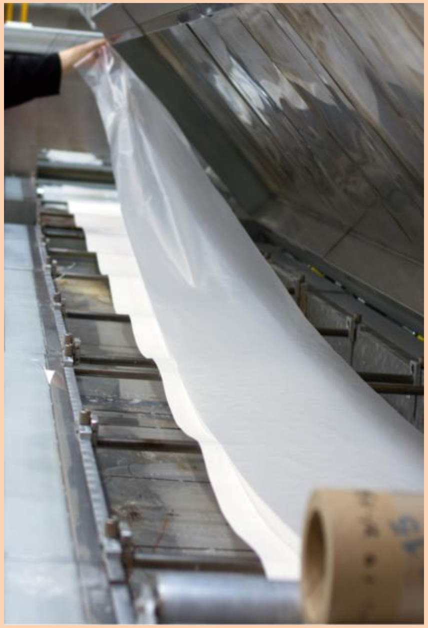
Specialty Cements

- Foamed
- Panel
- Siding
- …

Cao et al.

Commercial Application Areas II

Nonwovens Sheets

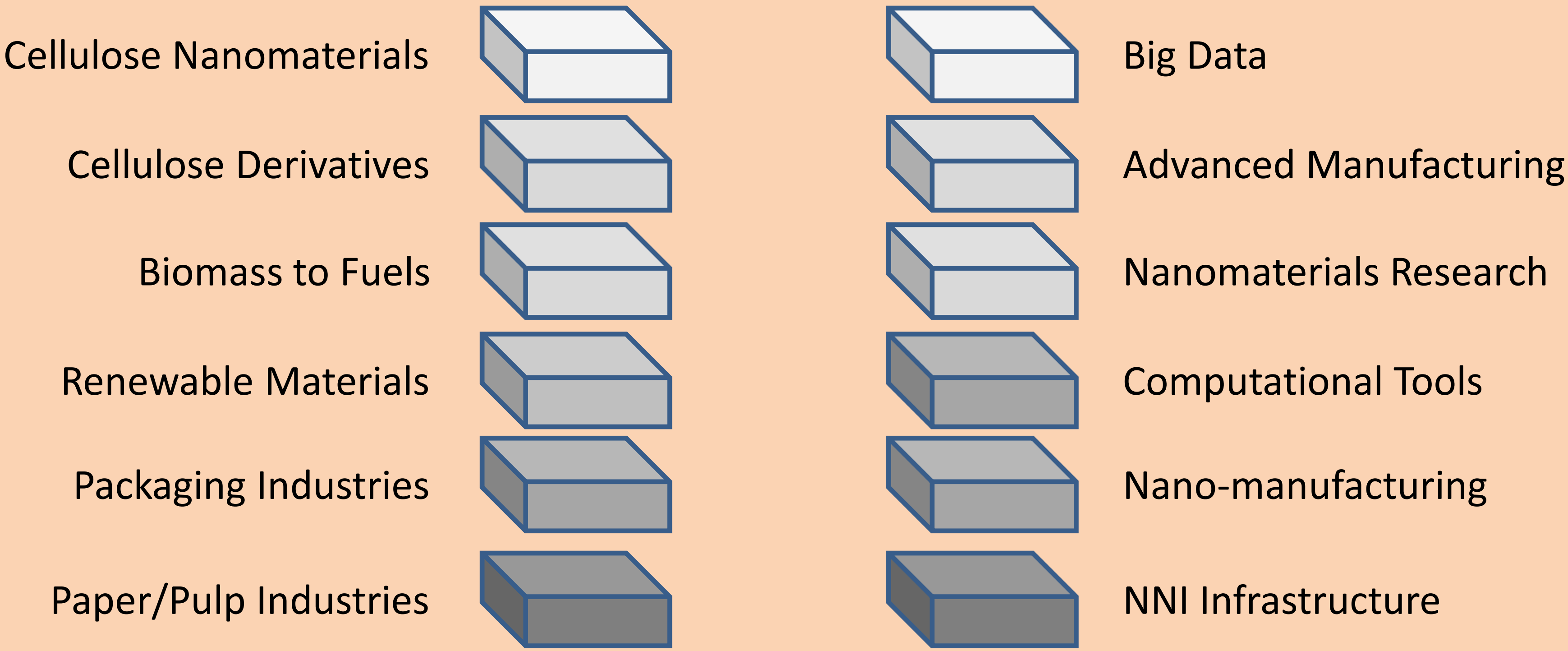


Vartiainen, et al… 2013

Gaps: Autonomous Efforts

Wide spread investment in R&D relevant to cellulose nanomaterials, but research efforts are not coordinated

Individual Research Blocks:



Example: Needs For R&D

Characterization

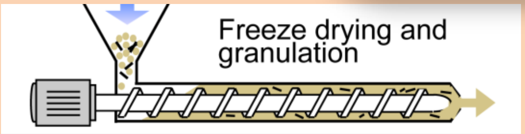
- New Techniques for Fundamental Research
- Online Characterization Techniques
- New Quality Control Methods
- Surfaces & Interfaces
- …

Composite Processing:

- Dispersion/Redispersion
- Non Aqueous Suspensions
- Low Energy Drying
- Hierarchical Design
- …

Prototyping:

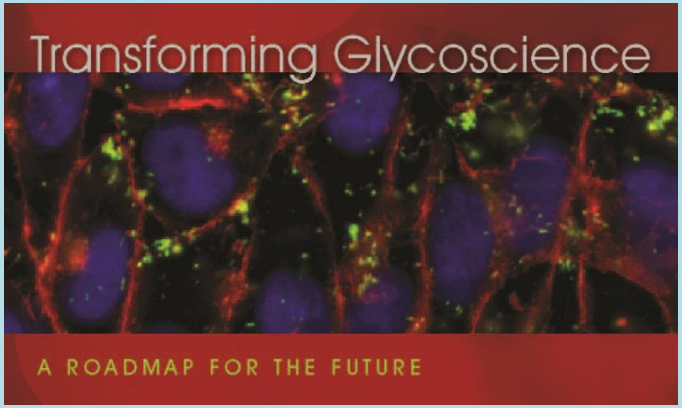
- Industrial Relevant Processes
- Melt-mixing
- Roll-to-Roll
- Advanced Manufacturing
- …



Oksman et al.

Identifying the Needs:

National Academies
National Research Council



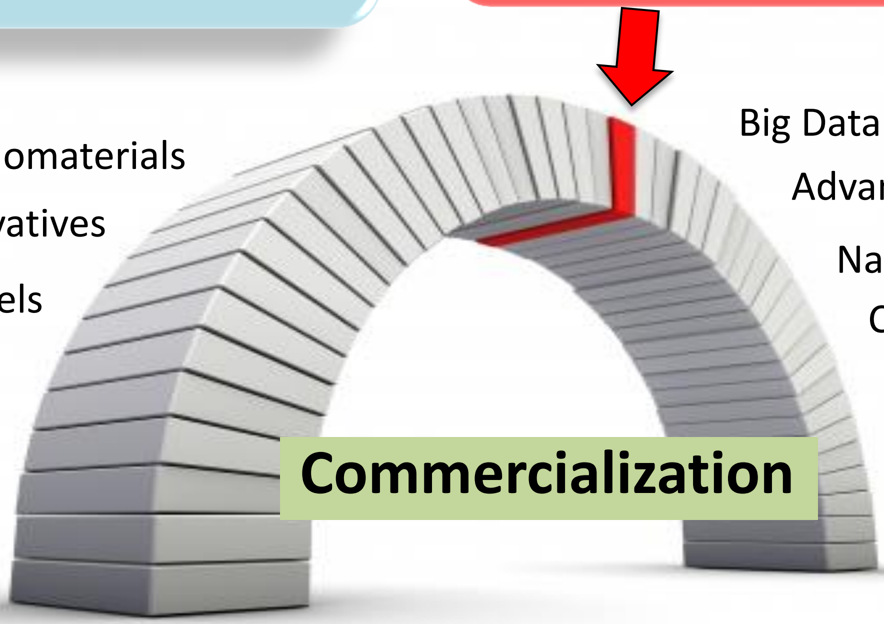
Role of glycans in:

- Medicine
- Bioenergy
- Materials Science

Center on Cellulose Nanomaterials

To make disruptive innovations we need to define and focus on bold longer term objectives and coordinated efforts.

Key Stone
- Bridge gap in existing infrastructure
- Define, Focus, Coordination,
- Research & Development



Critical Partnership:

Industry ⟷ Government ⟷ Academic

Funding in Cellulose Nanomaterials

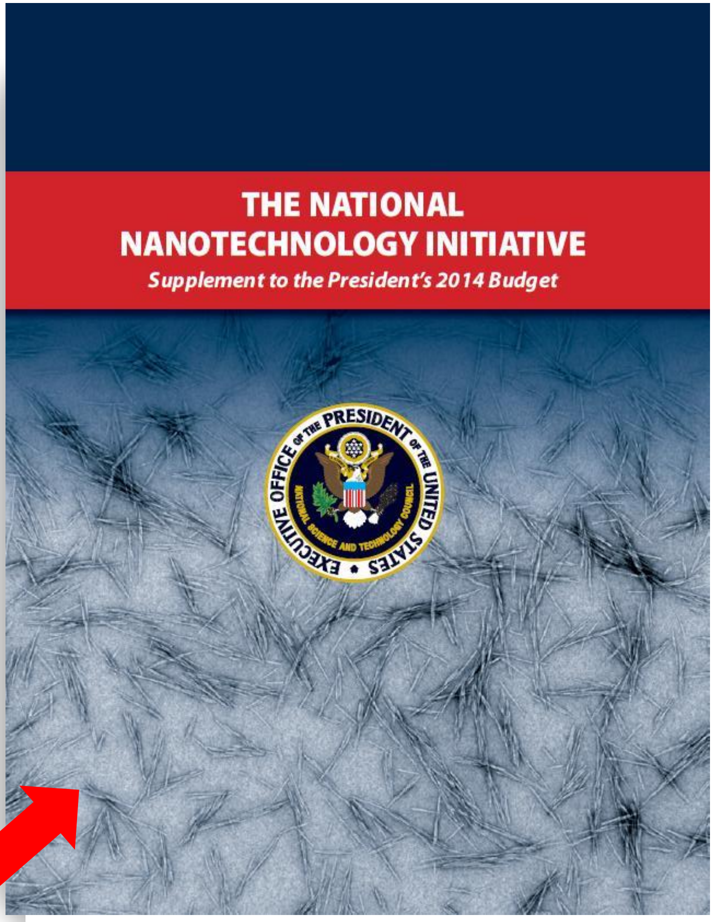
U.S. NNI Investment in Nanotech.:
- ~$17 B since 2000

U.S. Forest Service Investment:
- ~$20 M in R&D since 2009
- Focused under Ted Wegner

World Investment:
- ~$680 M in R&D since 2009
- Focused under Federal Programs

In Federal Funding Amounts, no one knew about us …

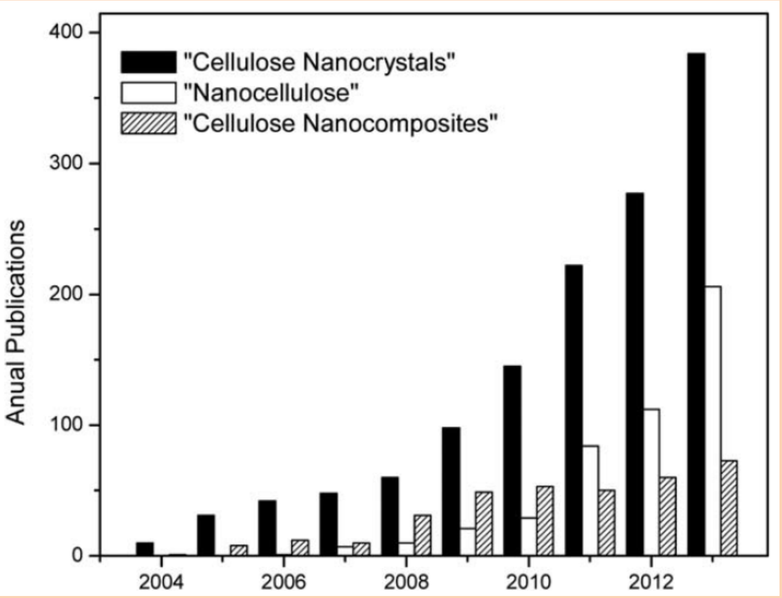
People Have Taken Notice



Cellulose Nanomaterial

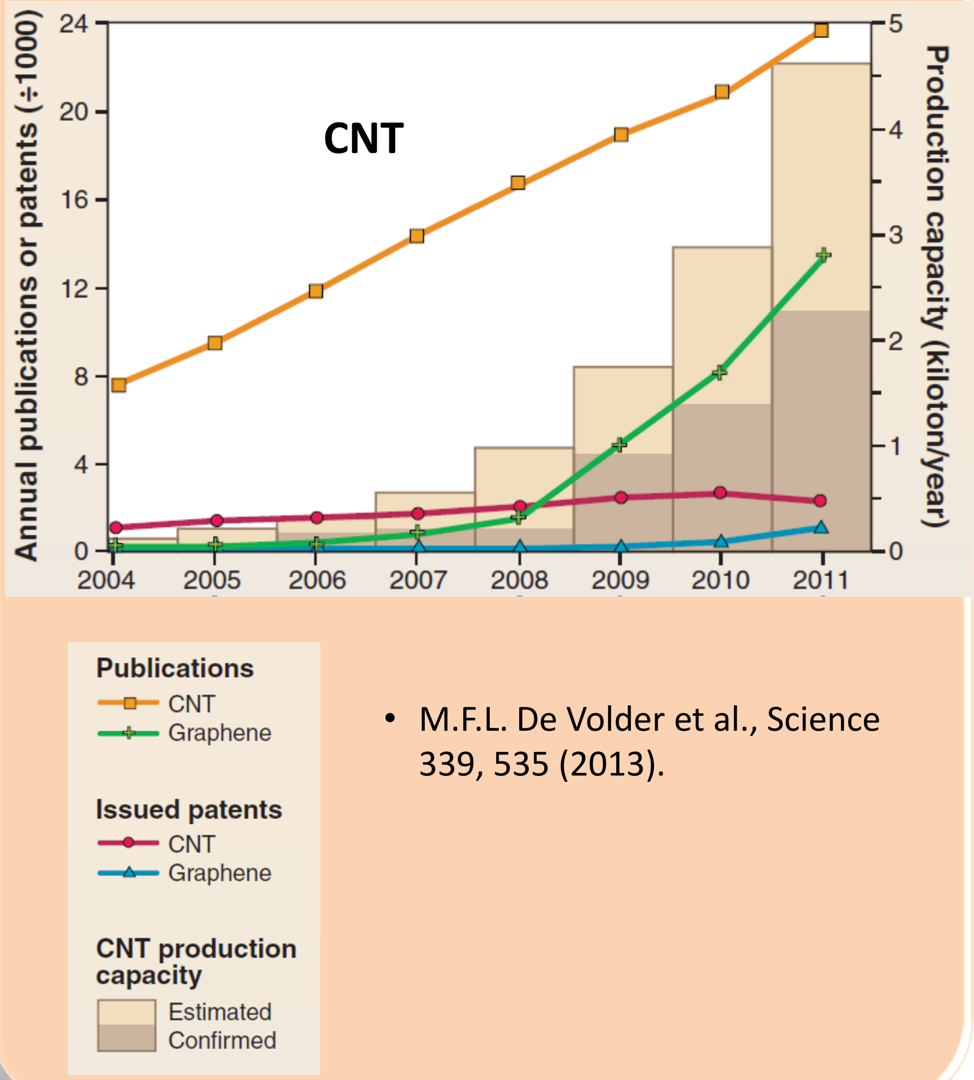
Funding Matters

Cellulose Nanomaterials



Mariano et al., J Poly Sci. poly physics,2014

Carbon Nanotubes



- M.F.L. De Volder et al., Science 339, 535 (2013).

Thank you for your Attention

To learn more about Cellulose Nanomaterials ***"State of the Art"***

Review Papers:

R J Moon, *Chemical Society Reviews*.(2011).
DOI:10.1039/C0CS00108B

Websites:

http://www.fpl.fs.fed.us/

http://www.tappinano.org/

Contact Me:

robertmoon@fs.fed.us