Grand Challenges of Characterization & Modeling of Cellulose Nanomaterials

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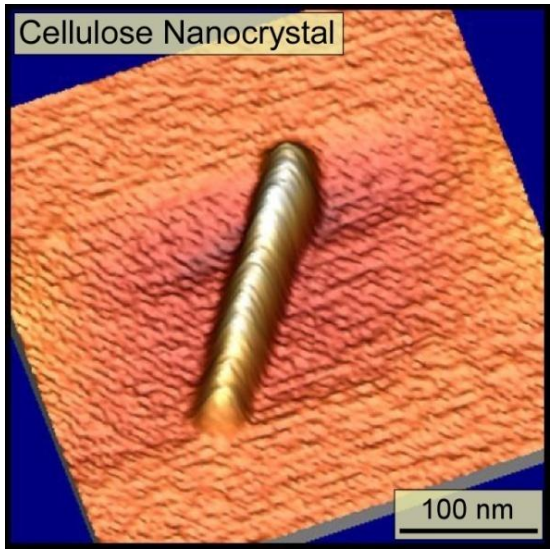
DOE- Sustainable Nanomaterials Workshop,
26 June, 2012

200nm

Cellulose Nanomaterials (CN)

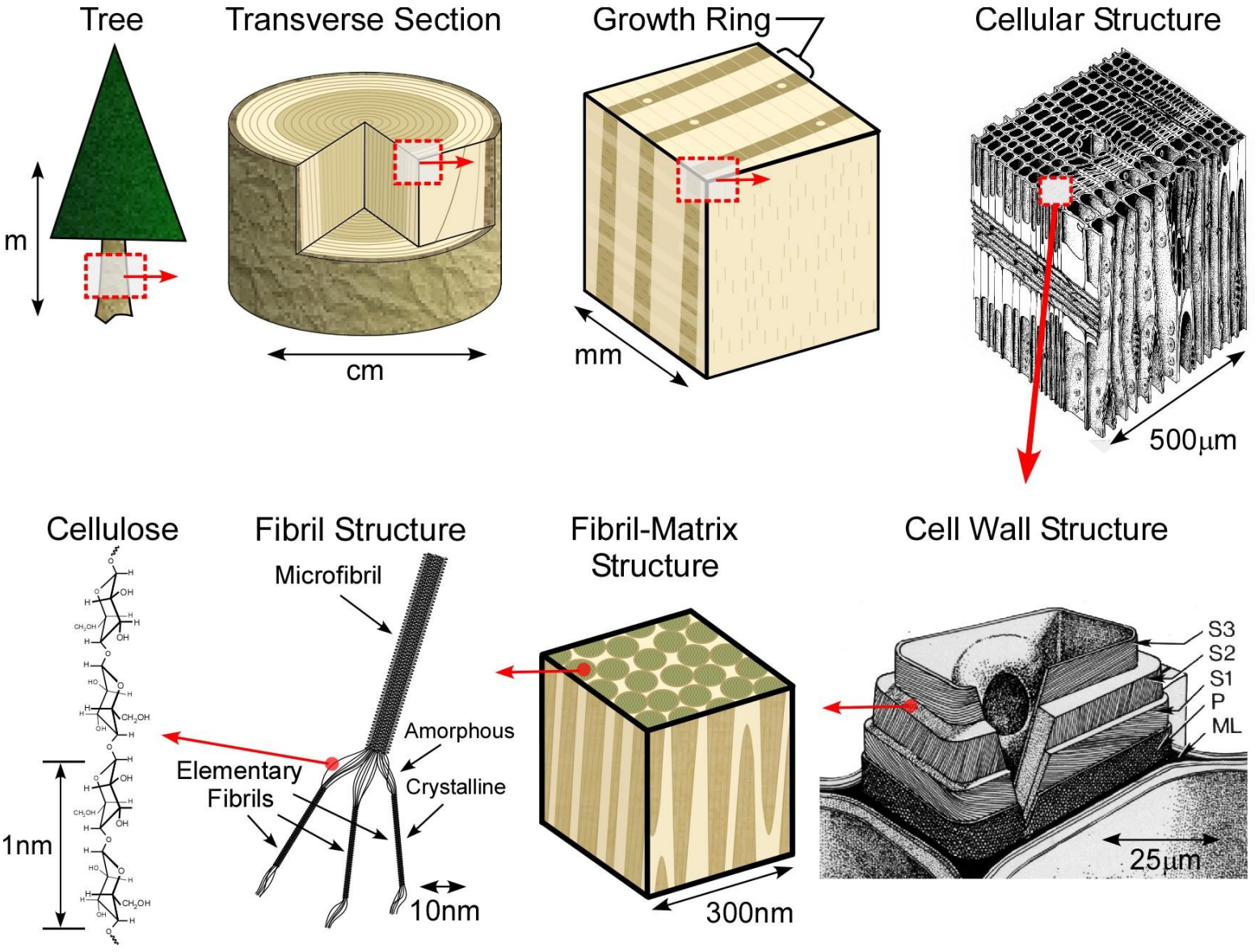
Char & Modeling:

- Extraction Process
  - Linked to bioenergy
- Extracted Materials
  - Chemicals
  - **Nanomaterials**
- Reassembly



- Influence:
  - Cellulose Source
  - Extraction Process
- Two Particle Morphologies:
  - Rod: **CNC**, NCC, NCW, NCXLS
  - Fibrillar: **CNF**, NFC, MFC, BC, AC
- Questions:
  - What to Characterize?
  - How to Characterize?
  - How to Model?

Wood- Cellulose Nanomaterials (CNs)



Moon et al., Chem Soc Rev 2011.

CN form Wide Variety of Sources

Trees

Plants

Wheat Straw

Cotton

Sugar Beet

Sisal

Ramie

Banana

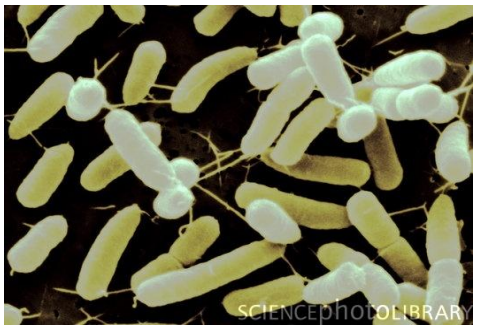
Alfa, Hemp, Flax, Jute, etc

Potato

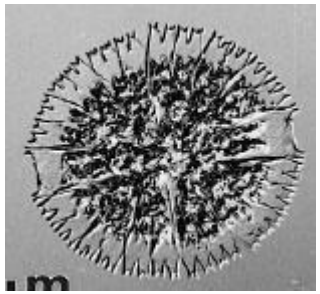
Other

Tunicate

Bacteria

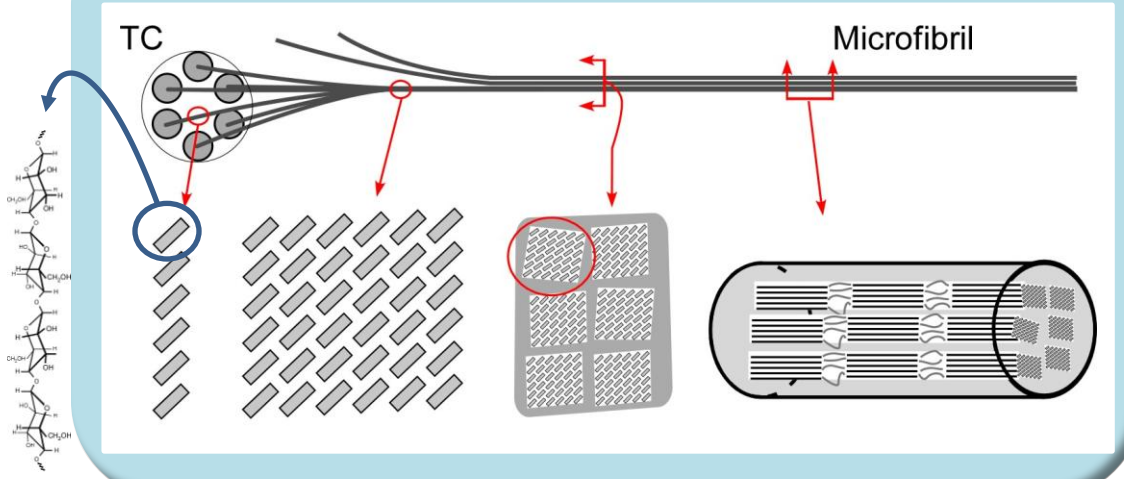


Algae

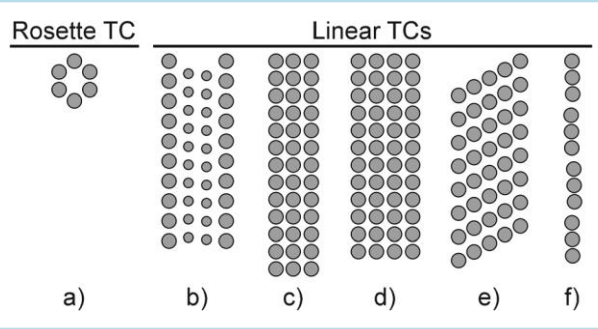


Biosynthesis

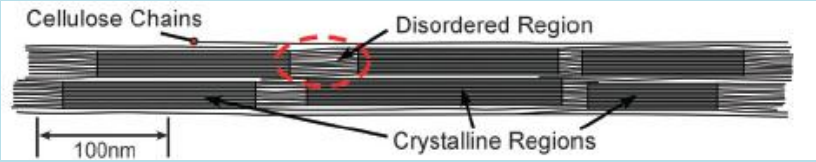
Wood/Plant Microfibril Synthesis



TC dependent on Source



Microfibril Structure



- Dependent on Source
- Hierarchical structure
- Crystalline/Amorphous, Bundling
  - Crystalline → high properties
- Structure not 100% quantified.

Influence on Extracted Particle

- Morphology
- Crystalline/Amorphous
- Surface Chemistry
- Uniformity

Moon et al., Chem Soc Rev 2011.

CNs Extraction Summary

Rod Types:

Pretreatment:

Fibrillar Types:

Acid Hydrolysis

Mechanical

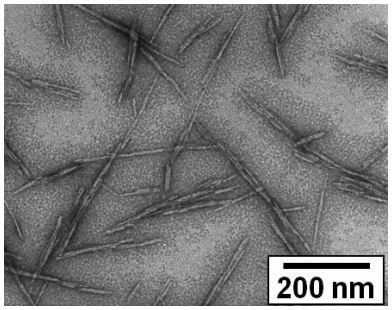
Fibrillation Treatment

Homogenizer

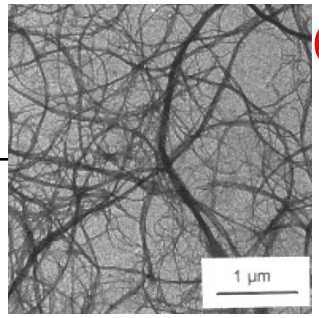
Microfluidizer

Mass Colloider

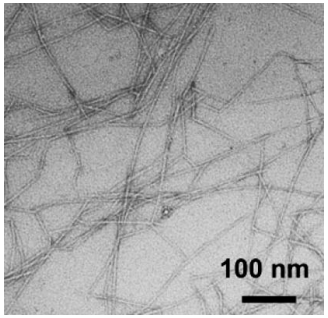
CryoCrushing



CNC



CNF I



CNF II

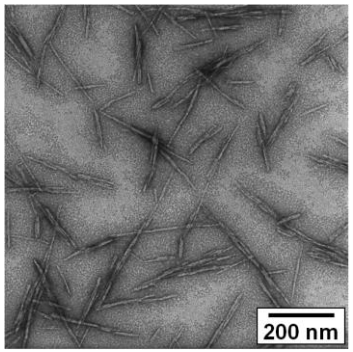
Moon et al., Chem Soc Rev 2011.

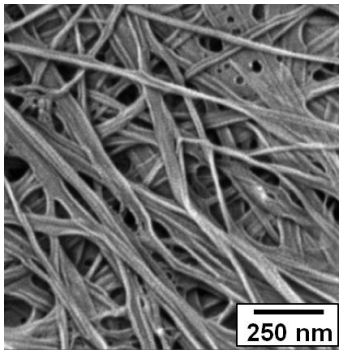
Dufresne et al., J. App. Poly. Sci., 1997

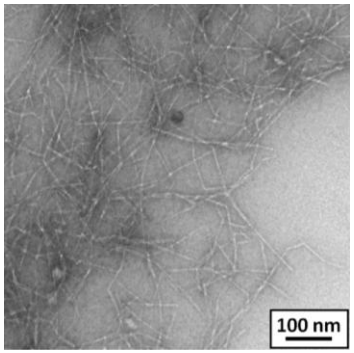
Saito et al., Biomacromolecules, 2007

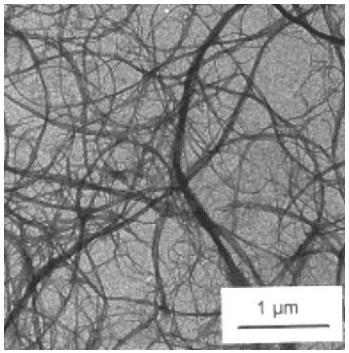
Degree of Branching

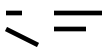
↑ **branching**

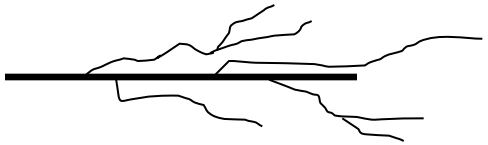












CNC	**BC**	**CNF II**	**CNF I**
•<u>Diameter:</u> 3-20 nm	•30-50, 6-10nm	•4-40 nm	•40-100 nm
•<u>Length:</u> 50-500 nm	•> 1µm	•> 1um, ?	•> 1um, ?
•<u>Branching:</u> low	•low	•med	•High

Ifuku et al., Biomacromolecules, 2007
Saito et al., Biomacromolecules, 2007
Dufresne et al., J. App. Poly. Sci., 1997

Moon et al., Chem Soc Rev 2011.

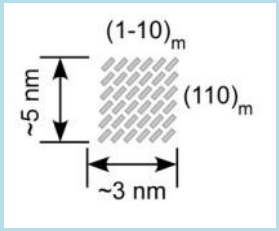
Differences in CN Morphology

Result From:

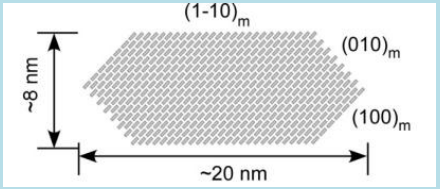
- Biosynthesis process
- Extraction process

Cross-Sectional Shape:

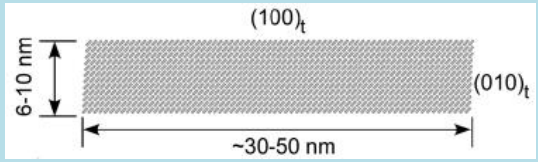
CNC, CNF-wood/plant

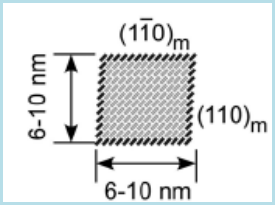


CNC-tunicate

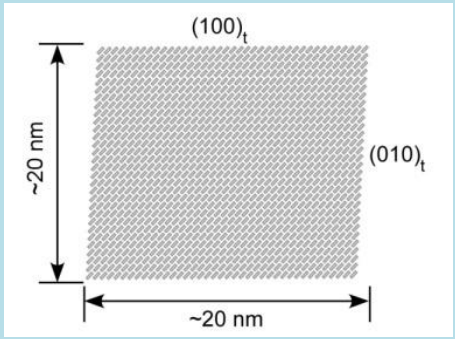


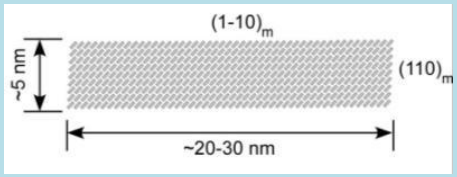
Bacterial Cellulose (BC)





Algae Cellulose (AC)





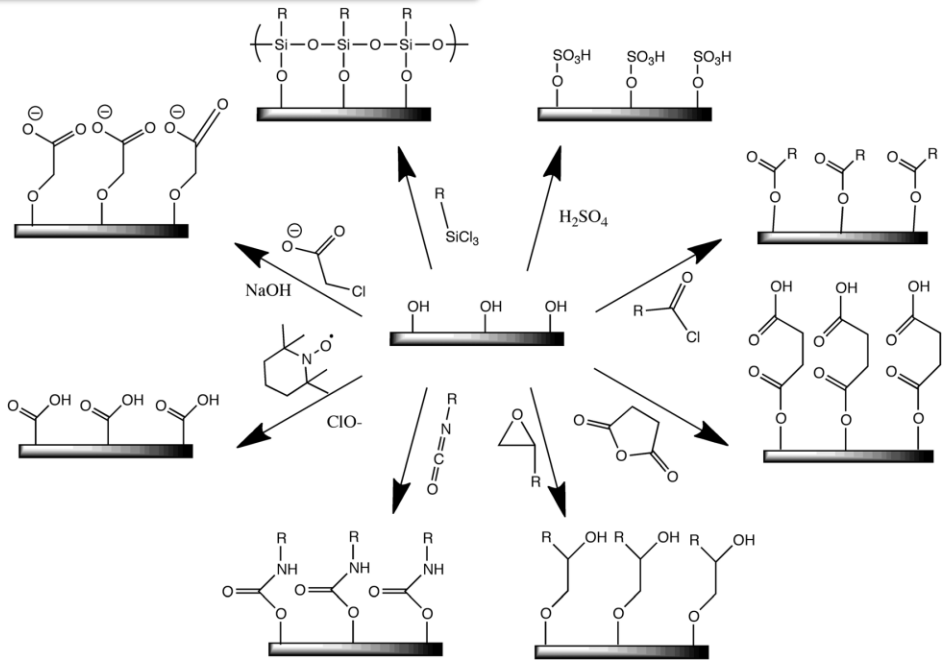
Moon et al., Chem Soc Rev 2011.

Surface Modification:

Induce New Functionality

- Readily Reactive Surface: -OH
- Alter Particle-Particle, & Particle-Matrix

Covalent Bonding

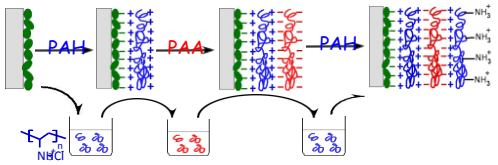


- TEMPO regioselective oxidation
- sulfonation
- halogenated acetic acids
- carboxylic acid halides
- acid anhydrides
- epoxides
- isocyanates
- chlorosilanes

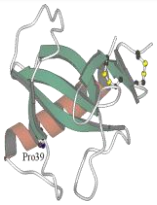
Moon et al., Chem Soc Rev 2011.

Surface Modification:

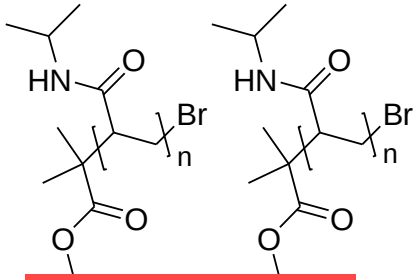
Polyelectrolyte multilayers



Proteins



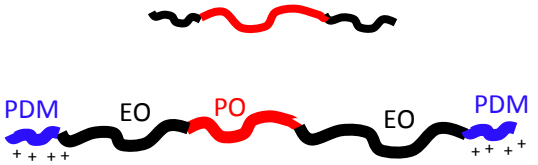
Polymer grafting

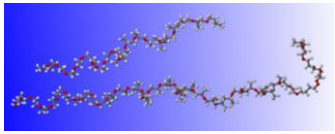


poly(NiPAAm)-g-CNCs

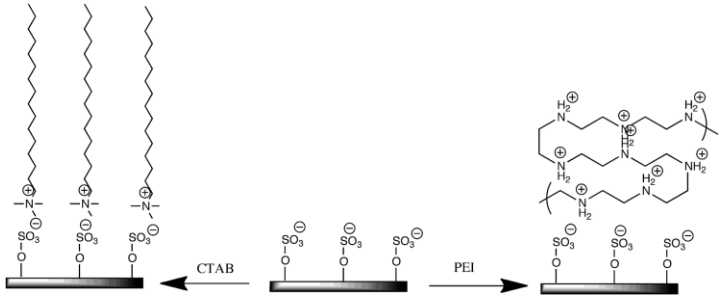
Roy et al., Chem Soc Rev, 38, 2046-2064,2009

Amphiphilic copolymers



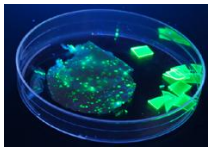


Surfactants

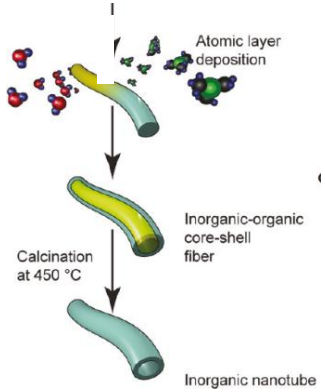


Moon et al., Chem Soc Rev 2011.

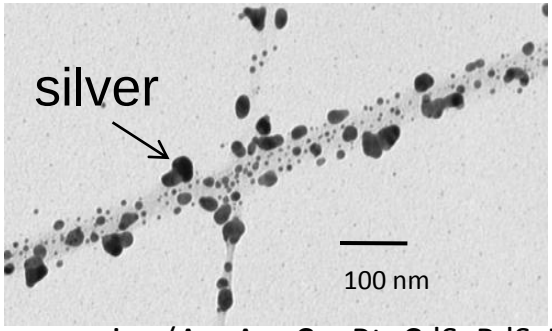
NPs, ALD, QDs



D. Grey
http://www.mcgill.ca/pprc/members/gray/quantum/



Korhonen, ACSNano 2011



- processing (Ag, Au, Cu, Pt, CdS, PdS, ZnS)

Padalkar et al., Langmuir, 2010,

Grand Challenge: CN Characterization

Key Challenges:

- Increased Fidelity
- Quantification
- Anisotropy Effects
- Application
  - high Throughput
  - Representative volume
  - Combination of Techniques

Technique Summary:

- Microscopy: light, e-, ion, scanning probe
- Diffraction: e-, neutron, x-ray
- Inelastic Scattering: Raman
- Scattering: DLS,
- Spectroscopy: NMR, IR, FTIR,
- Rheology:
- Thermal: TGA/DTA
- Etc

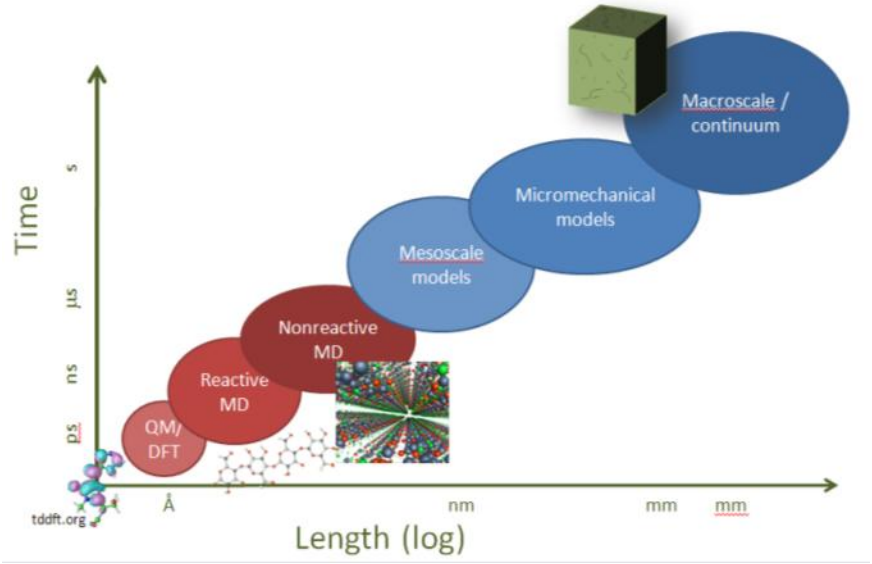
Needed Information:

- Morphology
  - Size, aspect ratio, uniformity
  - Degree of Branching
  - distribution, etc
- Surface Chemistry
  - Functional Group
  - Charge, etc.
- Surface Area
- Crystallinity
- Molecular Mass
- Rheology
- Material Properties
  - Mechanical, Thermal, Electrical

Grand Challenge: Modeling

Key Challenges:

- Multiple-Length Scales
  - Atoms → Structures
  - Atomistic → Analytical
- Validation/Verification
  - Linked to experiments
  - Linked to other modeling
- Predictive Capabilities

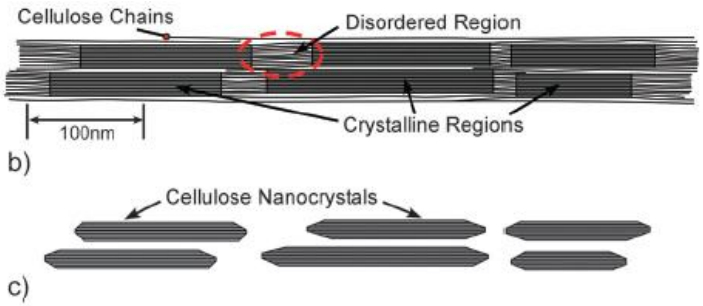


Modeling Areas:

- CN Particles
  - Size, aspect ratio, uniformity
  - Structure
  - H-bonding
  - Defects & Branching
- CN Suspensions
  - Water Interactions
  - Chemical interaction
  - Surface Reactivity
- CN Composites
  - CN-CN interactions
  - CN-Matrix Interactions
  - interfaces

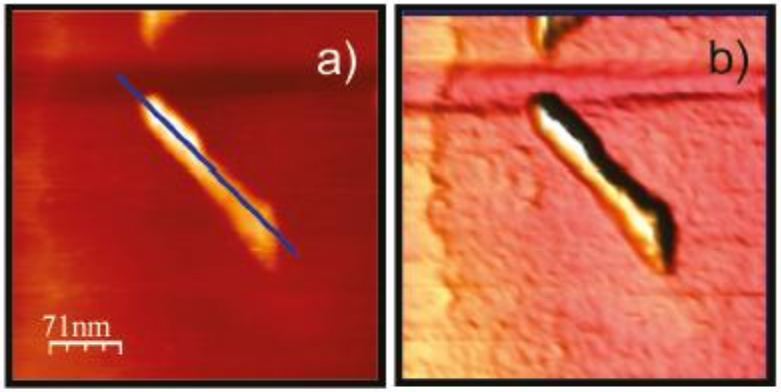
Thank YOU

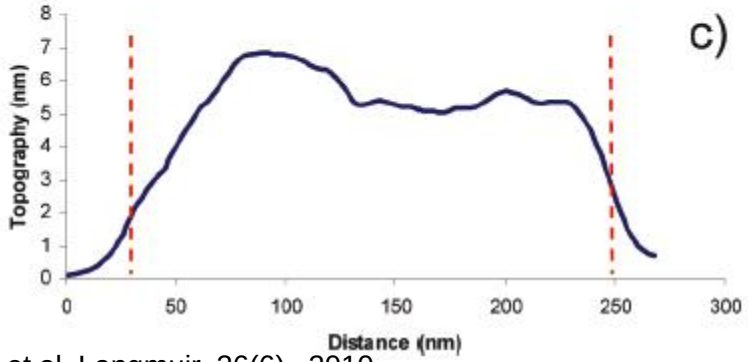
Ideal CNC Morphology?

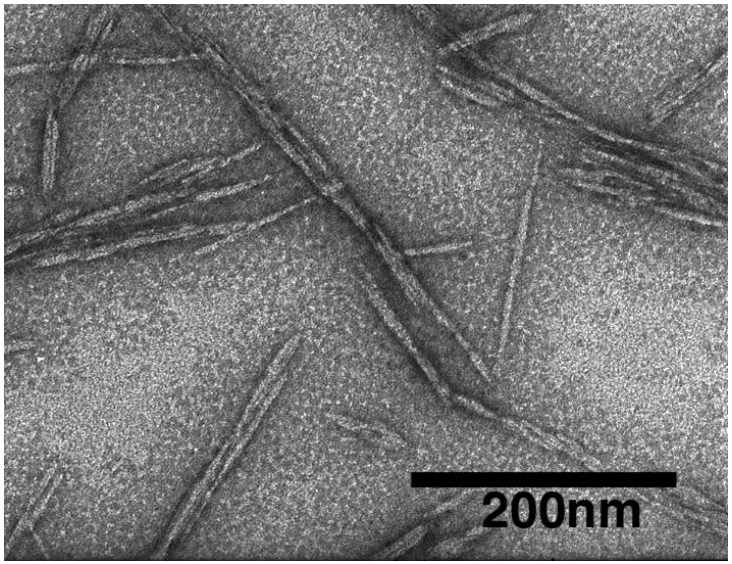


In Reality:

- Steps
- divots







Lahiji et al. Langmuir, 26(6) , 2010