International Conference on Nanotechnology for Renewable Materials

Improving Cellulose Nanocrystal Performance via a Sugar Precipitation Modification Route

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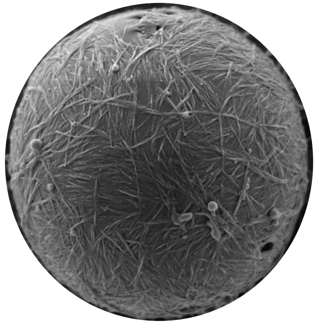
Introduction to Cellulose Nanocrystals (CNCs)

Emulsion stabilizers[a]



Ultra-lightweight aerogels[c]

Structural colours[b]

Challenges for CNC Utilization:

- **Hydrophilicity prevents** nanocelluloses from being used to their **full potential** in several **applications**.
- The **colloidal stability of nanocellulose** is **sensitive** to its environment.

[a] Kalashnikova et al. *Biomacromolecules* **2012**, *12*, 1, 267.; [b] Blonder et al., *Art Exhibition, Eretz Israel Museum* 2017.; [c] Yang & Cranston *Chem. Mat.* **2014**, *26*, 20, 6016.

The Motivation for Polymer Surface Modification of CNCs

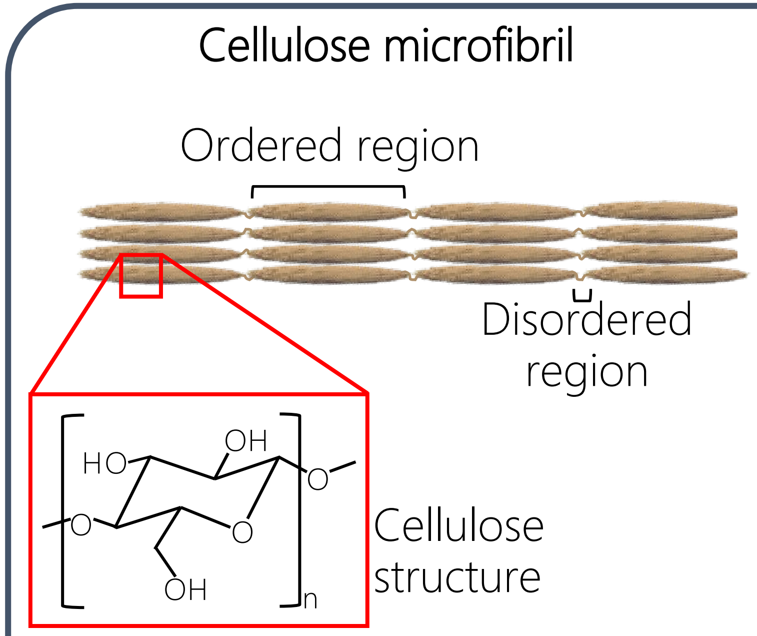
1. Induce steric stability
2. Impart hydrophobicity or enhance amphiphilicity

Categories of Polymer Surface Modification:

covalent

non-covalent

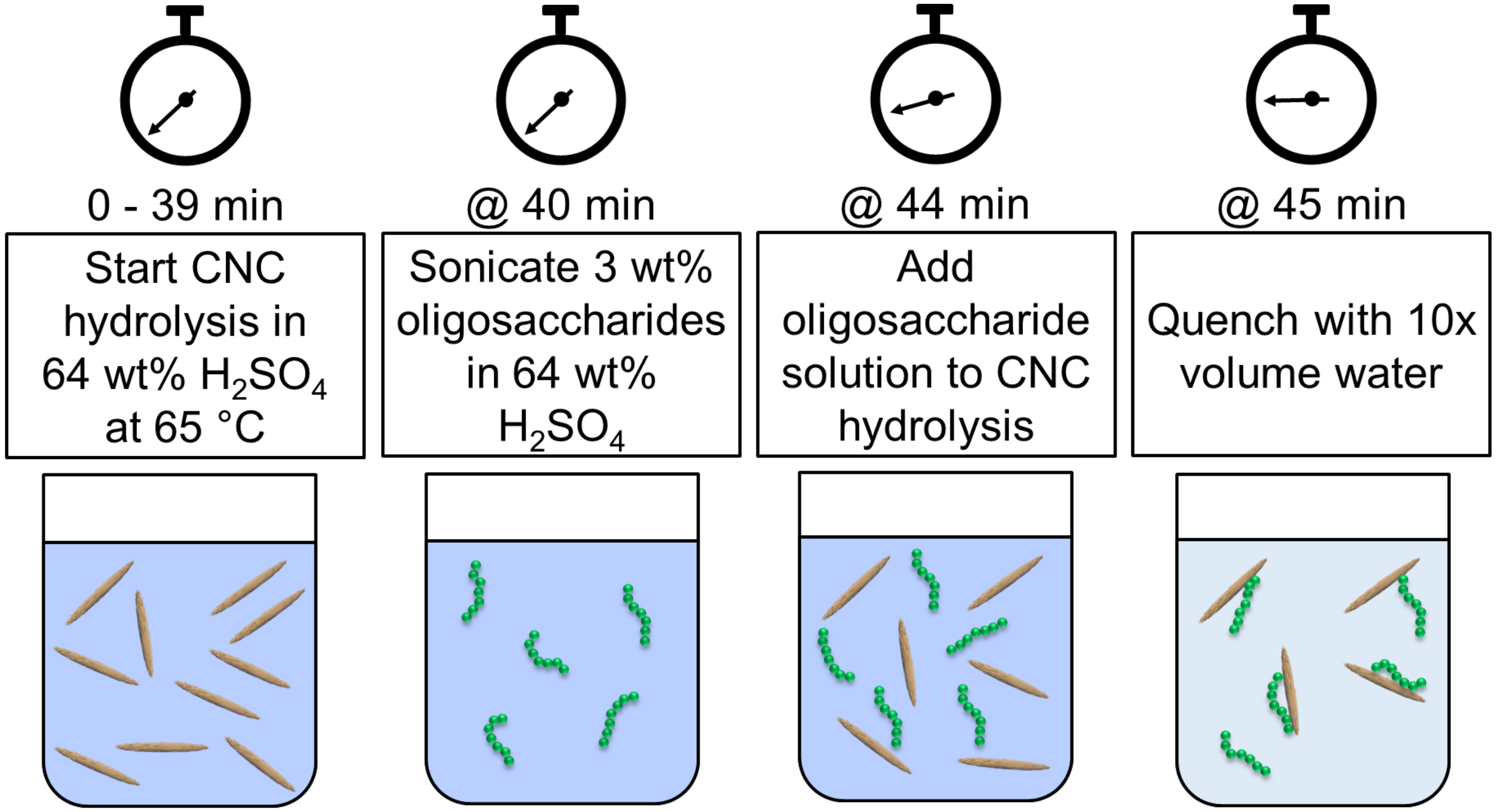
Oligosaccharides Are a Byproduct of CNC Hydrolysis



Byproduct oligosaccharides **decrease** suspension **viscosity**,[a] **improve colloidal stability** in high ionic strength media,[a] alter **self-assembly** behaviour,[a,b] and **hinder reproducibility** of surface modification chemistries.[c]

[a] Bouchard et al. *Cellulose*, **2016**, *23*, 3555.; [b] Beck et al. *Biomacromolecules*, **2011**, *12*, 167.; [c] Labet & Thielemans *Cellulose*, **2011**, *18*, 607.

In-situ Oligosaccharide Surface Modification of CNCs

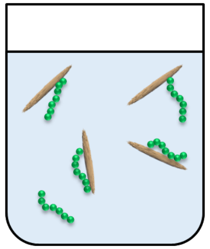


No harsh chemicals or additional **post-production clean up** is required!

Easy to scale up or implement in **existing production lines**!

Niinivaara, et al. *Biomacromolecules* **2021**, *22*, 8, 3284.

Confirming Oligosaccharide Presence on CNC Surfaces



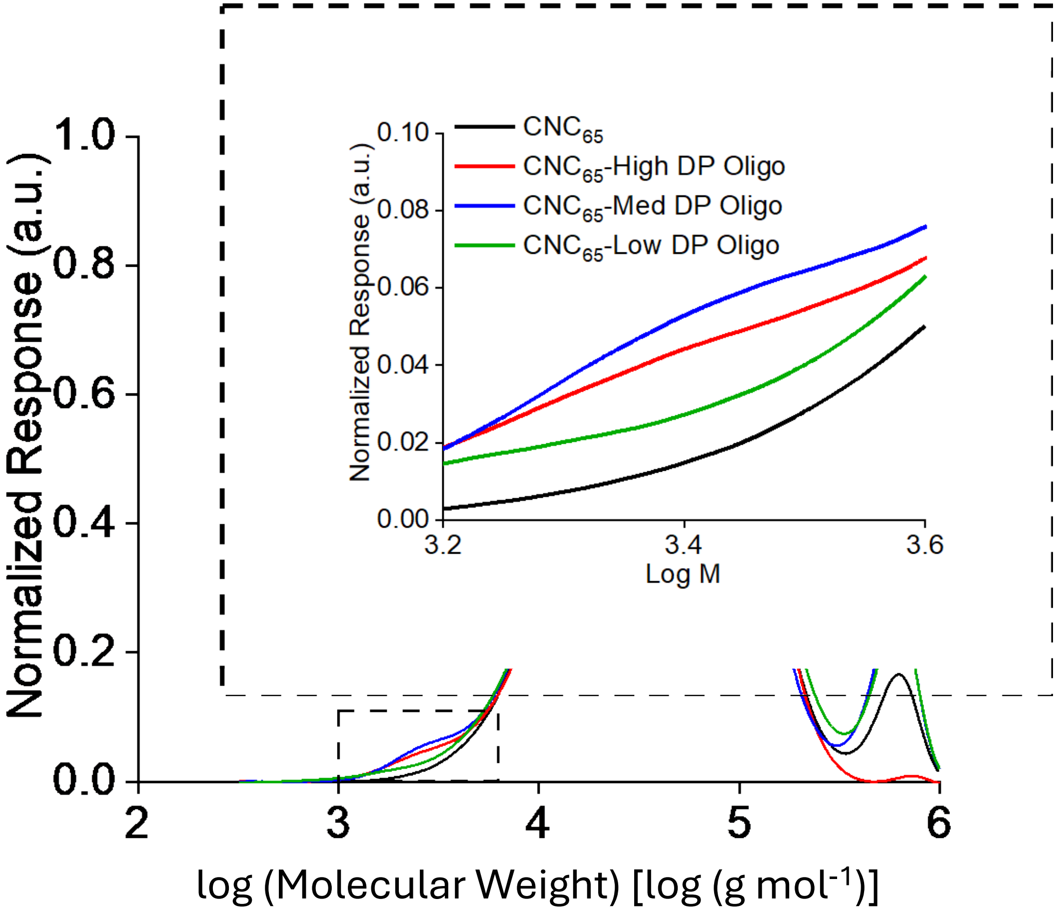
Change in molecular weight distribution confirms presence of oligosaccharides but oligosaccharide content on CNC does not increase with DP!

CNC Surface coverage:

High DP Oligo: 27 %

Medium DP Oligo : 84 %

Low DP Oligo: 10 %

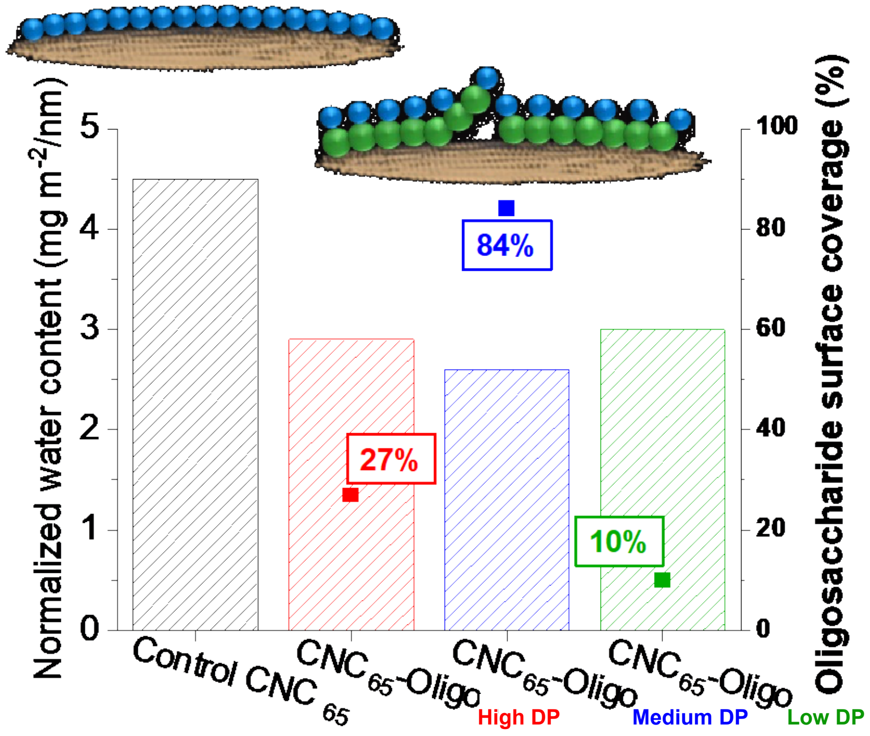


Medium-DP oligosaccharide exhibited the **best CNC-surface coverage**!

Niinivaara, et al. *Biomacromolecules* **2021**, *22*, 8, 3284.

How Oligosaccharides Change CNC Performance

Water Uptake Capacity:



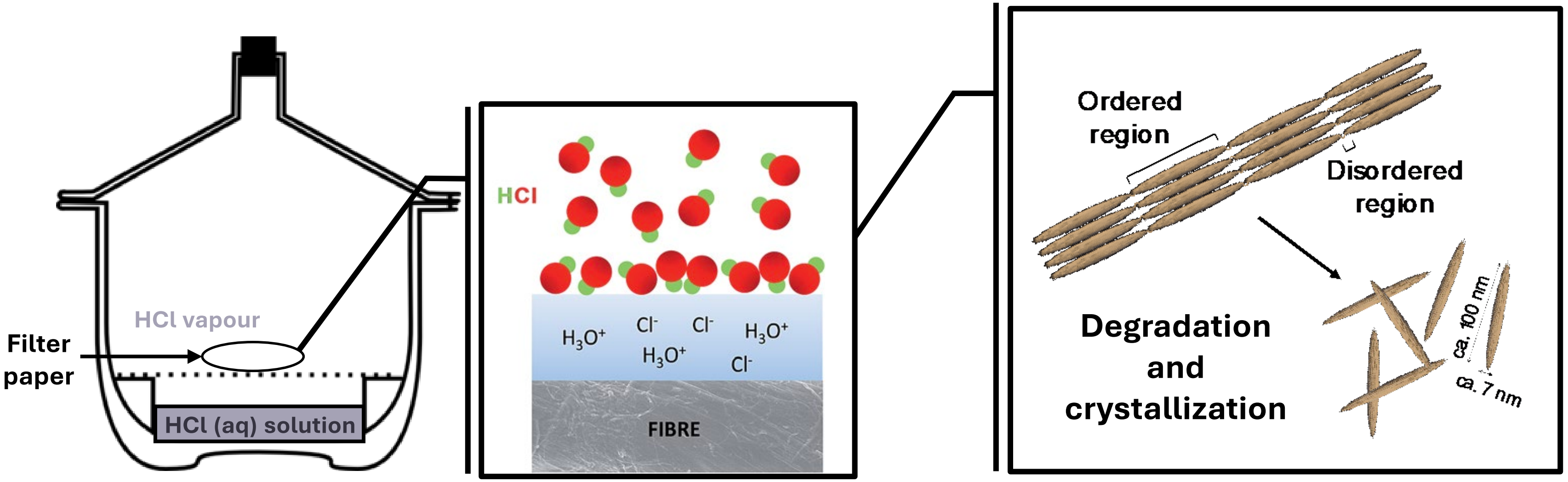
Presence of oligosaccharides **decreases water adsorption** as **surface coverage increases**.

In addition, there was **no observable difference** to the **thermal behavior** of control and modified CNCs.

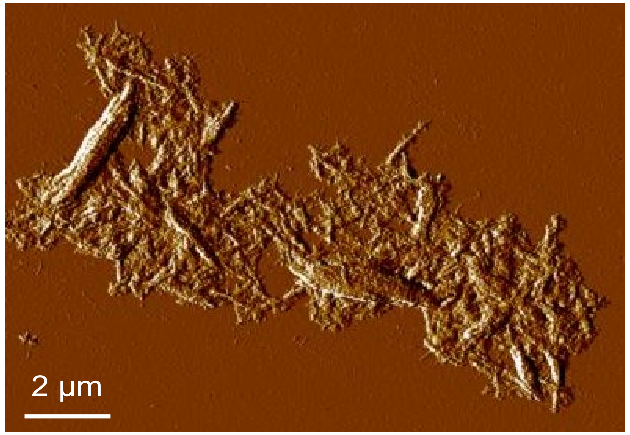
But, surface oligosaccharides did **slightly reduce the viscosity** of CNC suspensions in line with expectations.

Shifting Gears: HCl Vapour-Hydrolyzed CNCs

HCl vapour hydrolysis is an extremely efficient method to produce uncharged CNCs:



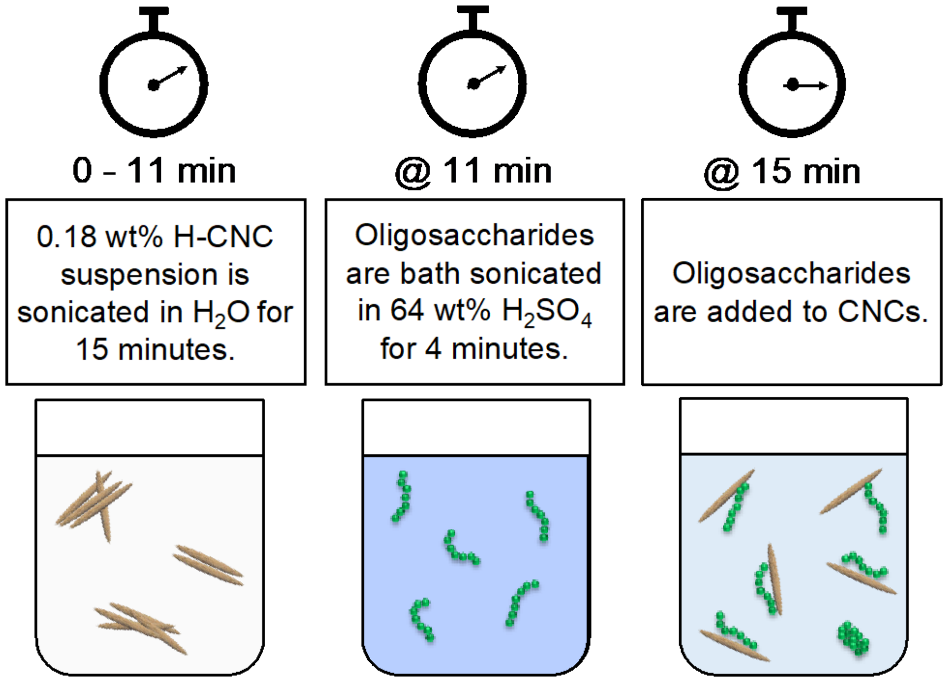
HCl vapour-hydrolyzed Whatman + 15 min sonication



This method does not involve any mass transfer, so the **yield is almost 100%** but CNCs can **not be easily isolated or dispersed in water** due to lack of charge.

Lorenz, et al. *Faraday Discuss.* **2017**, *202*, 315.; Kontturi, et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 14455.

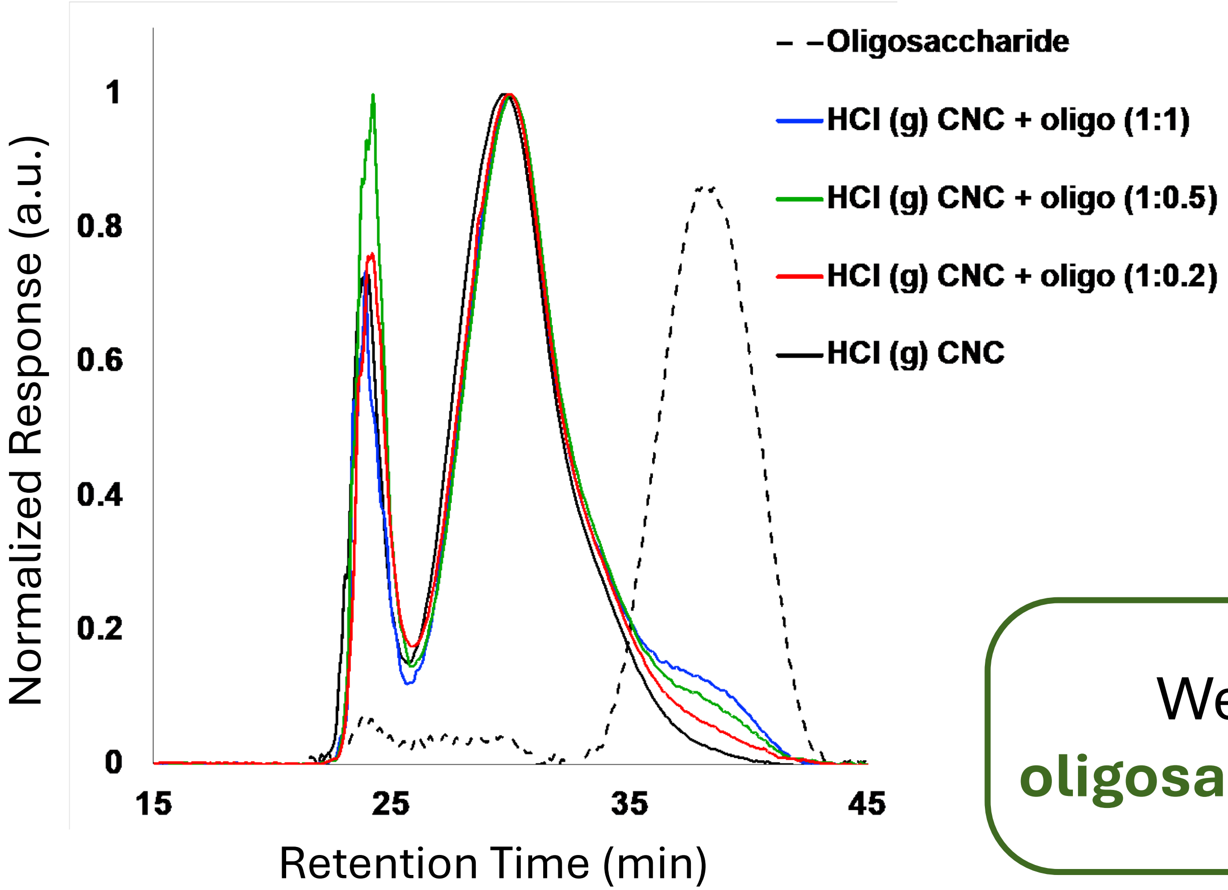
Post-Hydrolysis Oligosaccharide Surface Modification of CNCs



The sudden **change in pH** causes the solubilized **oligosaccharides to immediately precipitate** and crystallize on the **surface of HCl-hydrolyzed CNCs**.

Confirming Oligosaccharide Presence on CNC Surfaces

Size Exclusion Chromatography



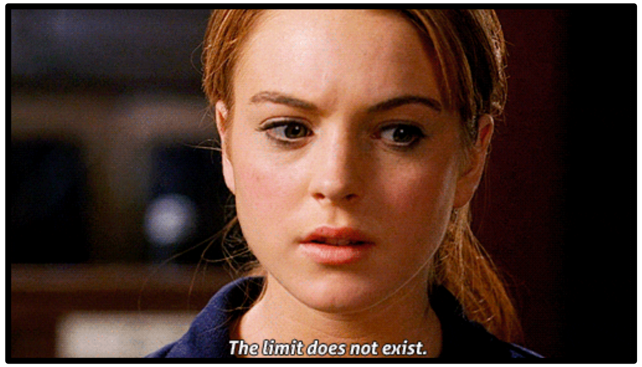
Elemental Analysis

Note the oligosaccharides were hydrolyzed using H_3PO_4 (aq)

	ppm ^{15}P
HCl (g) CNC	6 ± 1
HCl (g) CNC + oligo (1:0.2)	39 ± 9
HCl (g) CNC + oligo (1:0.5)	99 ± 6
HCl (g) CNC + oligo (1:1)	170 ± 10

We are able to **control the amount of oligosaccharides** on the HCl-hydrolyzed CNCs!

Pushing the Limit of this Modification



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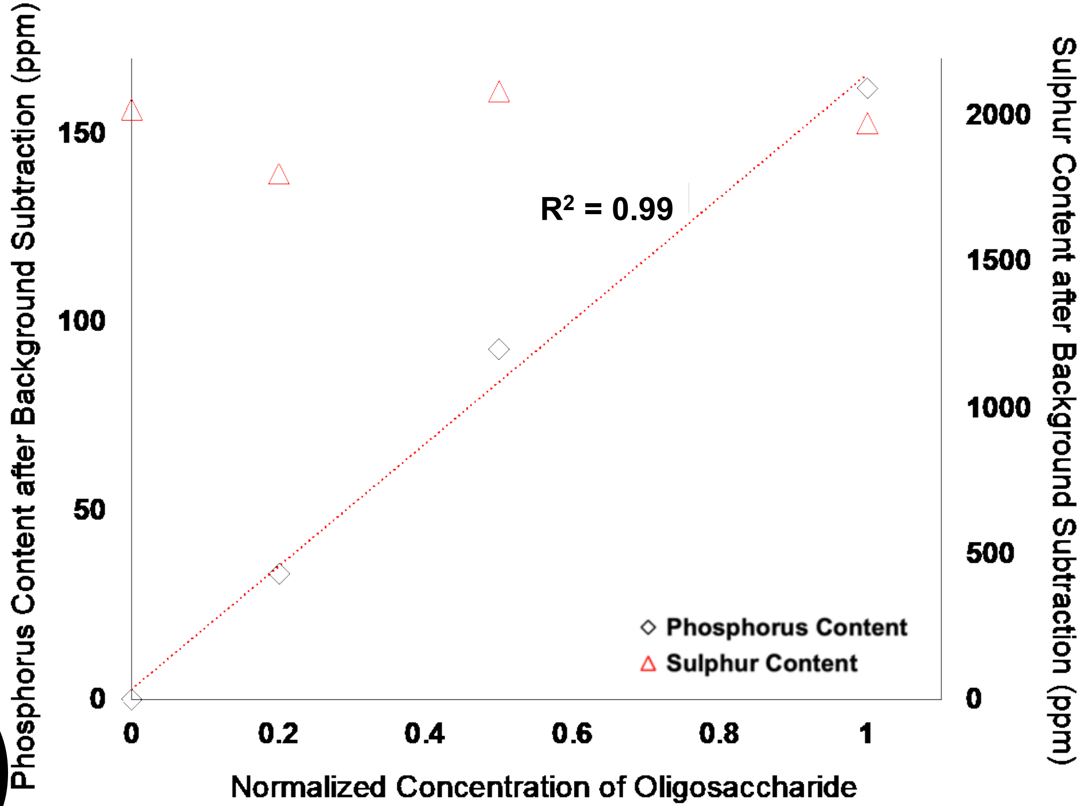
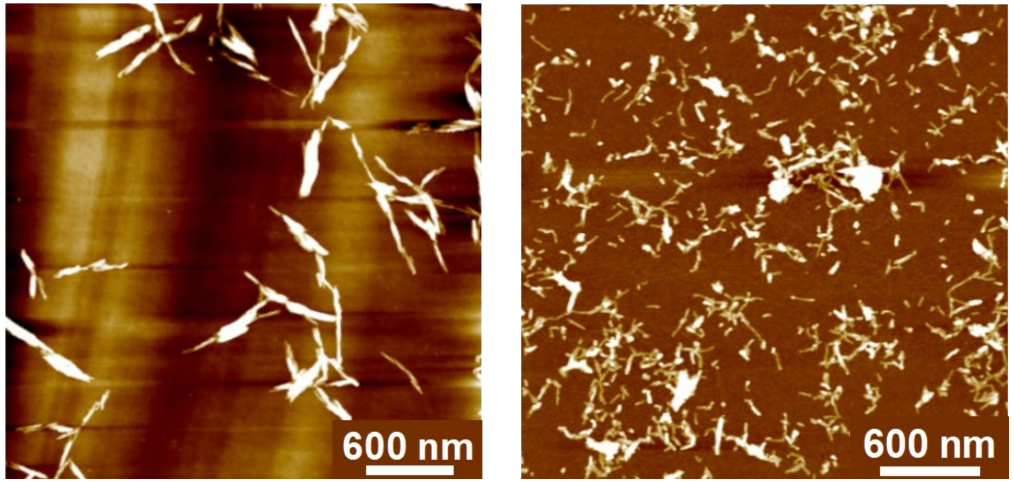
* The values for % yield are approximations. They are calculated by comparing the measured phosphorus content against the theoretical yield (i.e., if all the oligosaccharide added ends up on the CNC surface).

The **efficiency** of the surface modification **increases with oligosaccharide concentration.**



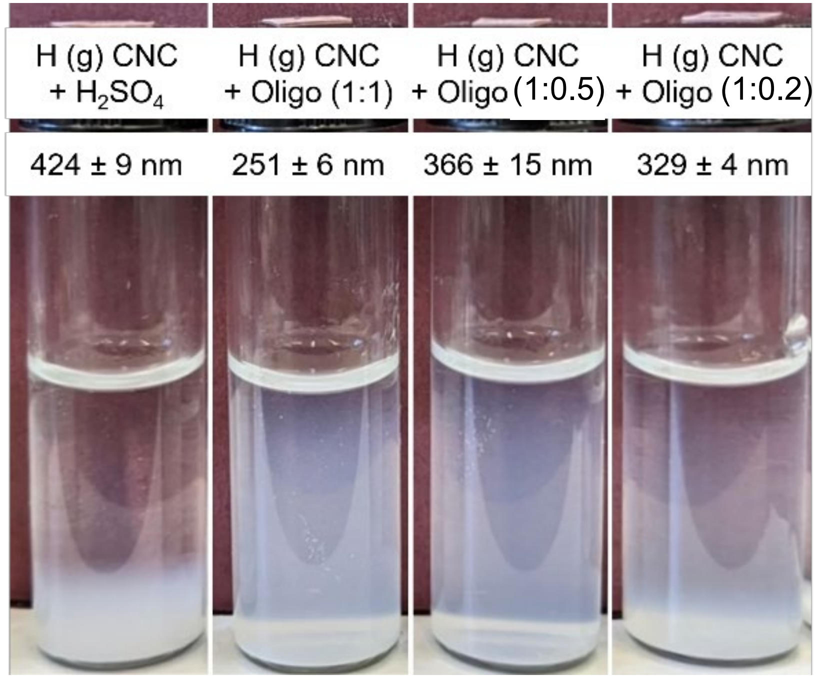
Improving HCl (g) CNC Dispersibility

HCl (g) CNC + H_2SO_4 HCl (g) CNC + oligo (1:1)



D = 424 ± 9 nm; ζ = -11 ± 3 mV D = 251 ± 6 nm; ζ = -11 ± 4 mV

Solutions of CNCs after 1 month on the bench



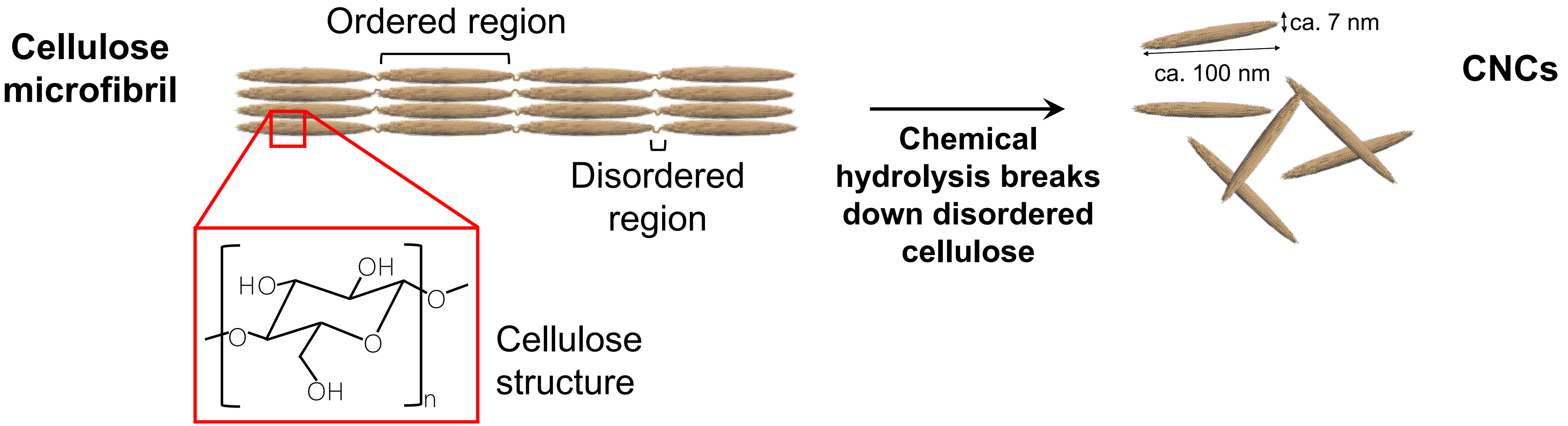
Presence of oligosaccharides on uncharged CNCs:

- Enables isolation of ‘individual’ CNCs
- Decreases the apparent particle size in without affecting ζ-potential

Dispersity **is maintained** by the presence of oligosaccharides.

Extending Modification to Aqueous HCl-Hydrolyzed CNCs

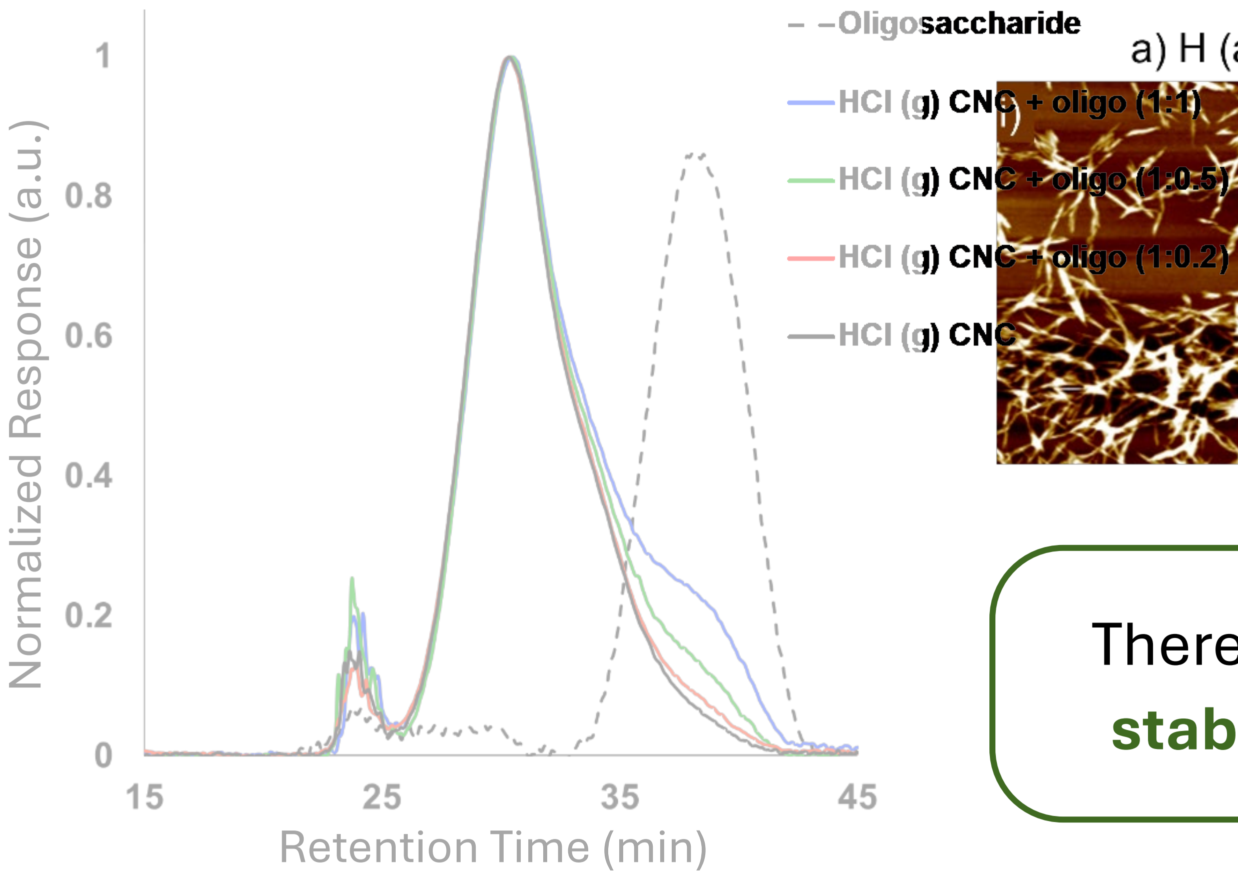
Aqueous HCl hydrolysis is a more common method to produce uncharged CNCs.



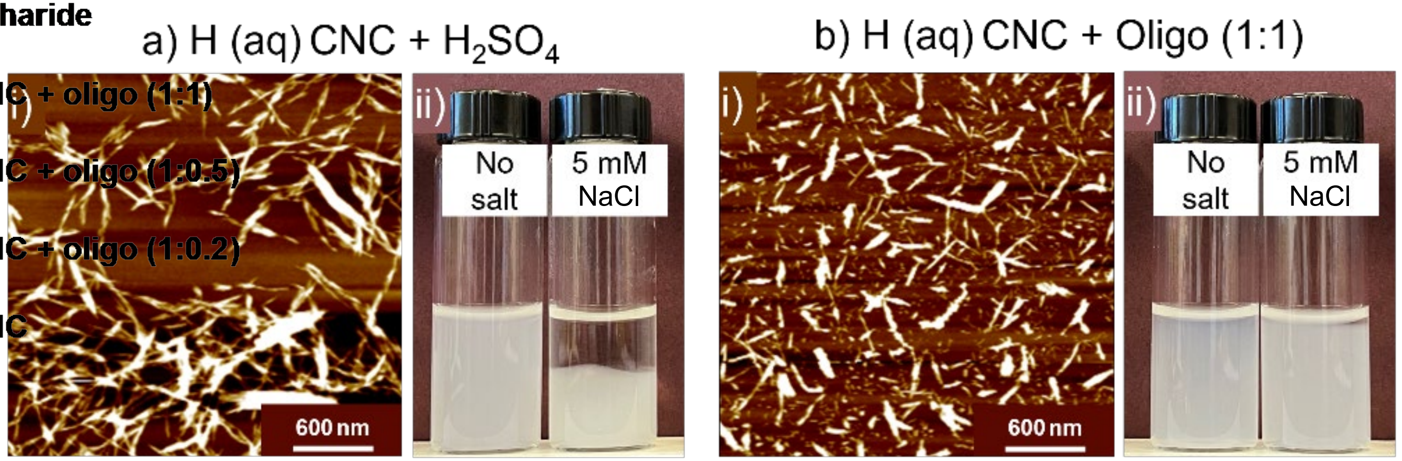
The **yields of this reaction are high** but not quantitative. The resulting material is similar in dimension and crystallinity to sulphated CNCs but **less colloidally stable**.

Improving HCl (aq) CNC Colloidal Stability

Size Exclusion Chromatography



Visualizing Colloidal Stability



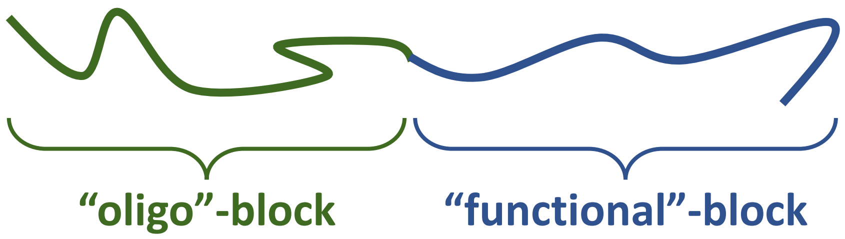
There is **increased resistance of colloidal stability to ionic strength** after 24 hours.

Summary

- Oligosaccharides can be precipitated onto CNC surfaces after their production
- We are able to control the amount of oligosaccharides that precipitate on CNCs
- This modification can be used to improve the dispersibility of uncharged CNCs produced using HCl Vapour and the colloidall stability of uncharged CNCs produced using aqueous HCl.

What's Next?

Attempt synthesis of oligosaccharide-based block copolymers without sacrificing selective solubility.



These block copolymers may be used to impart new properties to CNCs including:

1. Enhanced steric stability;
2. Hydrophobicity; or,
3. Other more complex chemistries!

Thank You!

THE UNIVERSITY OF BRITISH COLUMBIA

Prof. Emily Cranston
Dr. Elina Niinivaara
Cameron King

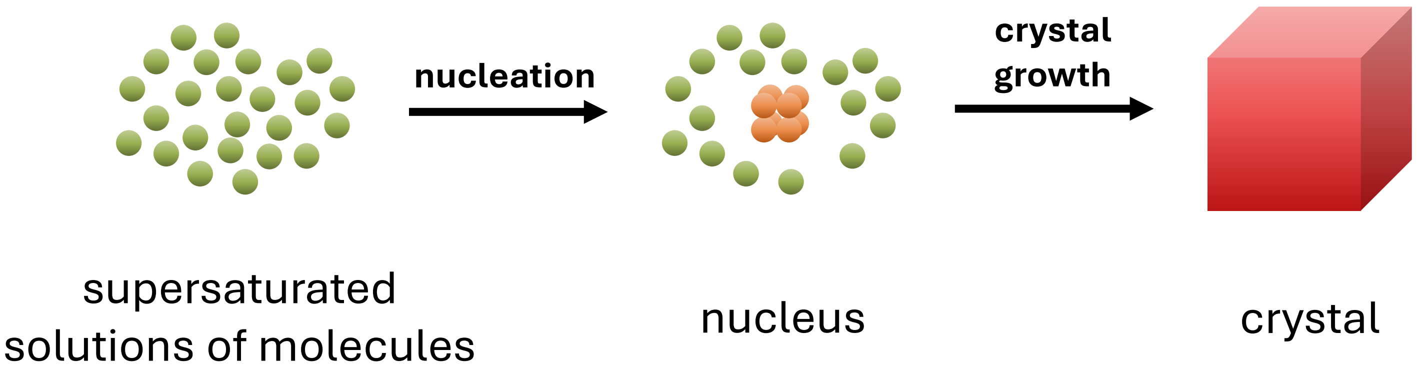
All group members past and present!

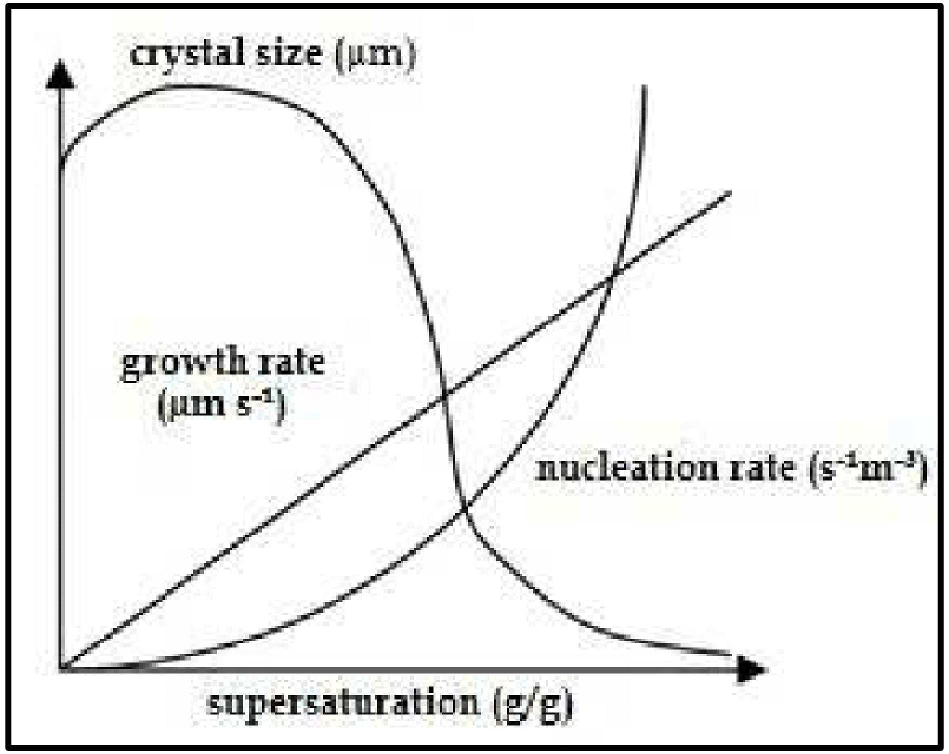
NSERC
CRSNG

BioProducts Institute

Questions?

How Can This Behaviour Be Explained?





Supersaturation is a condition that gets met as physical environments change. It is **necessary** for both **crystallization and precipitation**. Increasing solution concentration increases supersaturation.