Cellulose Nanomaterials
– Technical State of Art –

Industry
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Academia
Robert J Moon

Government
Robert J Moon, Ted Wegner, World Neih

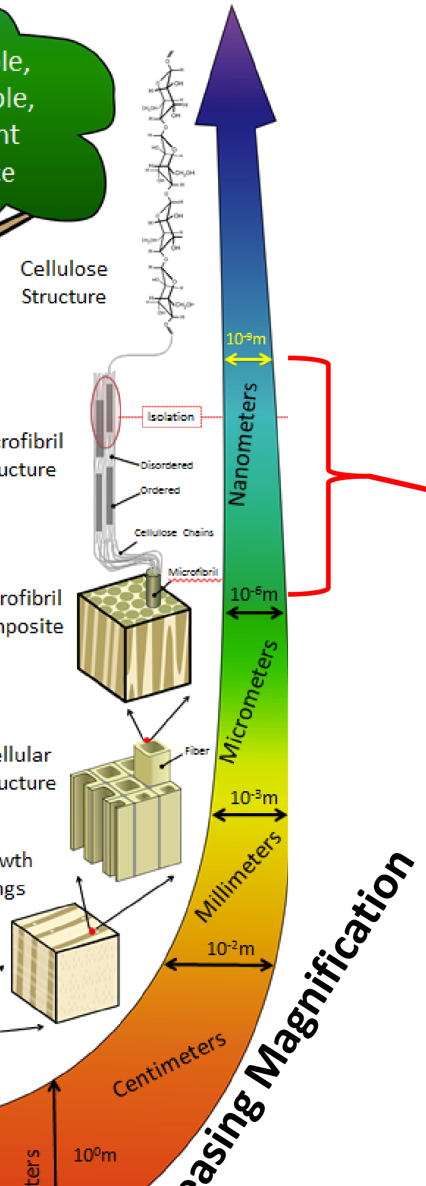
NNI and USDA-Forest Service Workshop on
Cellulose Nanomaterials – A Path Towards Commercialization
Washington DC, 20-21 May, 2014

200nm

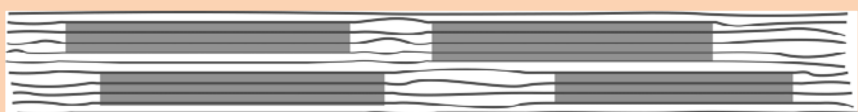
Outline of Talk

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

hat 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

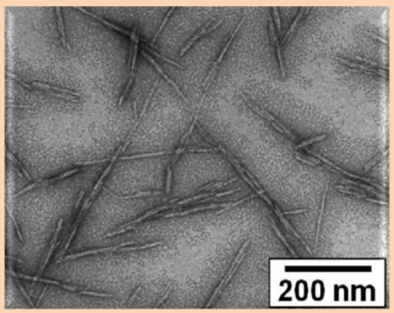
Many "Flavors" of CNs

Acid
Hydrolysis

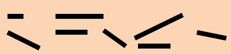
Chem/Mech

hanical

Cellulose Nanocrystals (CNC)

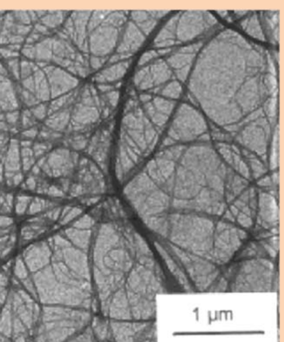


Rod-like

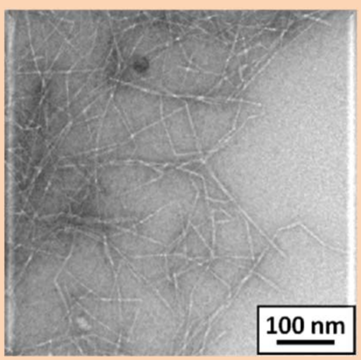


Particles:
- Source
- Method

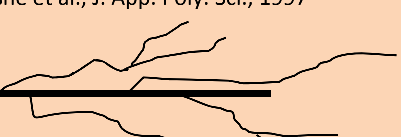
Cellulose Nanofibrils (CNF)

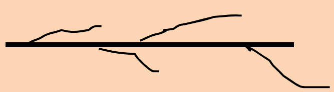


sne et al., J. App. Poly. Sci., 1997



Fibril-like:





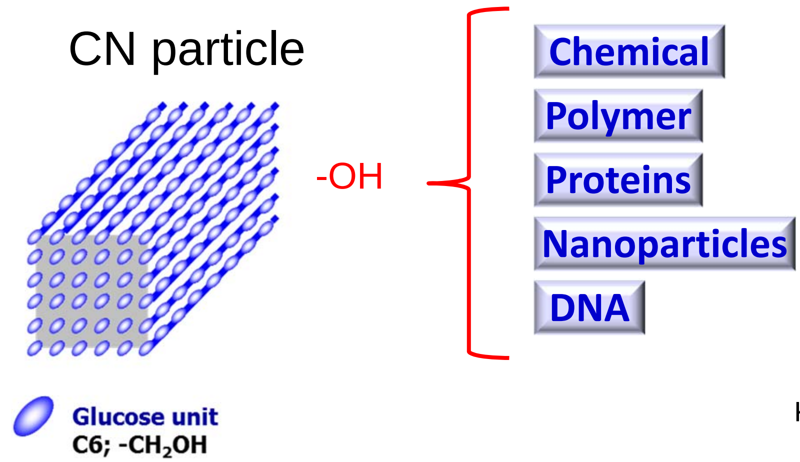
Properties:
- Length
- Aspect Ratio
- Branching
- Crystallinity

y "Sprinkles" of Surface Modification

/ Functionality

- eactive Surface: -OH
- mple Chemistry
- ter Properties:
  - Interfaces: CN-CN, CN-Matrix
  - Self Assembly
  - Function: e^{-}, antimicrobial,

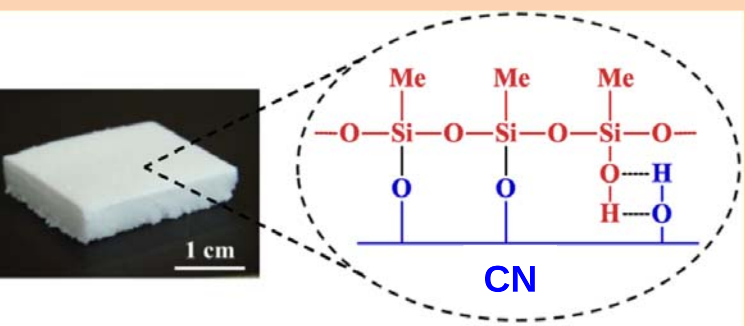
CN particle

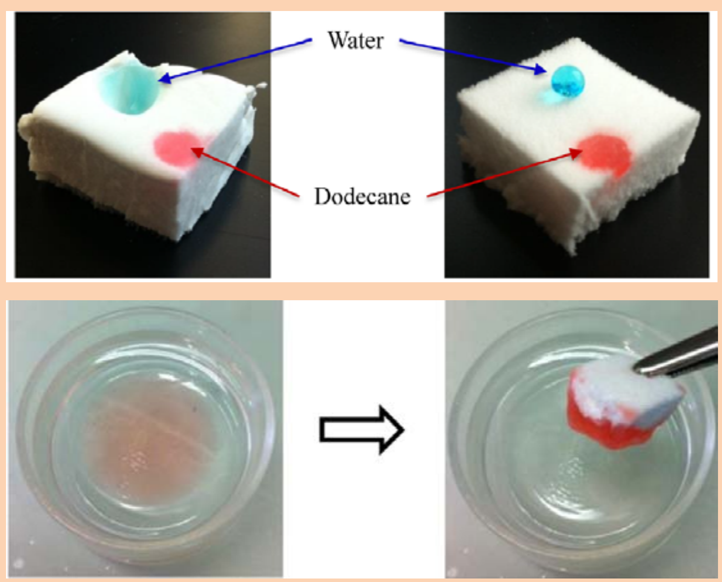


Koga et al.

ponges: Remove Oil from Water

w chemistry alters behavior





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

Why Cellulose Nanomaterials?

can CNs do that no other nanoparticle can do?

ght/Stiff/Strong
ptical
urface Chemistry

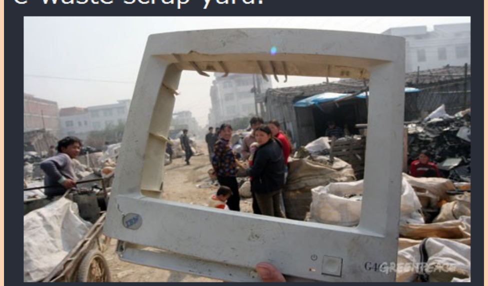
It is not one specific property that sets Nanocellulose apart from the rest, rather the unique combination of relevant characteristics that gives these materials utility

igh Production Potential
ow Cost Potential
S Source → Local Jobs

Societal Needs

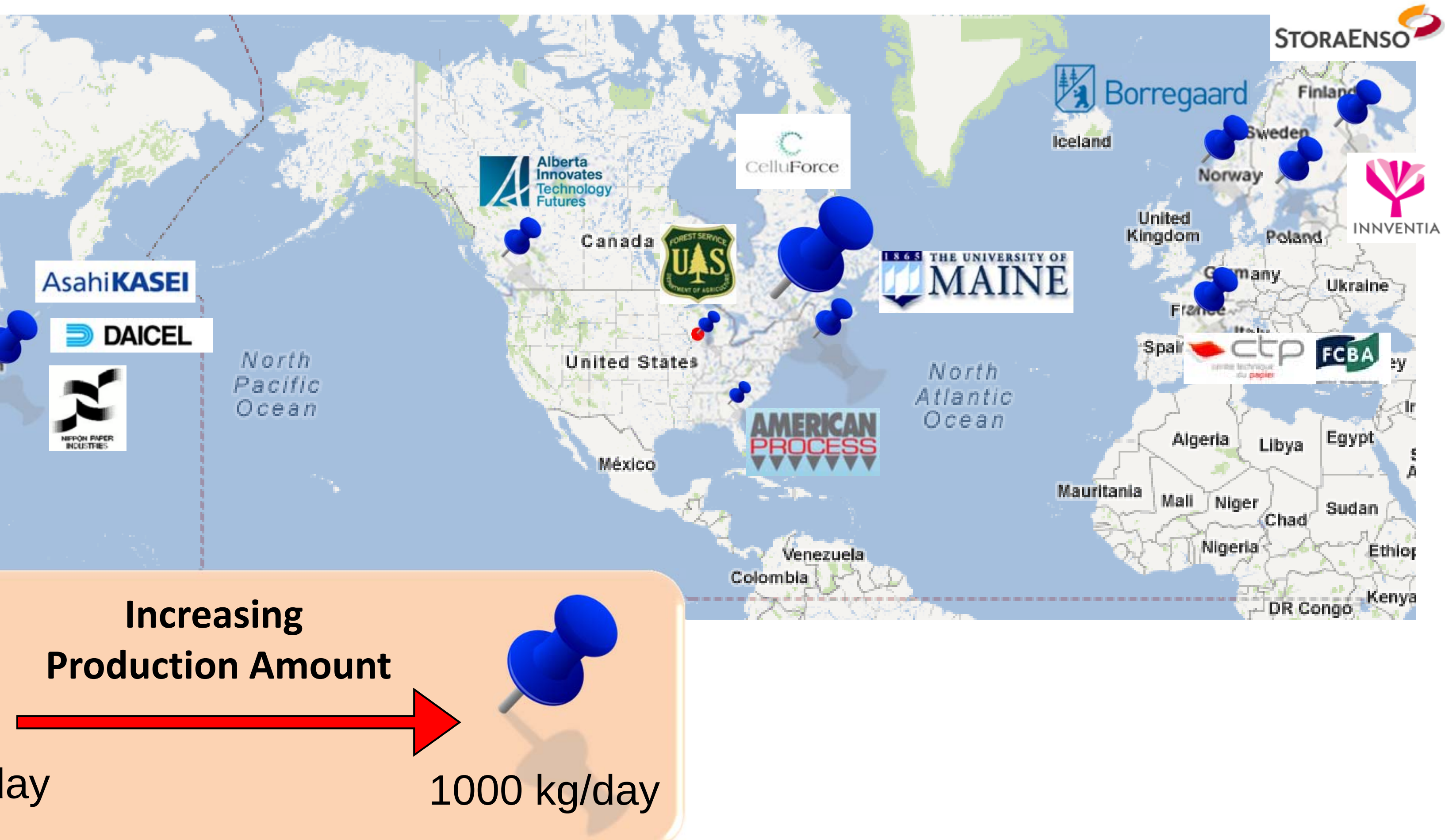
Profit

ew EHS Concerns
enewable
ustainable
odegradable



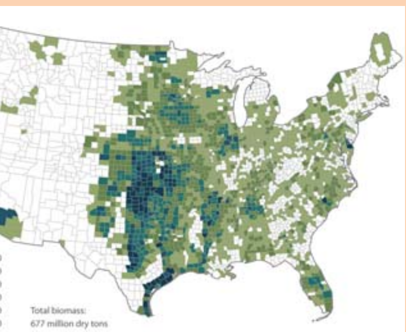
Part of a IBM computer at a Chinese e-waste scrap yard.

World Production of Nanocellulose



$ Billions of Infrastructure in Place

ainable Biomass
Management



Forestry
Agriculture
Biomass for Fuel

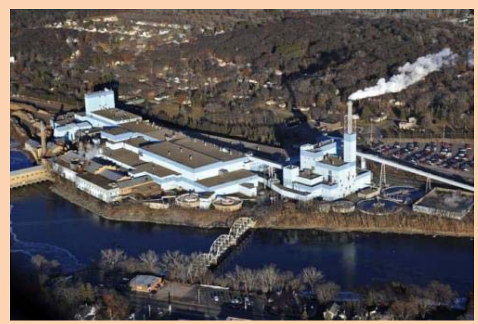
infrastructure is in
ce for LARGE scale
duction of cellulose
nanomaterials

Harvesting

Distribution

Refining: Trees to Particles

- Pulp fiber
- Water, Energy
- Waste Streams



Environment

Pro

Gap:
Needed for Cellulose
Nanomaterials

Disposal/Recycle

Opportunity for Mass Production

terial		Production US	Production World	Cost
Demand		60 M ton/yr	175M ton/yr	~$0.75-1.0 / kg
od Demand		~187 M ton/yr	????	
od capacity		~405 M ton/yr	????	
current capacity		7.5 ton/yr (est)	50 ton/yr (est)	$4-40 /kg
current capacity		1.25 ton/yr (est)	30 ton/yr (est)	$2-15 /kg
er Nanomaterials				
(multiwalled) 2011		?	2000 ton/yr	~$100/kg

.L. De Volder et al., Carbon Nanotubes: Present and Future
nmercial Applications, Science 339, 535 (2013).

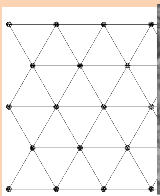
Ma et al., Dispersion and Functionalization of carbon nanotubes for
ymer-based nanocomposites: A Review, Composites: Part A 41:
5-1367 (2010)

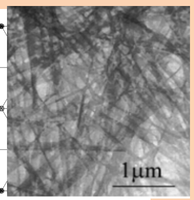
In Addition…

***2Billion tons** of*
Beetle killed wood
looking for a use

Industrially Relevant Structures from Cellulose Nanomaterials

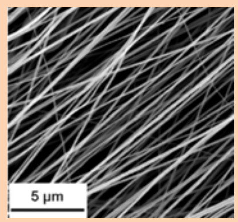
elf-Assembly





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

Continuous Fibers

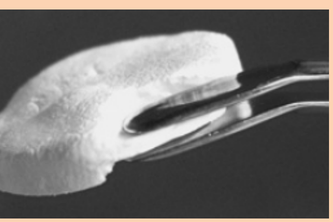


Dong et al., Carb. Poly., 2012, 87, 2488-2495

Films

Nogi et al., Adv. Mater, 2009

ams/Aerogels

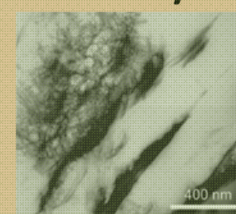


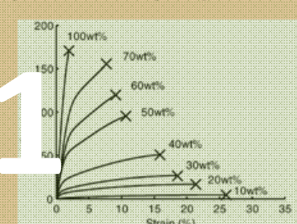
et al., Soft Matter, 2008, 4, 2492-2499

Hydrogels

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

Polymer Fillers

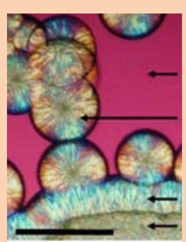




Bondeson et al., Comp. Inter., 2007, 14, 617-630
Svagan et al., Biomacromolecules,2007

eology Modifier

Nucleation Agent



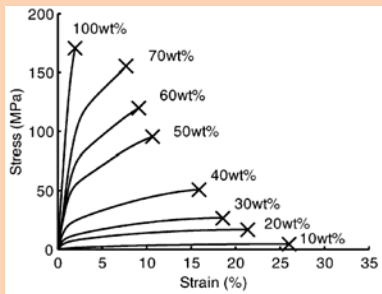
Reaction Pathway

cement

ample I: Expand Materials Applications

ment Properties of Existing Polymer Platforms

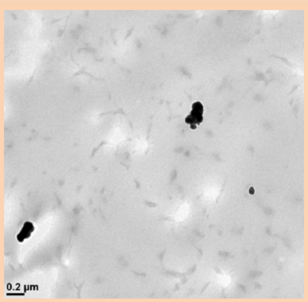
echanical Properties
trength
tiffness
longation



Svagan et al., Biomacromolecules,2007

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

rrier Properties
)xygen, water
hemicals



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

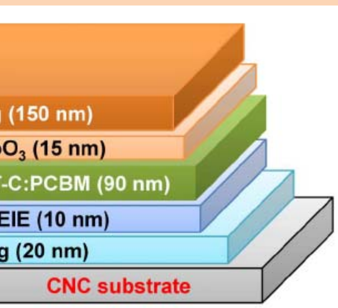
Fortunati et al., J Food Eng,2013

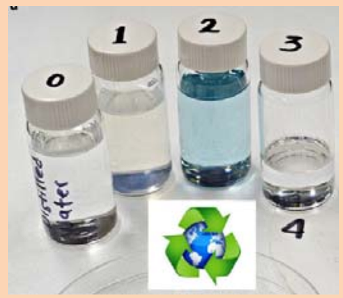
ermal Properties
otical Properties
eological Properties

CNC-Epoxy: 5, 2, 0%

Example II: Enabling Technology

r Device: Reduce Environmental Footprint!!





Substrate material facilitates recovery of device components

Key Features:

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

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

xample III: Better Properties & Safer

C Additions to Cement
- -30% Increase in Flexural Strength
  - @ 0.2wt% CNC additions
- odified Cement Reaction
  - Increased Degree of Hydration
  - Altered Microstructure

Vin: More durable cement while maintaining Low Environmental Impact

Cellulose Nanomat

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

Gap:
Needed for Cellulose
Nanomaterials

Nano to Bulk Reality

The Nano Potential

Realities of Manufacturing

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

The Bulk Reality

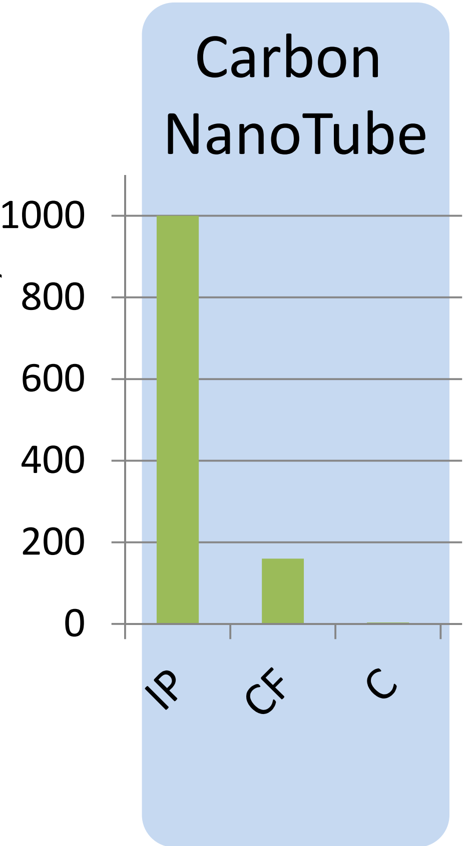
Hulk Hogan

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

- Improved performance
- Rough arou... ...ges
- N... ...ing potential

Gap:
Needed for Cellulose Nanomaterials

Example I: Nano > Bulk Properties

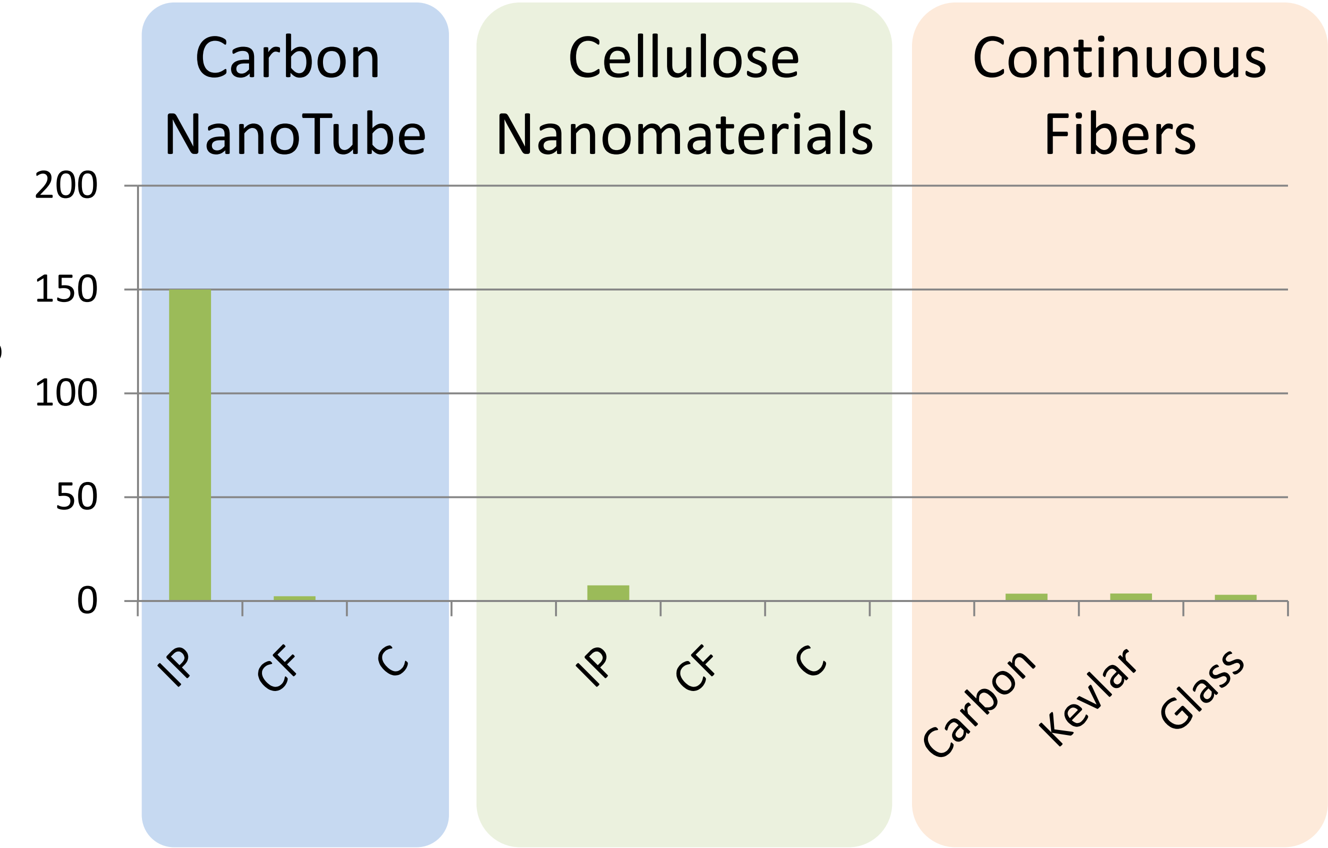


Properties of bulk structures much lower then individual Nanoparticle

Individual Particle
Continuous Fiber
Composite -5% nanoparticles

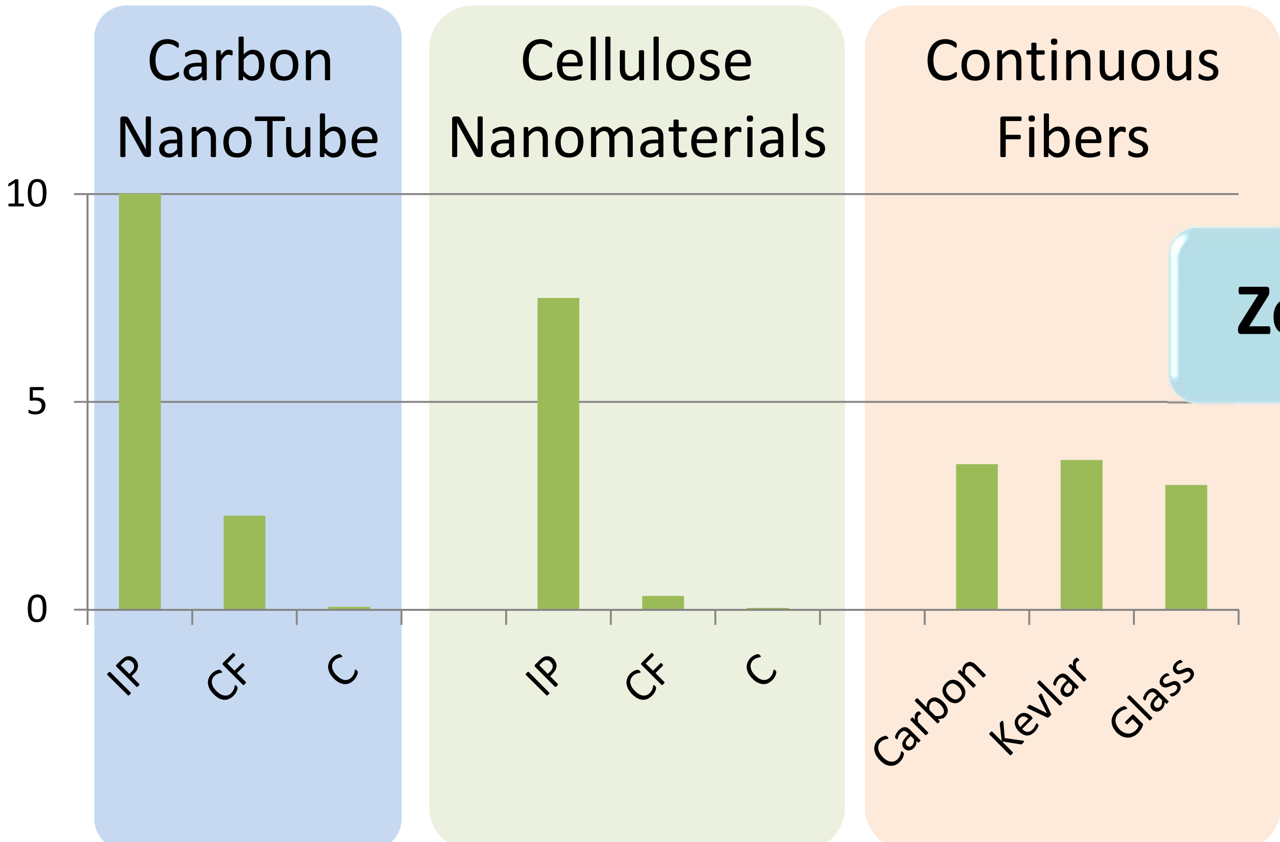
- M.F.L. De Volder et al., Science 339, 535 (2013).
- P-C Ma et al., Composites: Part A 41: 1345-1367 (2010)
- International assessment of research and Development of carbon nanotube manufacturing And applications, World Technical Evaluation Center report , P Eklund, P Ajayan, R Blackmon, A.J. Hart,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

xample II: Nano > Bulk Properties



Individual Particle
Continuous Fiber
Composite -5% nanoparticles

xample II: Nano > Bulk Properties

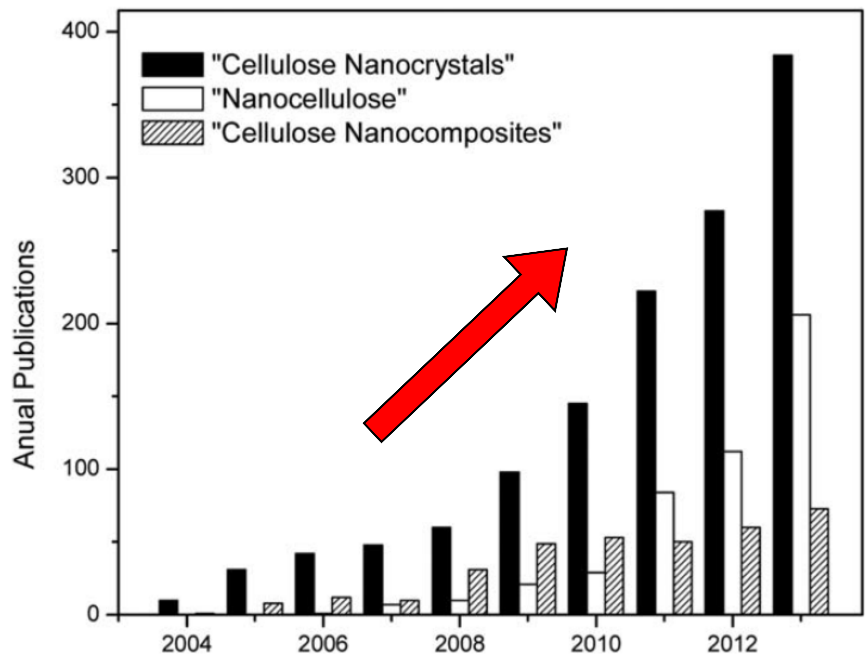


Zoomed in

Individual Particle
Continuous Fiber
Composite -5% nanoparticles

Current state of the art

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



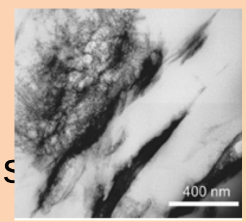
Mariano et al., J Poly Sci. poly physics,2014

Academic/Fed Lab Research Areas

Production
urces
lds
w methods
eze drying

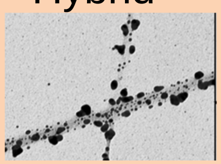
Character
- Particles & C
- Properties
- Distribution
- Interfaces

Composites
persion
erface
ability
w systems
uctures

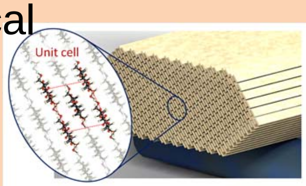


n et al., Comp. Inter., 2007, 14, 617-630

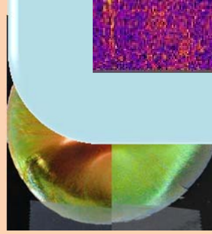
Template St
- Sacrificial
- Hybrid



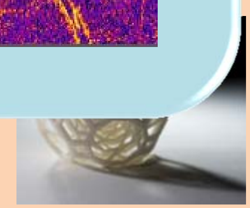
dictive Modeling
rarchical
chanical
ermal
rface



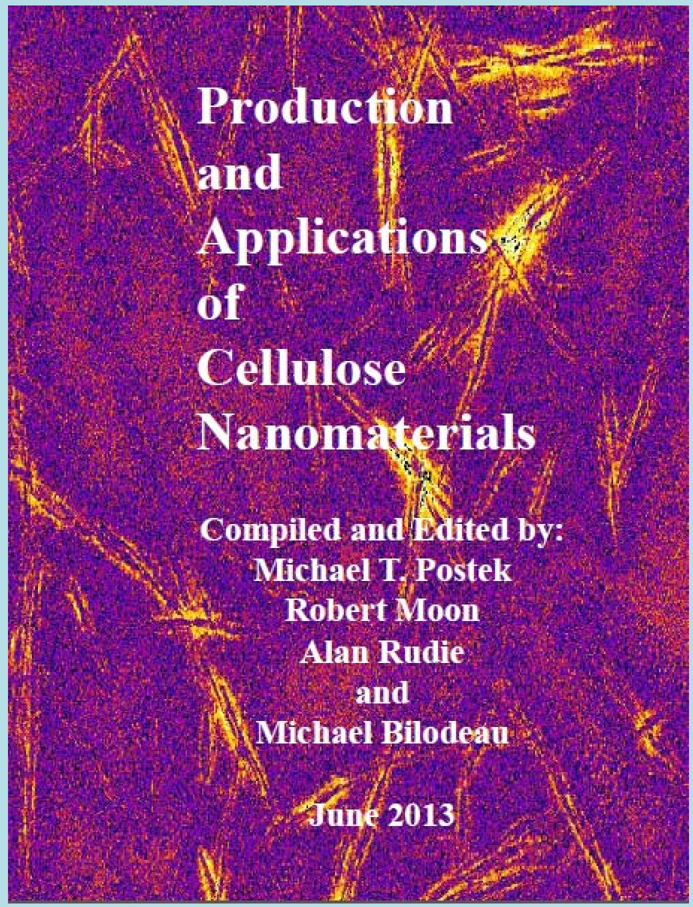
Opti
- Transparent
- Colors
- …



- Fibers
- Foams



Summarized in:



Production and Applications of Cellulose Nanomaterials

Compiled and Edited by:
Michael T. Postek
Robert Moon
Alan Rudie
and
Michael Bilodeau

June 2013

Commercial Application Areas

Production

- ds
- cess
- sts

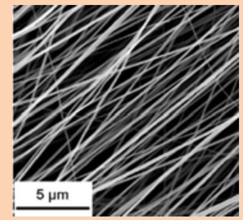
Foams

- Acoustic
- Structural
- Thermal
- …

Paakko et al., Soft Matter, 2008

Continuous Fibers

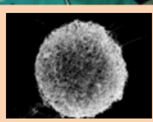
- Reinforcement
- Textiles
- Woven
- …



Dong et al., 2012

sue Engineering

- affolds
- ndages
- ament
- od Vessels
- g Delivery



Deng et al.

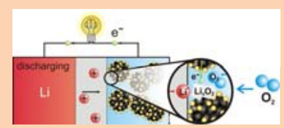
Flexible Electronics

- Self Powered
- Display
- Solar
- LED
- …

Yano et al.

Separators/Barrier

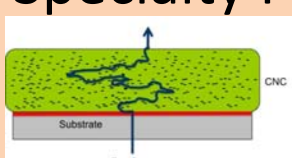
- Filtration
- Batteries
- Pumps
- …



eology Modifier

- nts
- smetics
- od

Specialty Packaging



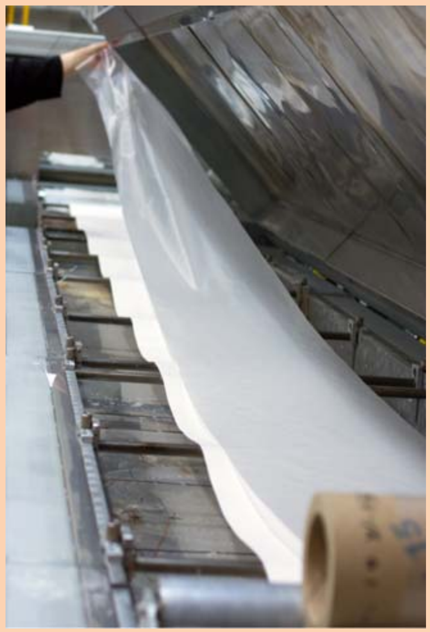
Herrera et al.

Specialty Cements

- Foamed
- Panel
- Siding
- …

Commercial Application Areas II

nwovens Sheets



Vartiainen, et al… 2013

INNOVATECH
ENGINEERING

Gaps: Autonomous Efforts

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

dividual Research Blocks:

ulose Nanomaterials
Cellulose Derivatives
Biomass to Fuels
Renewable Materials
Packaging Industries
aper/Pulp Industries

Big Data
Advanced Manufacturing
Nanomaterials Research
Computational Tools
Nano-manufacturing
NNI Infrastructure

Example: Needs For R&D

aracterization

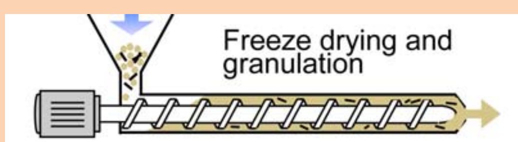
- ew Techniques for Fundamental Research
- nline Characterization Techniques
- ew Quality Control Methods
- urfaces & Interfaces
- .

mposite Processing:

- ispersion/Redispersion
- on Aqueous Suspensions
- ow Energy Drying
- ierarchical Design
- .

ototyping:

- dustrial Relevant Processes
- elt-mixing
- oll-to-Roll
- dvanced Manufacturing
- .

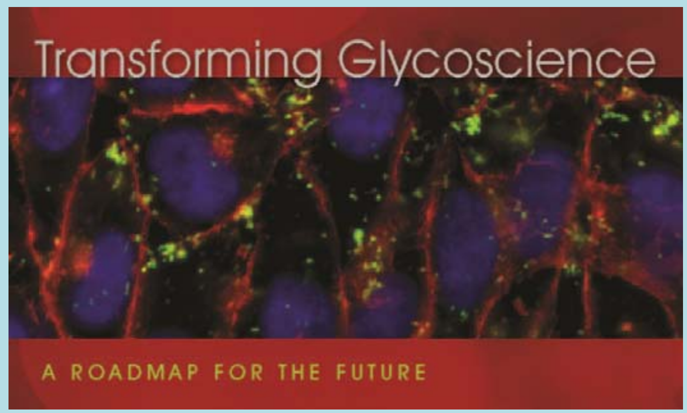


Oksman et al.

Identifying the Needs:

National Academies

National Research Council



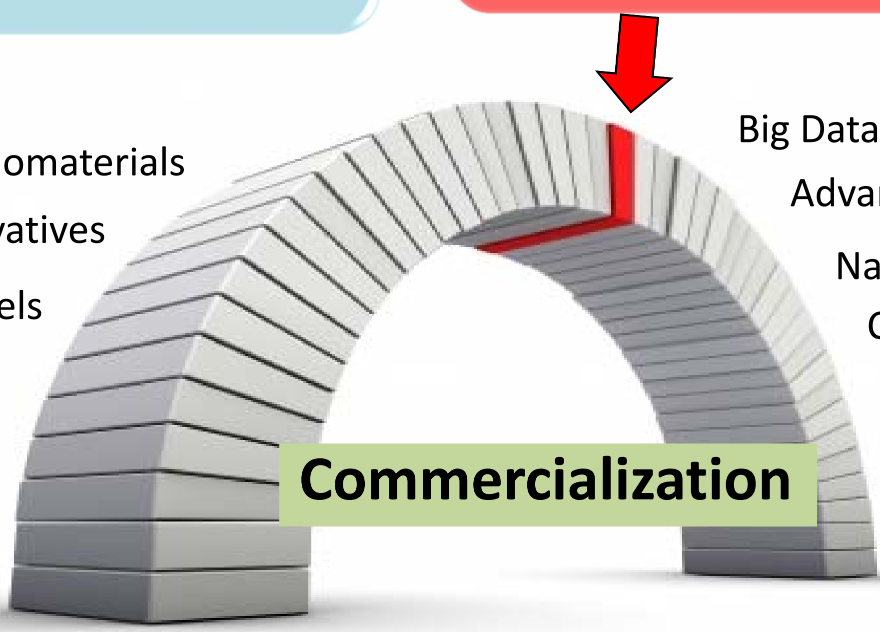
Role of glycans in:

- Medicine
- Bioenergy
- Materials Science

…enter on Cellulose Nanomaterials

…ke disruptive innovations we …o define and focus on bold … term objectives and …nated efforts.

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



…tical Partnership:

Industry ⟷ Government ⟷ Academic

unding in Cellulose Nanomaterials

. NNI Investment in Nanotech.:

- ~$17 B since 2000

. Forest Service Investment:

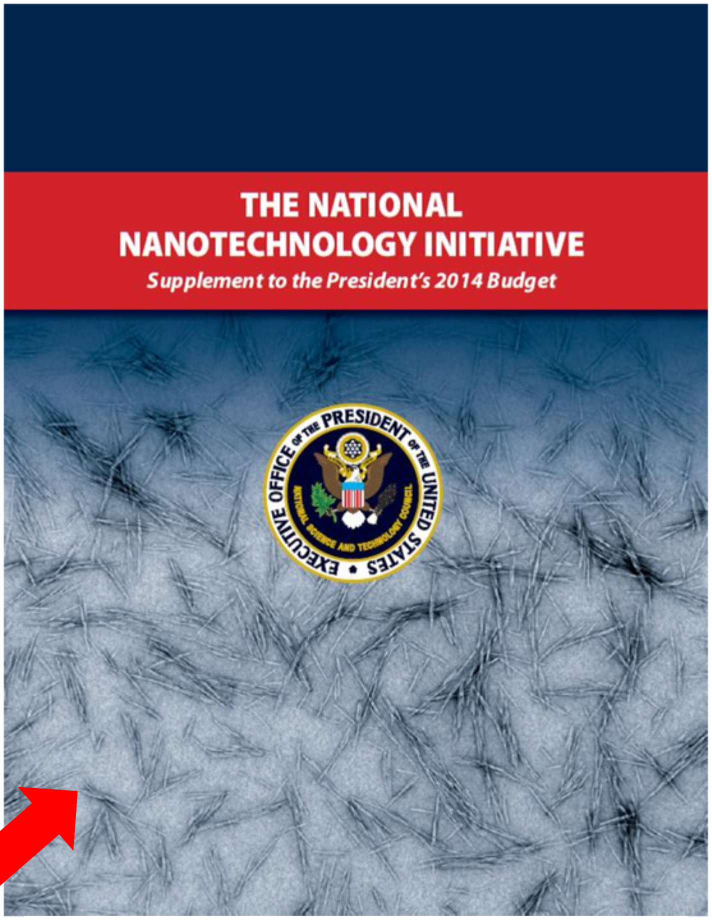
- ~$20 M in R&D since 2009
- Focused under Ted Wegner

rld Investment:

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

Federal Funding Amounts, no one
ew about us …

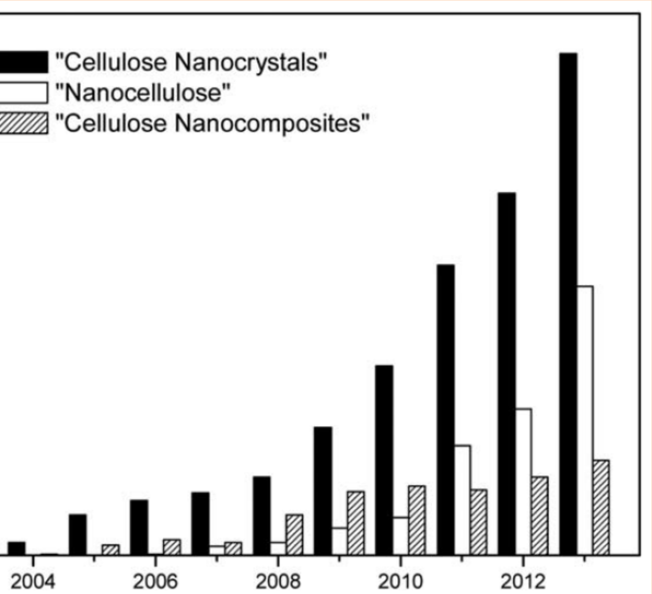
People Have Taken Notice



Cellulose Nanomaterial

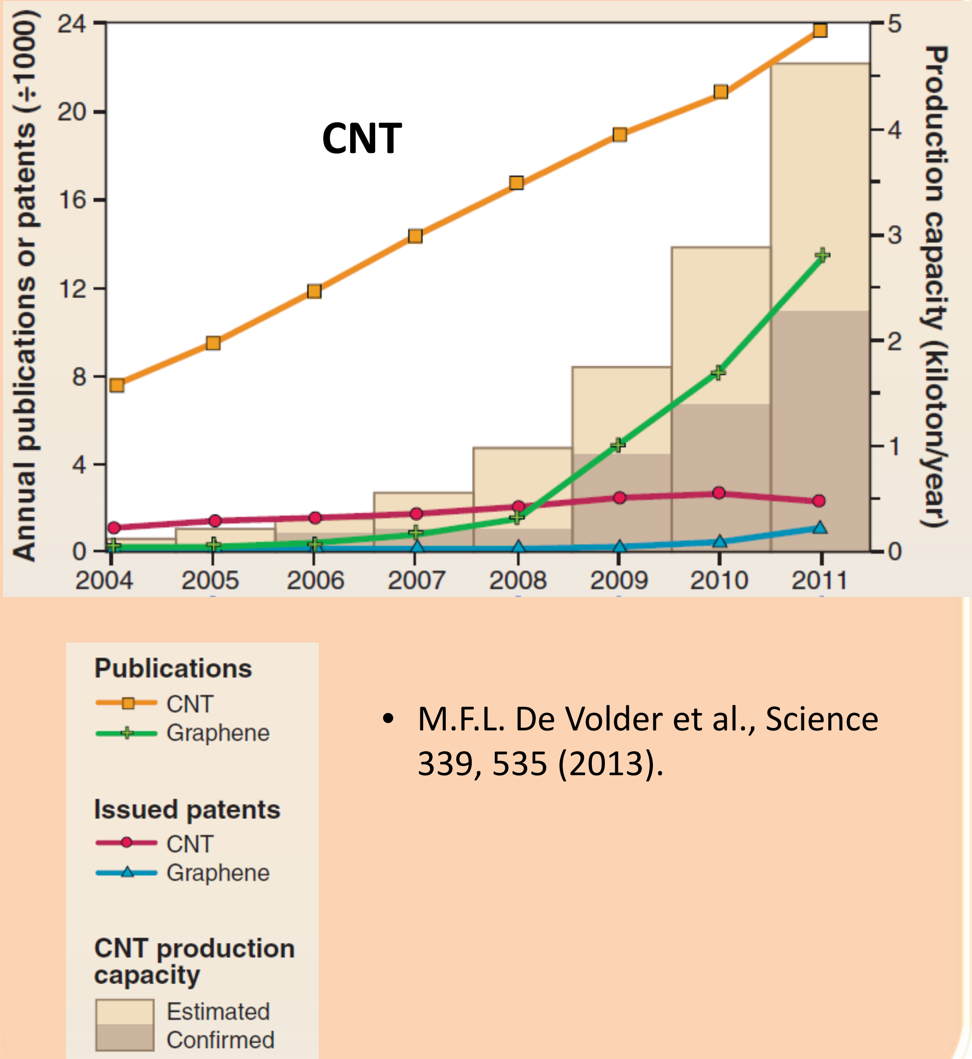
Funding Matters

Cellulose Nanomaterials



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

Carbon Nanotubes



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

hank you for your Attention

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

view Papers:

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

ebsites:

- http://www.fpl.fs.fed.us/
- http://www.tappinano.org/

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