Benchmarking Cellulose Nanocrystals Part II: New Industrially-Produced Materials

Sustainable NaNO BiO Composites

UBC

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TAPPI NANO DIVISION

Research Program: Bridging the Gap

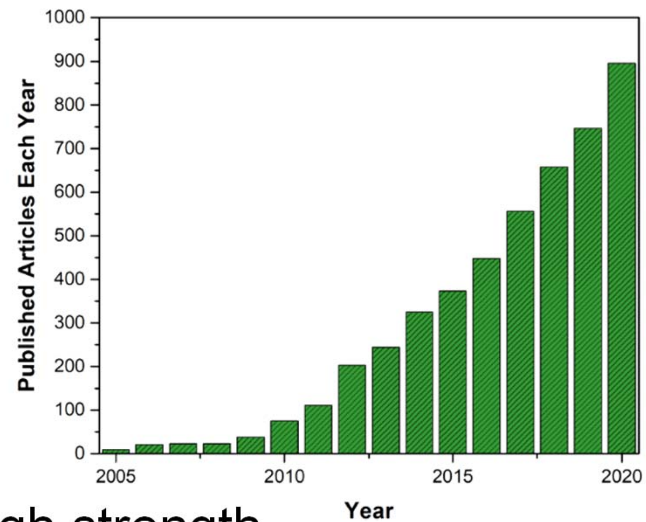
Establish cellulose nanocrystals (CNCs) as a material platform

New CNC properties for strategic industries:
Mechanical, thermal, rheological, optical, adhesive, colloidal stability, absorbency, bio-interactions, etc.

New science & technology which will lead to new markets for wood pulp and biomass

Current Aspects of CNC Research

- Increased research in academia



- High strength
- Low density
- High aspect ratio
- Biodegradability
- Optical properties & self-assembly

- Increased interest in industry with an **increase in large-scale production** of CNCs

ALBERTA PACIFIC FOREST INDUSTRIES INC

BLUE GOOSE BIOREFINERIES INC.™

noram group

InnoTech ALBERTA

Melodea Bio Based Solutions

Anomera

- Oil and gas fluids
- Cement and concrete
- Adhesives
- Water remediation
- Coatings

Objectives

- Benchmarking study by Reid *et al.* in 2017
  - H_2SO_4 hydrolyzed CNCs only
  - Emphasis on CNC characterization protocols
  - Importance of knowing your starting material
  - Small differences can affect the performance of CNCs

Need for up-to-date information as new, industrial CNCs emerge!

LANGMUIR
Invited Feature Article
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Benchmarking Cellulose Nanocrystals: From the Laboratory to Industrial Production

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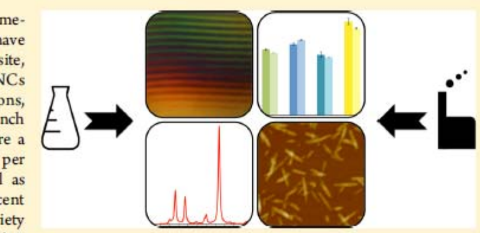
Supporting Information

ABSTRACT: The renewability, biocompatibility, and mechanical properties of cellulose nanocrystals (CNCs) have made them an attractive material for numerous composite, biomedical, and rheological applications. However, for CNCs to shift from a laboratory curiosity to commercial applications, researchers must transition from CNCs extracted on the bench scale to material produced on an industrial scale. There are a number of companies currently producing kilogram to ton per day quantities of sulfuric acid-hydrolyzed CNCs as well as other nanocelluloses, as described herein. With the recent intensification of industrially produced CNCs and the variety of cellulose sources, hydrolysis methods, and purification procedures, the characterization of these materials becomes critical. This has further been justified by the past two decades of research that demonstrate that the CNC stability and behavior are highly dependent on the surface chemistry, surface charge density, and particle size. This work outlines key test methods that should be employed to characterize these properties to ensure a "known" starting material and consistent performance. Of the sulfuric acid-extracted CNCs examined, industrially produced material compared well with laboratory-made CNCs, exhibiting similar charge density, colloidal and thermal stability, crystallinity, morphology, and self-assembly behavior. In addition, it was observed that further purification of CNCs using Soxhlet extraction in ethanol had minimal impact on the nanoparticle properties and is unlikely to be necessary for many applications. Overall, the current standing of industrially produced CNCs is positive, suggesting that the evolution to commercial-scale applications will not be hindered by CNC production.



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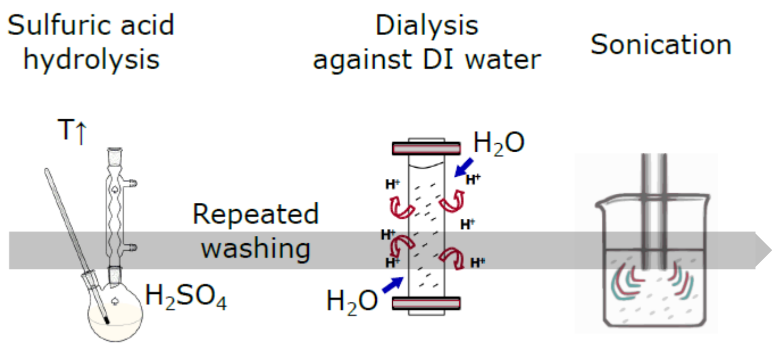
The Five CNC Samples

- **Lab-made CNCs (CNC-LM)**
  - Whatman filter paper (shredded)
  - 64 wt% H_2SO_4
  - 45 min
  - 45 °C
  - Quenched 10-fold
  - Dialyzed
  - Sonication + filtration



- **NORAM**
  - Hard- and softwood dissolving pulp
  - Sulfuric acid hydrolysis
  - 500 kg/day in a **continuous process**
  - 61 wt% H_2SO_4
  - 120 min
  - 55 °C
  - Received: 3 wt%, pH 6.8
  - Dialyzed: NORAM-D

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The Five CNC Samples

- **Melodea**
  - Sulphuric acid hydrolysis
  - 10 tonne/year
  - Received: 3.5 wt%, pH 4.5
  - **H_2SO_4 recovery program**
  - Dialyzed: Melodea-D

- **Anomera**
  - Carboxylated CNCs
  - **Hydrogen peroxide oxidation**
  - 1 tonne/year
  - Received: freeze-dried
  - Dialyzed: Anomera-D

- **Blue Goose Biorefineries (BGB)**
  - Carboxylated CNCs
  - **Transition-metal-catalyzed oxidative method**
  - Received: 8 wt%, pH 5.8
  - Dialyzed: BGB-D

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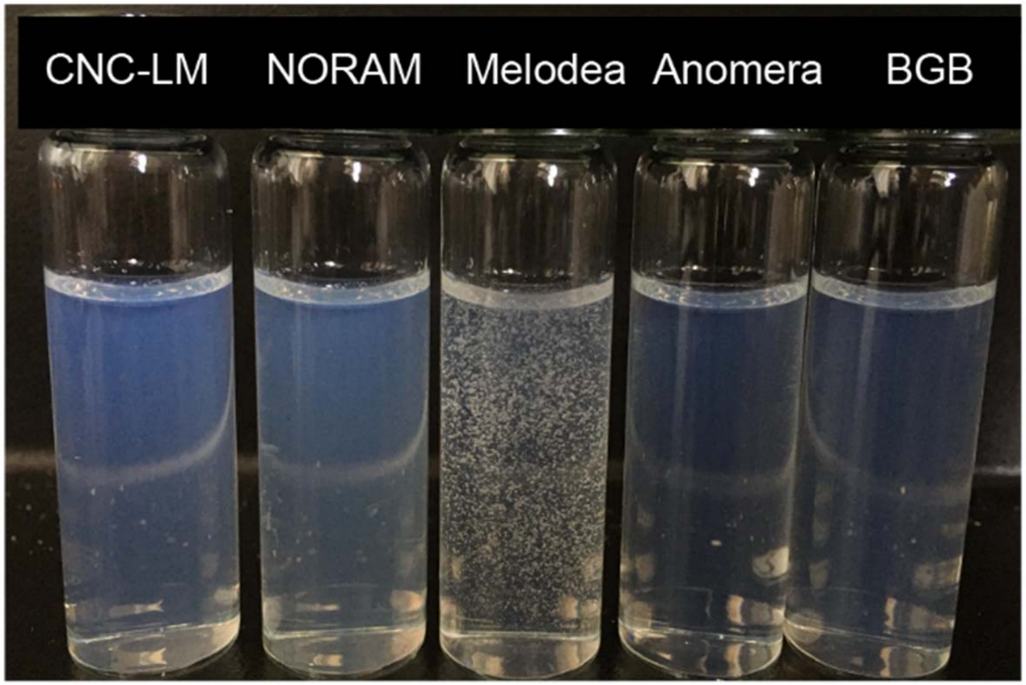
Physical Appearance of CNCs

- All CNCs can be easily dispersed and are colloidally stable
- Melodea CNCs are more viscous (trap air)

Sulfated CNCs　　Carboxylated CNCs



CNC suspensions at 1 wt%

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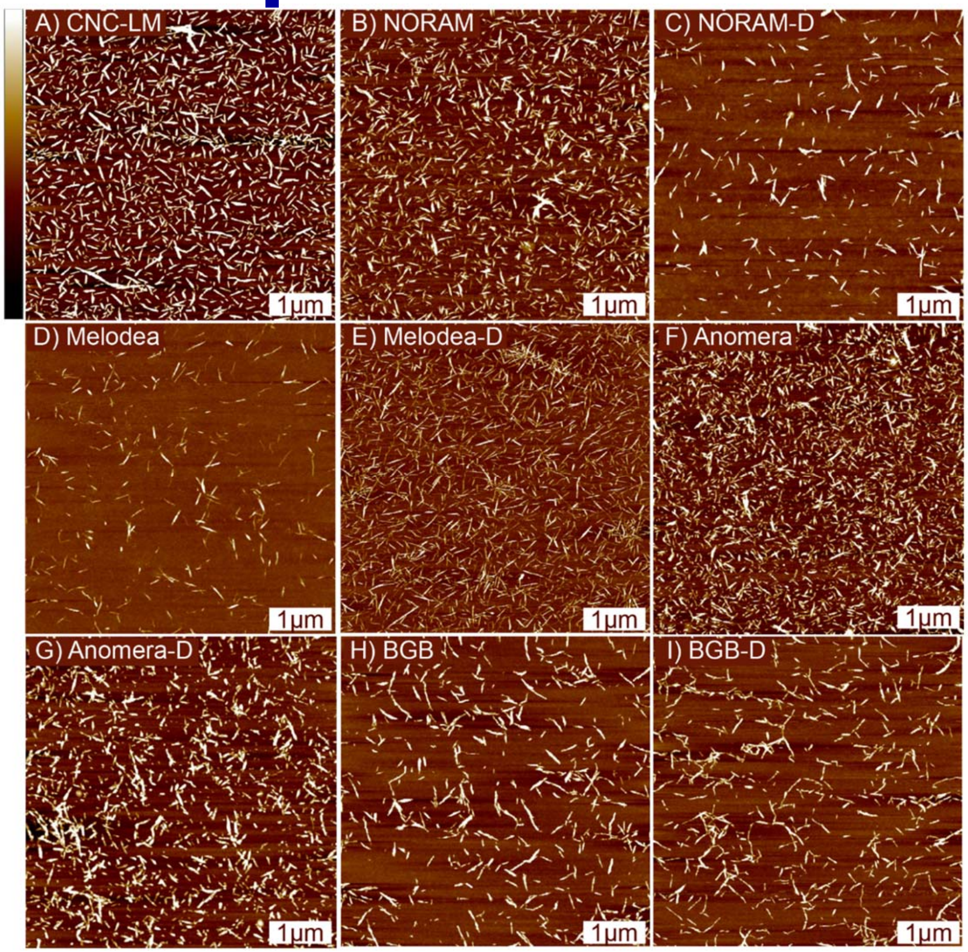
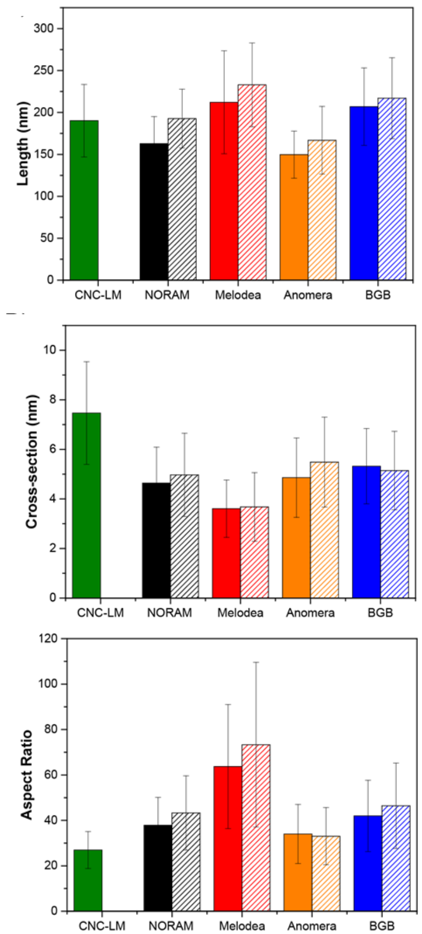
Nanoparticle Size & Structure





- All rod-shaped particles
- Aspect ratios 27 – 80
- Lowest: CNC-LM
- Highest: Melodea
- No change in size after purification

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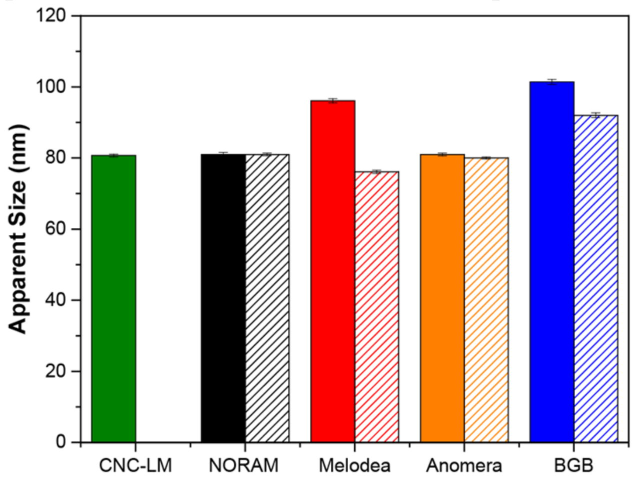
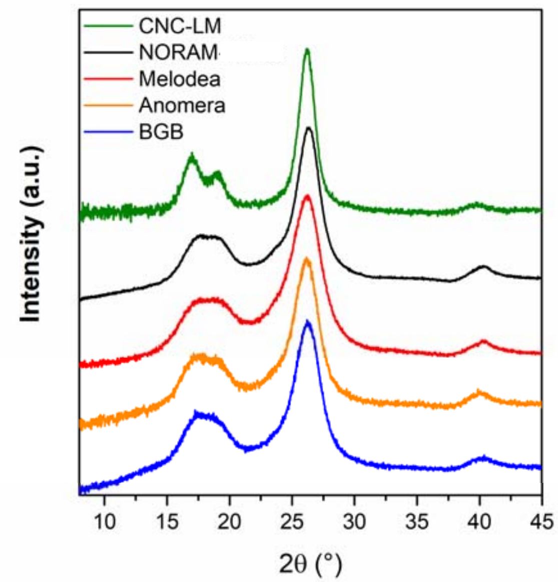
Nanoparticle Size & Structure

Apparent Size and Dispersion Quality



X-ray Diffraction



- CNC-LM, NORAM, and Anomera CNCs have similar apparent sizes
- Melodea and BGB show slight aggregation (residual ions)

- All samples are cellulose I (79 – 93%)
- Highest: CNC-LM & BGB

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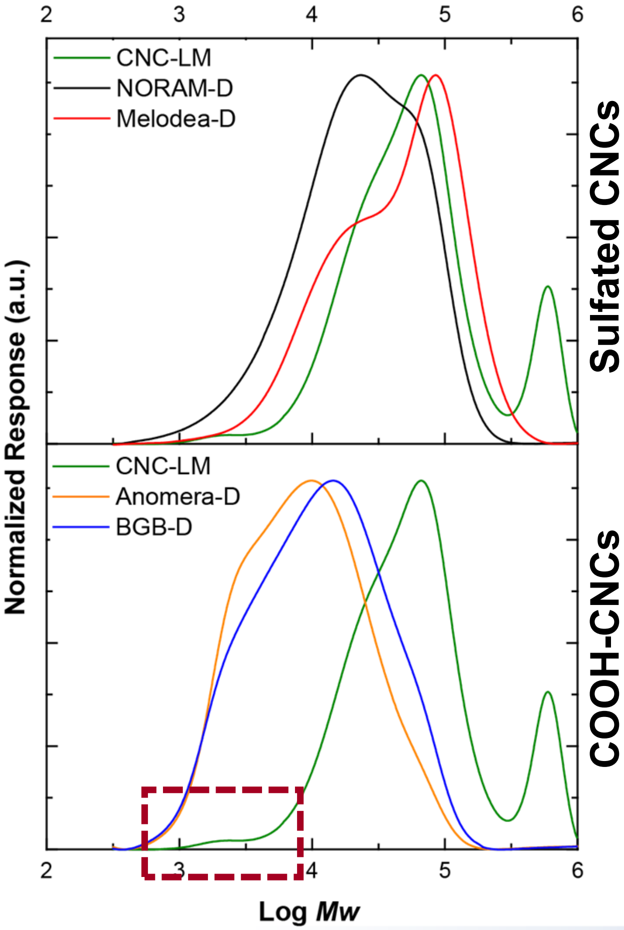
Cellulose Degree of Polymerization



- Cellulose in CNCs was derivatized and solubilized in DMSO for GPC
- M_w distribution of the cellulose chains is shifted to higher M_w for sulfated CNCs
  - Sulfated CNCs: breaking of β-1-4 glycosidic (ether) bond in the less ordered regions of cellulose
  - Carboxylated CNCs: oxidation routes break the C2-C3 bond of glucose (not necessarily in the disordered regions)
- CNC-LM has a low M_w peak ➔ surface oligosaccharides

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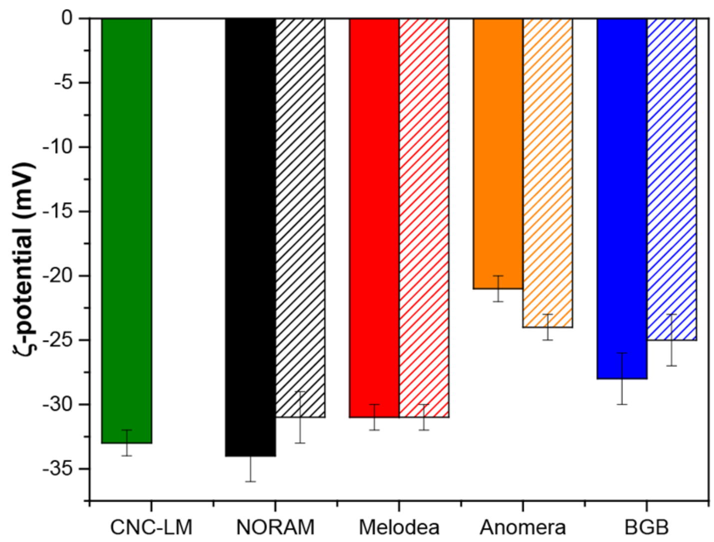
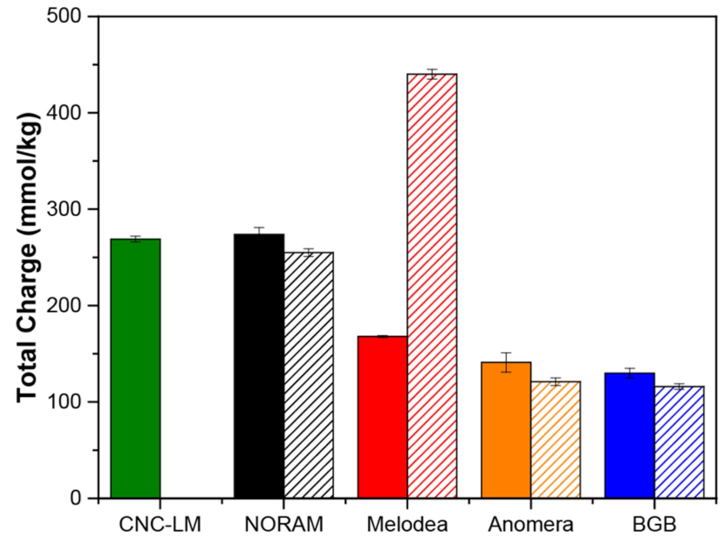
Colloidal Stability & Surface Charge



- Lower ζ-potential for carboxylated CNCs compared to sulfated CNCs
- Carboxylated CNCs are slightly less colloidally stable



- Lower total charge for carboxylated CNCs compared to sulfated CNCs
- Carboxylated CNCs are more sensitive to pH

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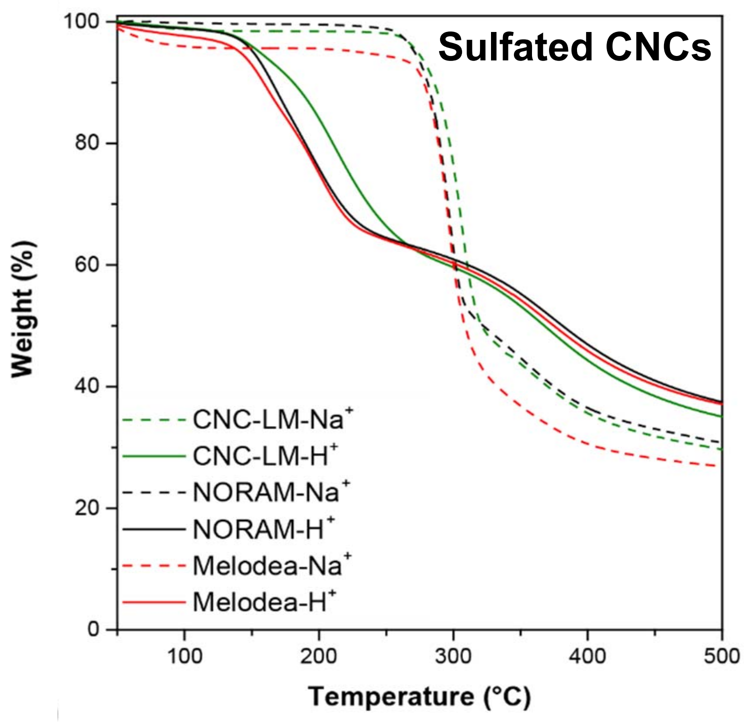
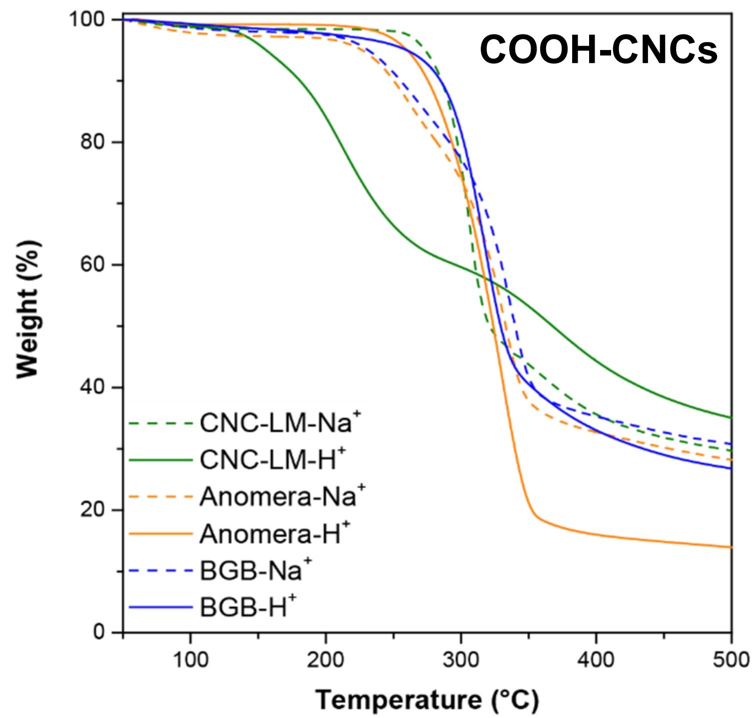
Thermal Stability





- Counterion is important for thermal stability

Vanderfleet et al. *Cellulose* **2019**, *26*, 507.
D'Acierno et al. *Biomacromolecules* **2020**, *21.* 3374.

- COOH-CNCs are more thermally stable than sulfated CNCs

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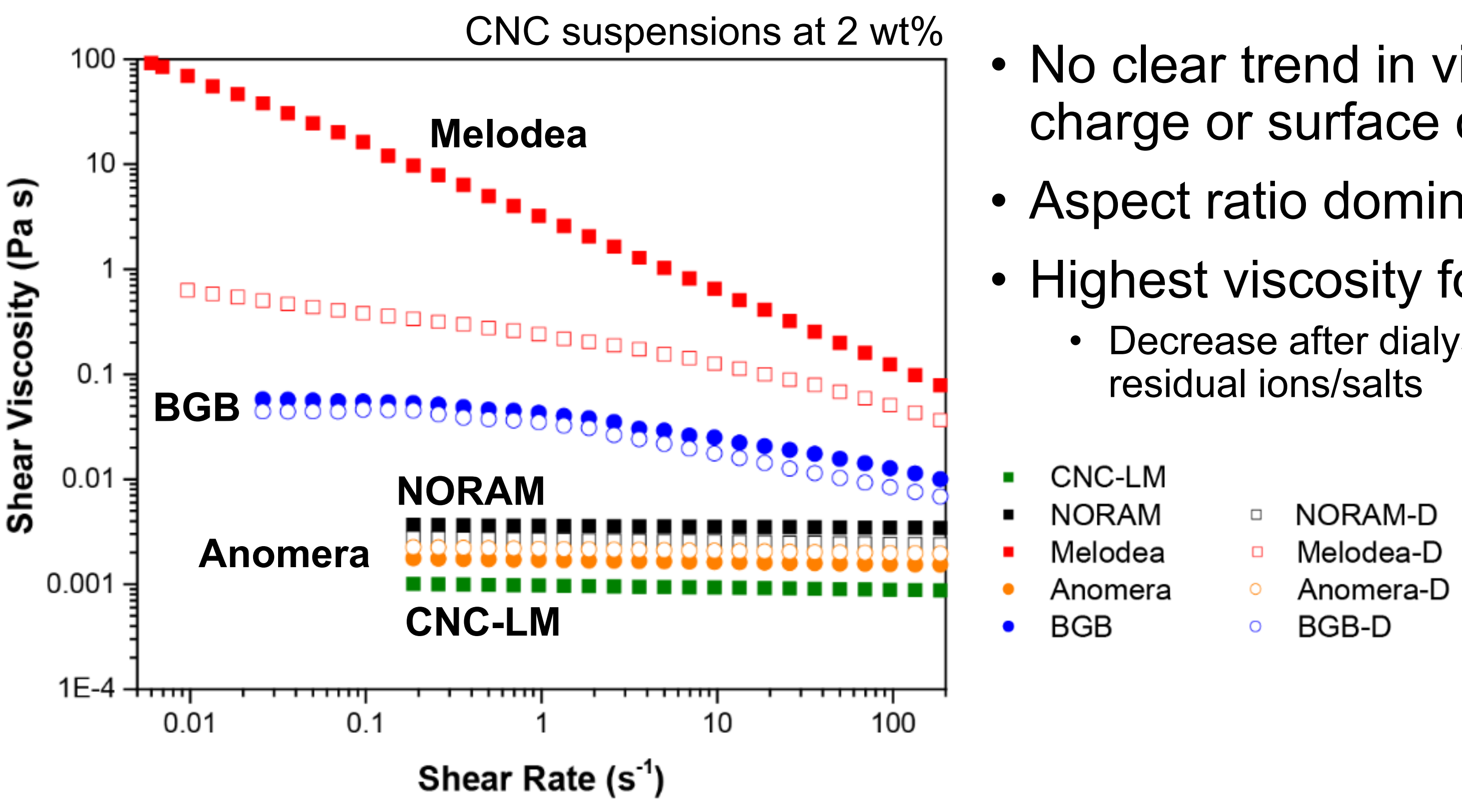
Rheology



- No clear trend in viscosity with surface charge or surface chemistry
- Aspect ratio dominates rheology
- Highest viscosity for Melodea CNCs
  - Decrease after dialysis due to removal of residual ions/salts

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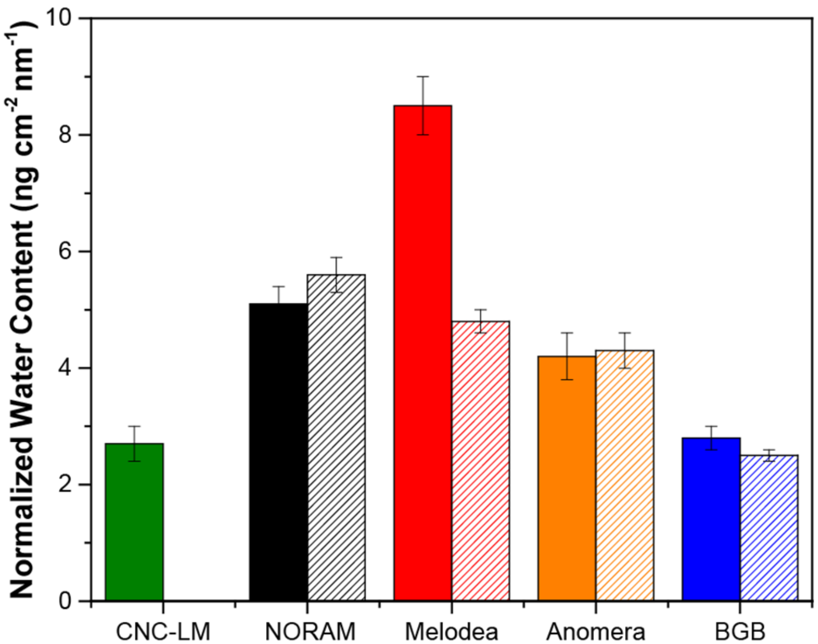
Water Binding Capacity



- Quartz crystal microbalance with dissipation monitoring was used with D_2O exchange to measure bound surface water
- CNC-LM: surface oligosaccharides ➔ low water binding capacity due to disruption of the bound water layer
- BGB CNCs: low surface charge (and a larger surface area than Anomera CNCs)
- Melodea CNCs: decrease of water binding capacity after dialysis

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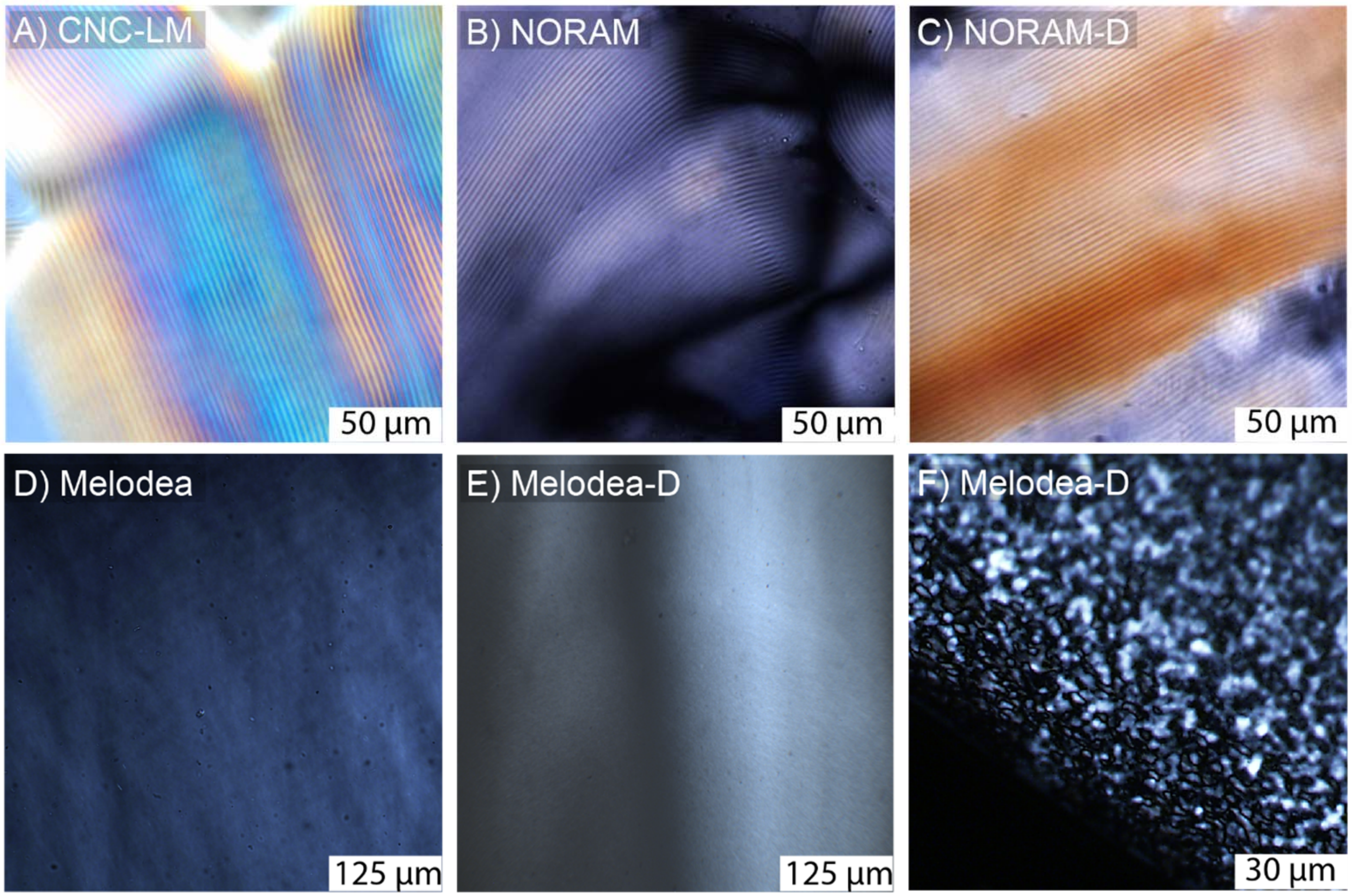
Liquid Crystals & Self-Assembly



- Sulfated CNCs (except Melodea) show chiral nematic self-assembly and phase separation above a critical concentration
- Melodea CNCs show a nematic liquid crystal phase
  - Probably due to high suspensions viscosity

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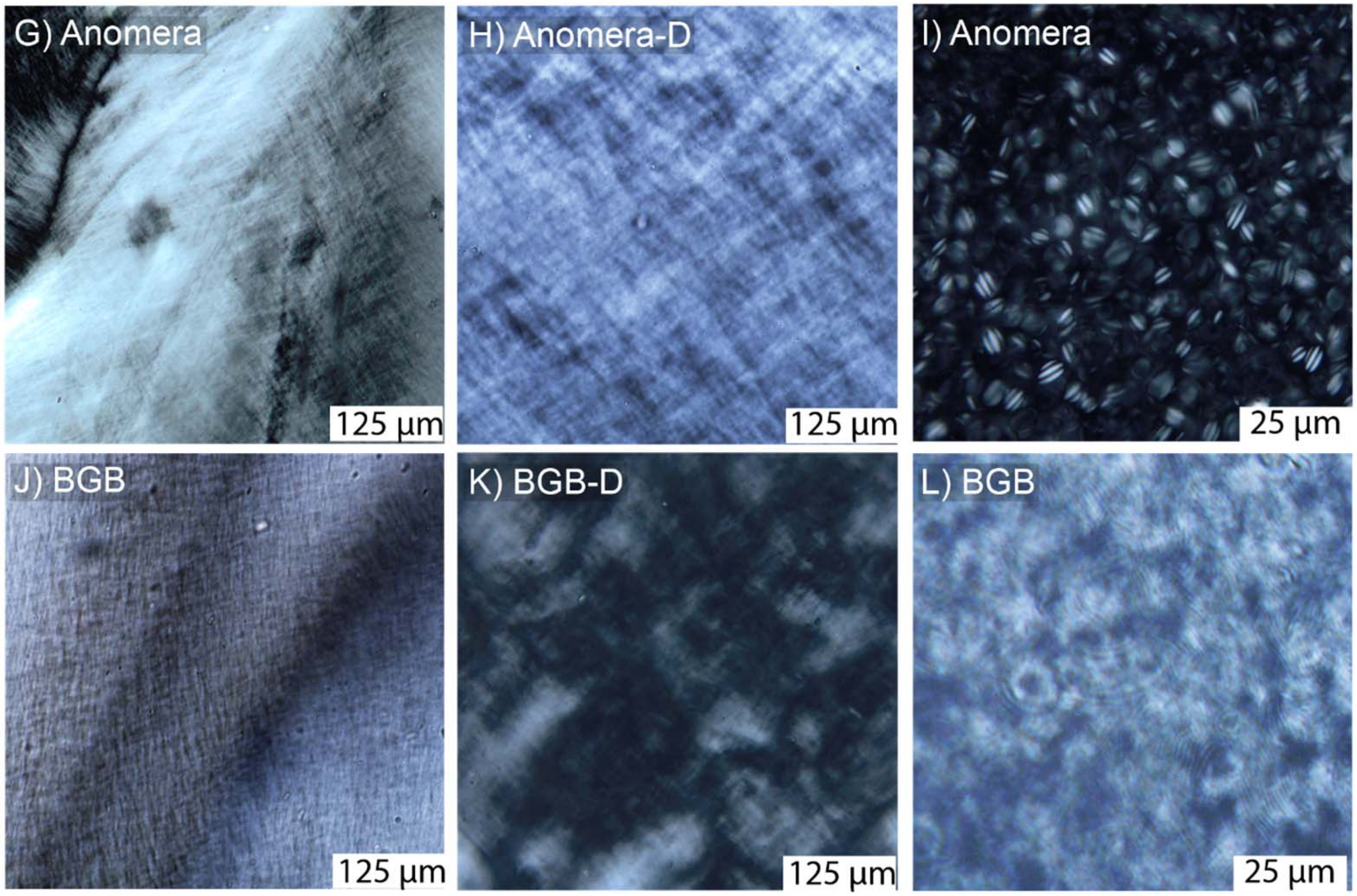
Liquid Crystals & Self-Assembly



- Carboxylated CNCs studied here do not phase separate
  - Probably due to the low surface charge density
- But…chiral nematic tactoids are observed upon drying droplets
  - Small pitch and/or the pitch might be under the microscope resolution

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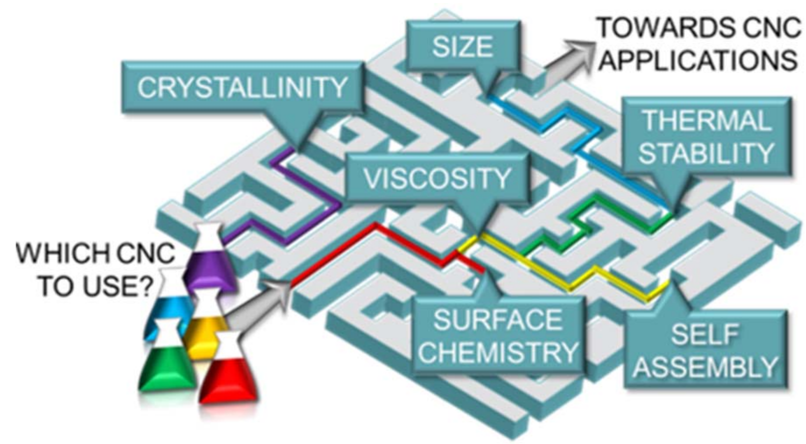
Conclusions

- We benchmarked 4 new industrially produced CNCs against sulfated lab-made CNCs
- **What are the main differences?**
  - Carboxylated CNCs have a lower surface charge density
  - Carboxylated CNCs are more thermally stable
  - Sulfated CNCs (except Melodea CNCs) self-assembled into chiral nematic liquid crystalline phases
- **What is the effect of process modifications on the properties of sulfated CNCs?**
  - NORAM CNCs are produced with a lower acid-to-pulp ratio in a continuous process, but have very similar properties to CNC-LM
  - Melodea uses a simplified cost-saving purification process, resulting in CNCs with slightly different properties



Guide for CNC-users looking to improve their CNC-based materials

Thank You!

- Gwenn for making the slides!
- Students & Collaborators
  - Tiffany Abitbol (RISE)
  - Clarite Azerraf (Melodea)
  - Geoff M. Clarke (AlPac)
  - James Lockhart (BCRI)
  - Sean McAlpine (BGB)
  - Timothy Morse (Anomera)
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- TAPPI staff, leadership & conference organizers

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