Aalto University
School of Chemical
Technology

Nanocellulose: modification during preparation

CHEM-L2010
Cellulose chemistry

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8th June 2023

Learning objectives

After this lecture, you should be able to:

- Explain why nanocellulose is important
- Distinguish cellulose nanofibres (CNFs) and cellulose nanocrystals (CNCs)
- List the main preparation routes to CNFs and CNCs
- List the main routes to modification during the preparation of nanocellulose

Outline

(1) Different types of nanocellulose: Terminological issues
(2) Preparation of nanocellulose:
- Cellulose nanofibres (CNF) (including bacterial cellulose)
- Cellulose nanocrystals (CNC)

(3) Modification of CNF
(4) Modification of CNC

Types of nanocellulose

(1) Cellulose nanofibres
- mechanically isolated microfibrils
- chemically isolated microfibrils (TEMPO-oxidation)
- bacterial cellulose

(2) Cellulose nanocrystals
- rods of highly crystalline cellulose, isolated by acid hydrolysis

Types of nanocellulose: terminological issues

(1) Cellulose nanofibres

Synonyms (used in literature) for mechanically isolated nanofibrillar cellulose:

- microfibrillar cellulose
- cellulose nanofibrils
- cellulose microfibrils

(2) Cellulose nanocrystals

Synonyms used in literature:

- cellulose whiskers
- cellulose nanowhiskers
- cellulose microfibrils
- microcrystalline cellulose
- nanocrystalline cellulose

Note: microcrystalline cellulose is in its more common use a completely different material (micron-sized cellulose crystals).

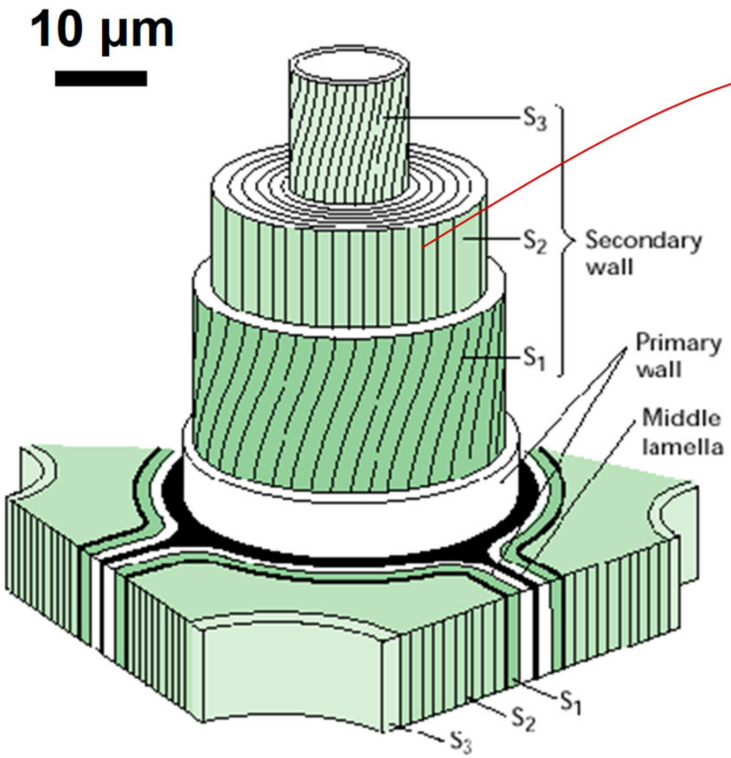
Cellulose nanofibres: preparation

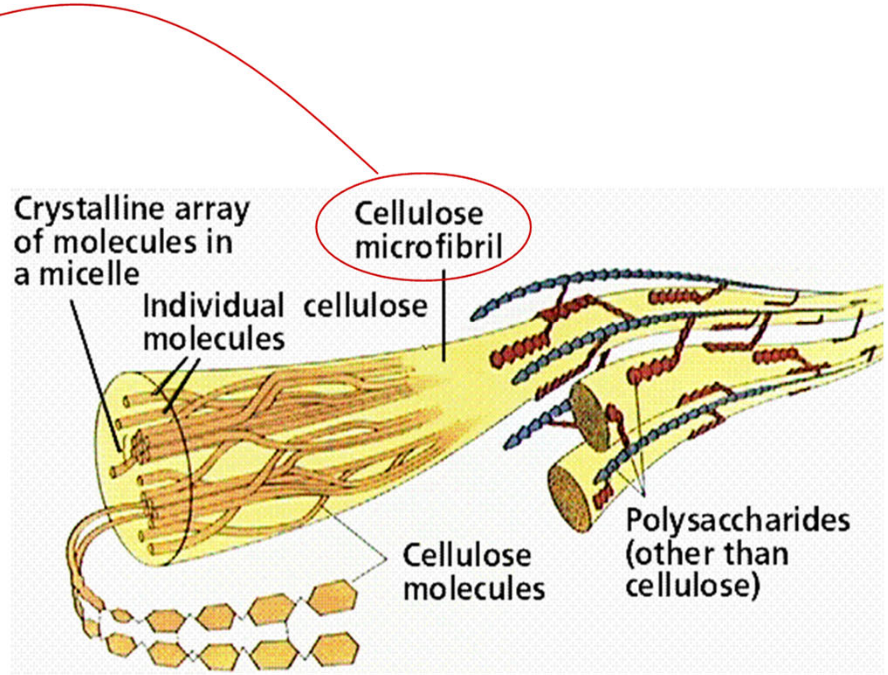
Ultrastructure of native cellulose

Individual fibre

Cellulose microfibril

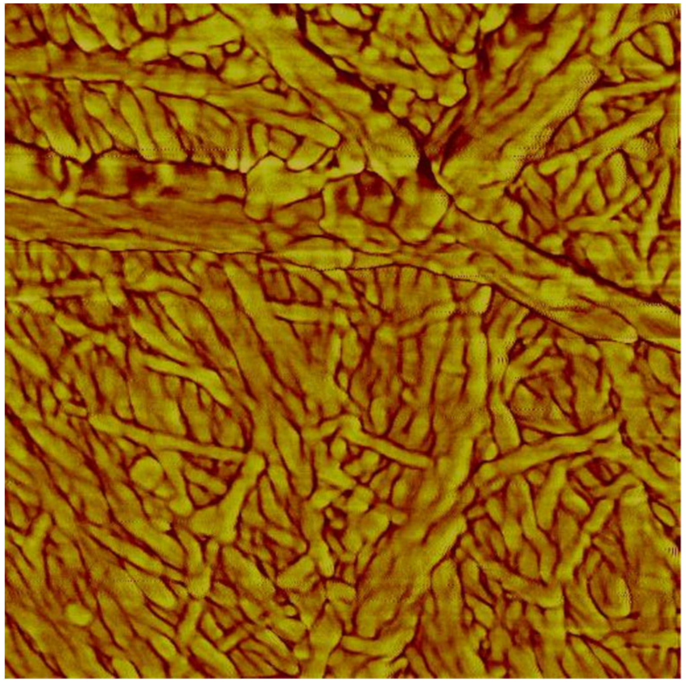
Diameter: 2-20 nm
(In wood: 3-4 nm)





Ultrastructure: cellulose microfibrils

Aggregates: 12-20 nm (or more)



AFM image of a surface of bleached birch kraft pulp; sample untreated.

Imaged by M. Suchy 2008.

Individual microfibrils: ~3.5 nm

TEM image of longitudinal cross-section of chlorite delignified pine cell wall; freeze-dried and stained.

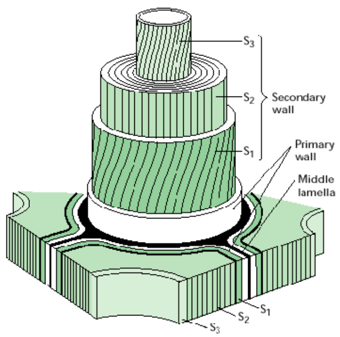
A. Heyn *J. Ultrastructure Res.* **1969**, *26*, 52.

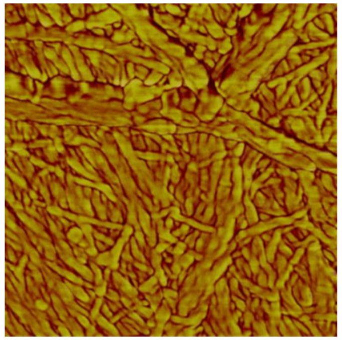
Cellulose nanofibres

Preparation of nanofibrillar cellulose aims at isolating the individual microfibrils (nanofibrils) from the cell wall structure.

Seminal challenges in isolation:

- **tight, hierarchical structure of the plant cell wall**
- **inherent tendency of cellulose to aggregate**





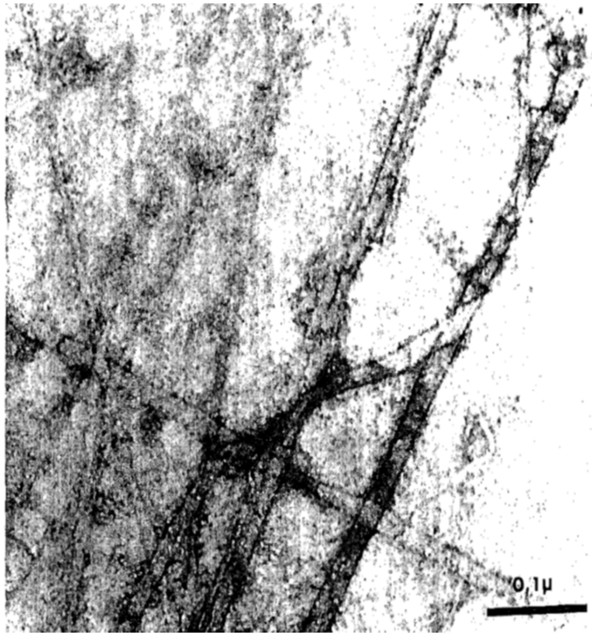
Preparation of cellulose nanofibres: mechanical disintegration

EARLY EXAMPLES OF INDIVIDUALIZATION OF MICROFIBRILS

METHOD: ULTRASONICATION

S.K. Asunmaa
Tappi **1967**, *49*, 319.

From aspen holocellulose



From valonia alga

Gardner and Blackwell
J. Polym. Sci. C
1971, *36*, 327.

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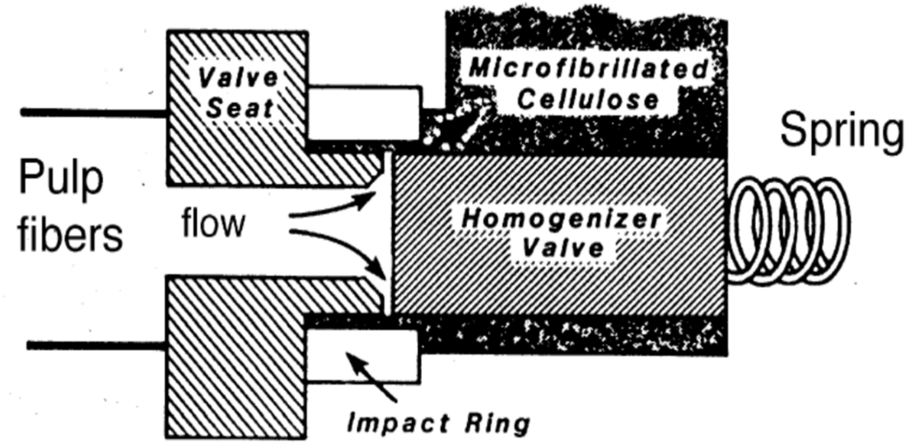
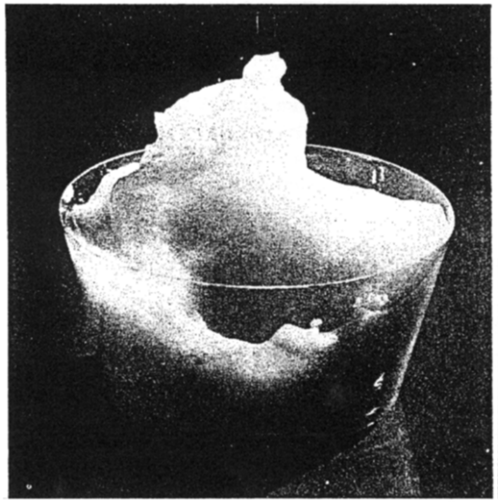
Preparation of cellulose nanofibres: mechanical disintegration

First attempt to isolate microfibrils for materials science purposes.



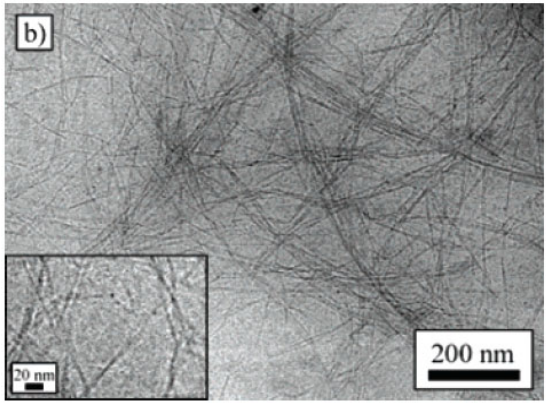


Turbak et al. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1983**, *37*, 815.

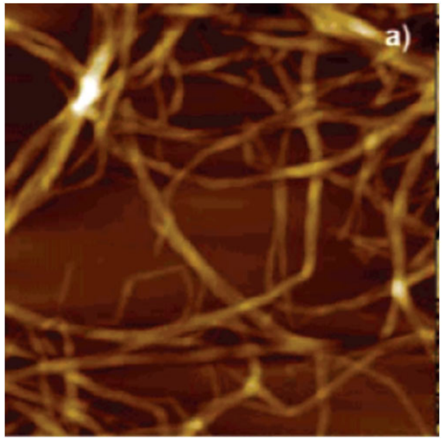
Preparation of cellulose nanofibres: mechanical disintegration

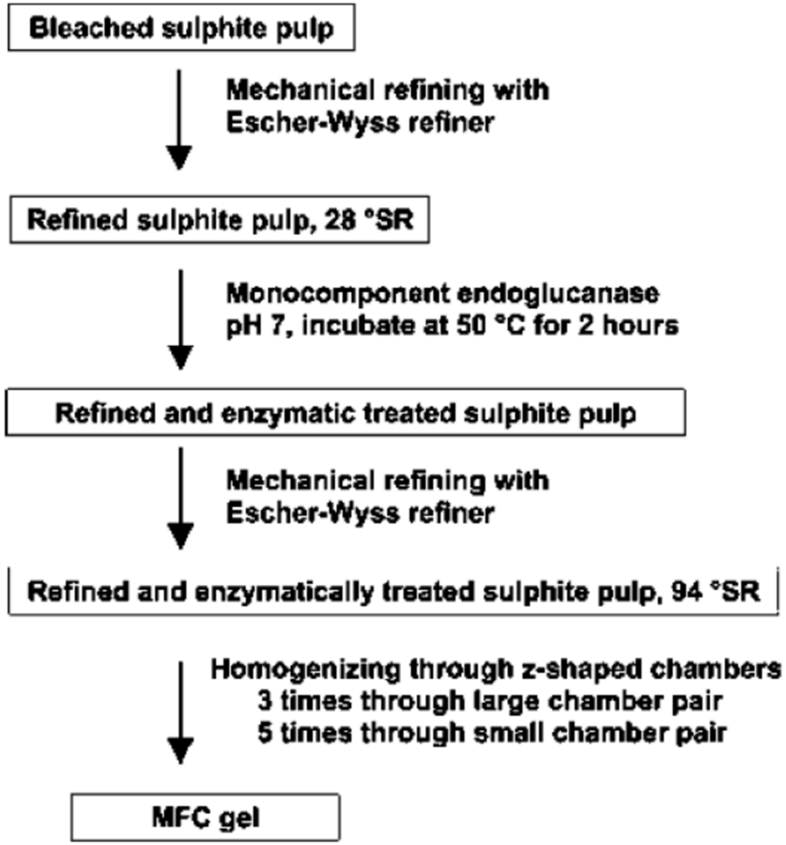
Enzymatic pretreatment to bleached sulphite pulp.

TEM



AFM



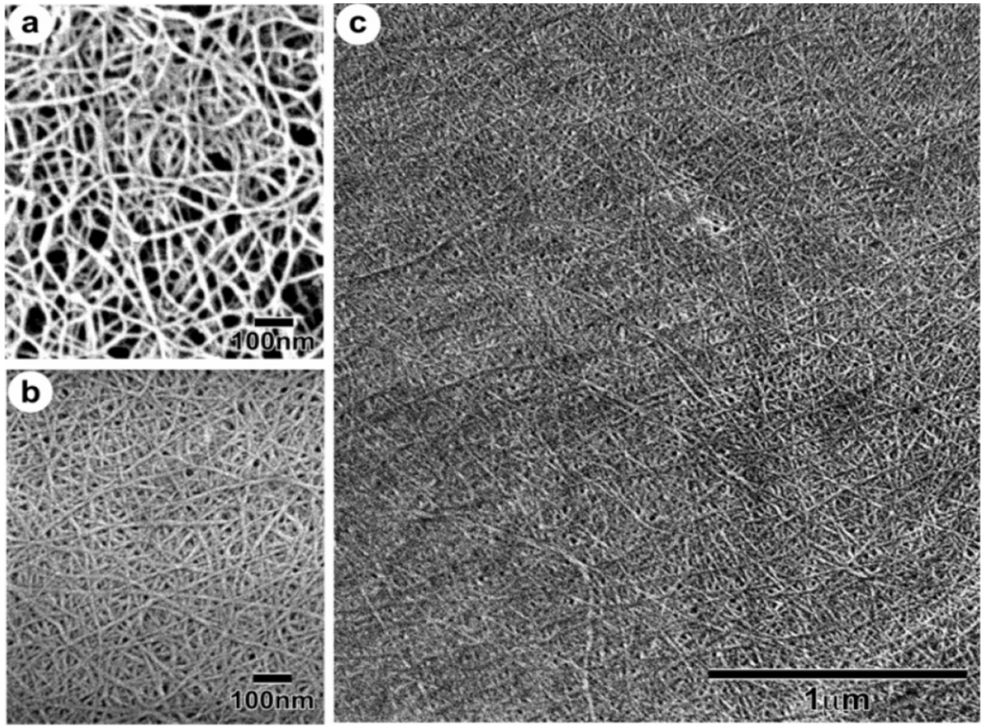


Microfibrils and microfibril aggregates, ca. 5-10 nm in size.

Pääkkö et al. *Biomacromolecules* **2007**, *8*, 1934.

Preparation of cellulose nanofibres: mechanical disintegration

Wood powder, delignified by chlorite, hemicellulose matrix leached out by alkaline treatment → 1 pass through Masuko grinder



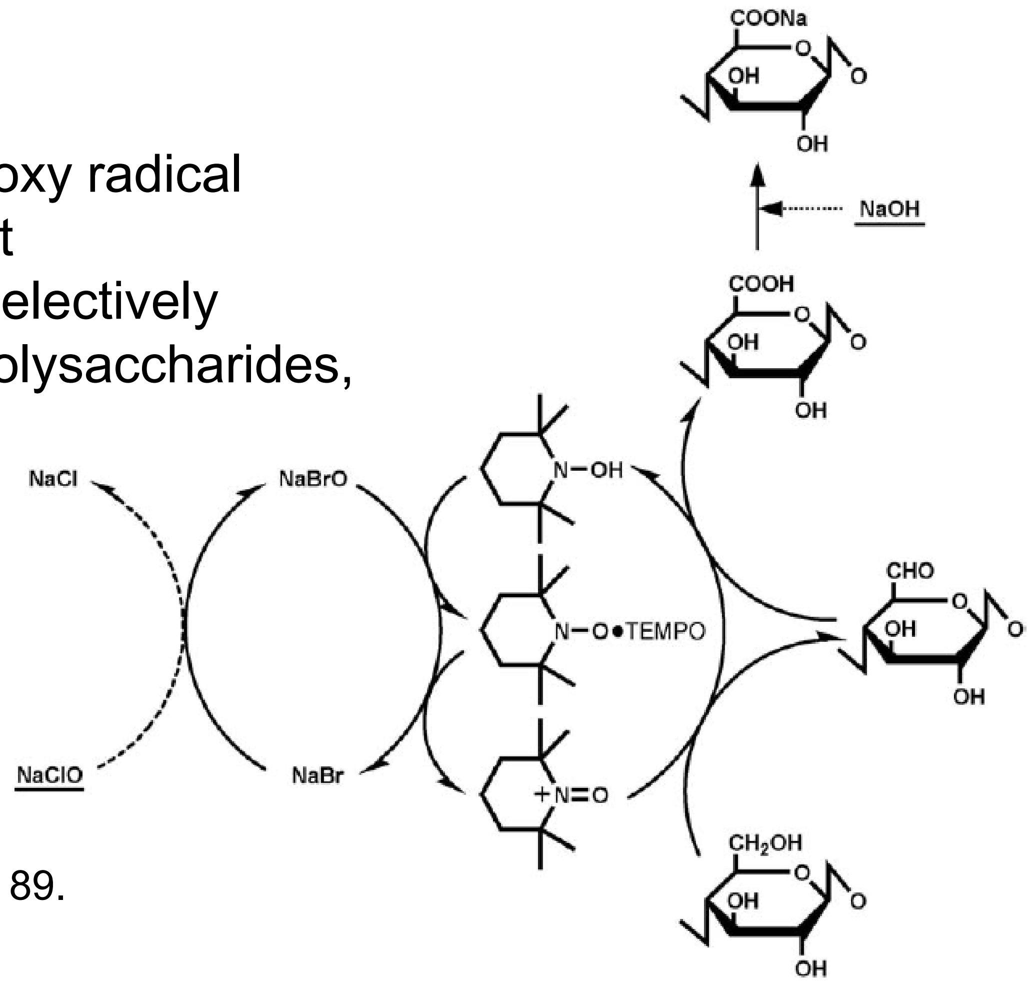
Highly monodisperse 15 nm wide microfibril aggregates

Abe et al. *Biomacromolecules* **2007**, *8*, 3276.

Preparation of cellulose nanofibres: chemical isolation

TEMPO-mediated oxidation

- 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) is an oxidation catalyst
- TEMPO-NaBr-NaClO –system selectively oxidized **primary alcohols** in polysaccharides, i.e., C6 position in cellulose



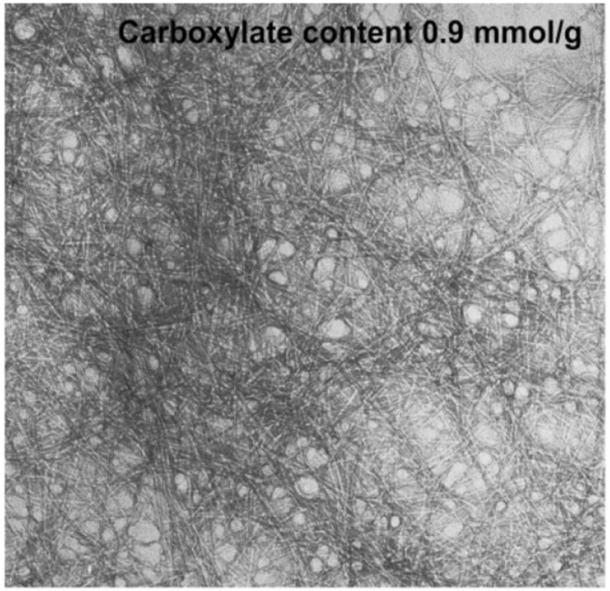
Pioneered for polysaccharides:
de Nooy et al. *Carbohydr. Res.* **1995**, *269*, 89.

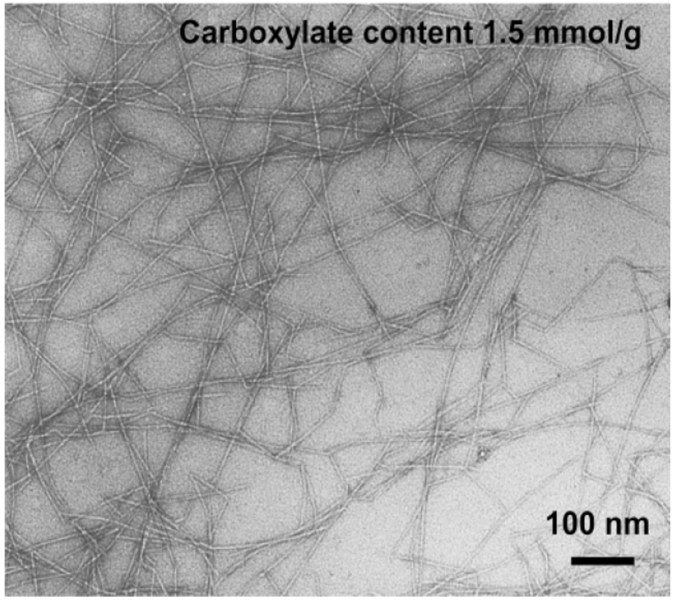
Pioneered for cellulose:
Isogai and Kato *Cellulose* **1998**, *5*, 153.

Preparation of cellulose nanofibres: chemical isolation

TEMPO-mediated oxidation of native fibres → **Mechanical stirring** → **Centrifugation**

↓ **supernatant**



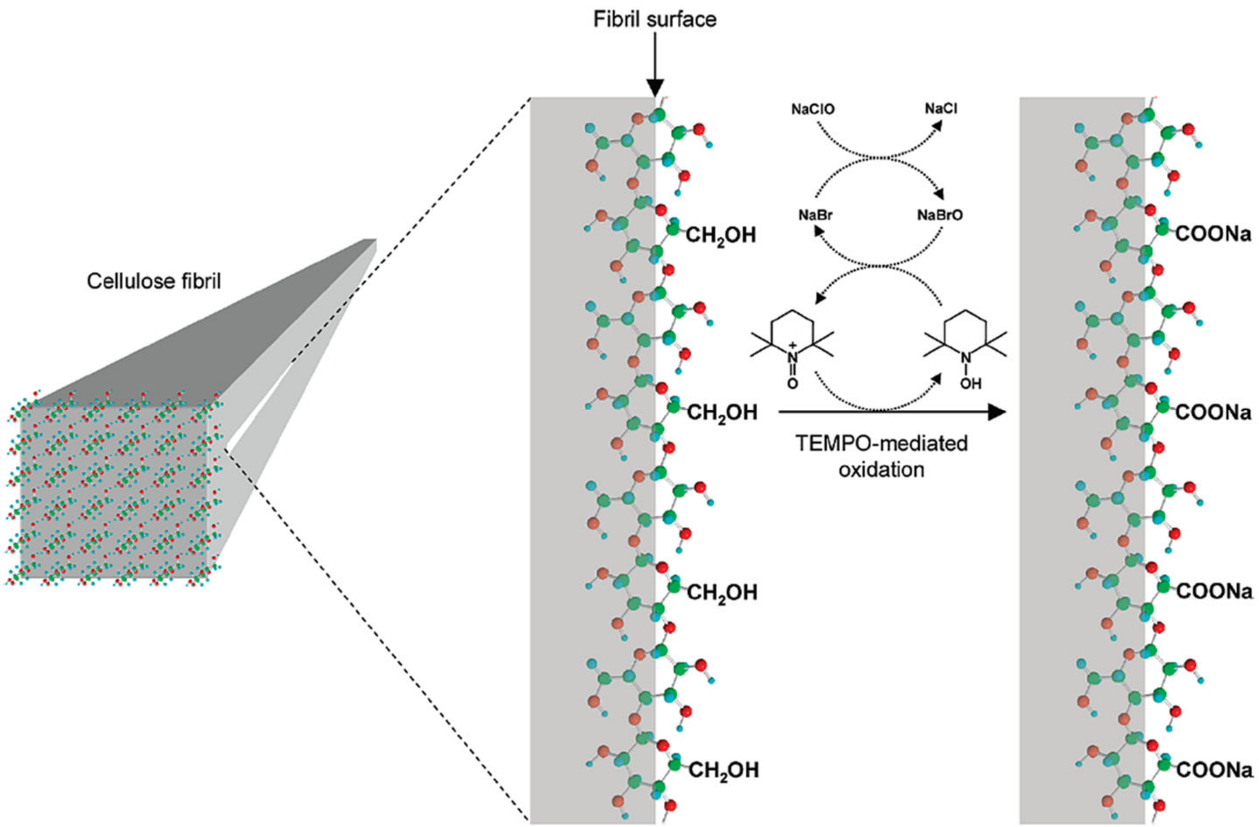


RESULT: highly monodisperse microfibrils (3-4 nm width)

Saito et al. *Biomacromolecules* **2006**, *7*, 1687.
Saito et al. *Biomacromolecules* **2007**, *8*, 2485.

Preparation of cellulose nanofibres: chemical isolation

Why do we get individual microfibrils from TEMPO-oxidation?



Only the surface of the microfibrils is oxidized → electrostatic repulsion.

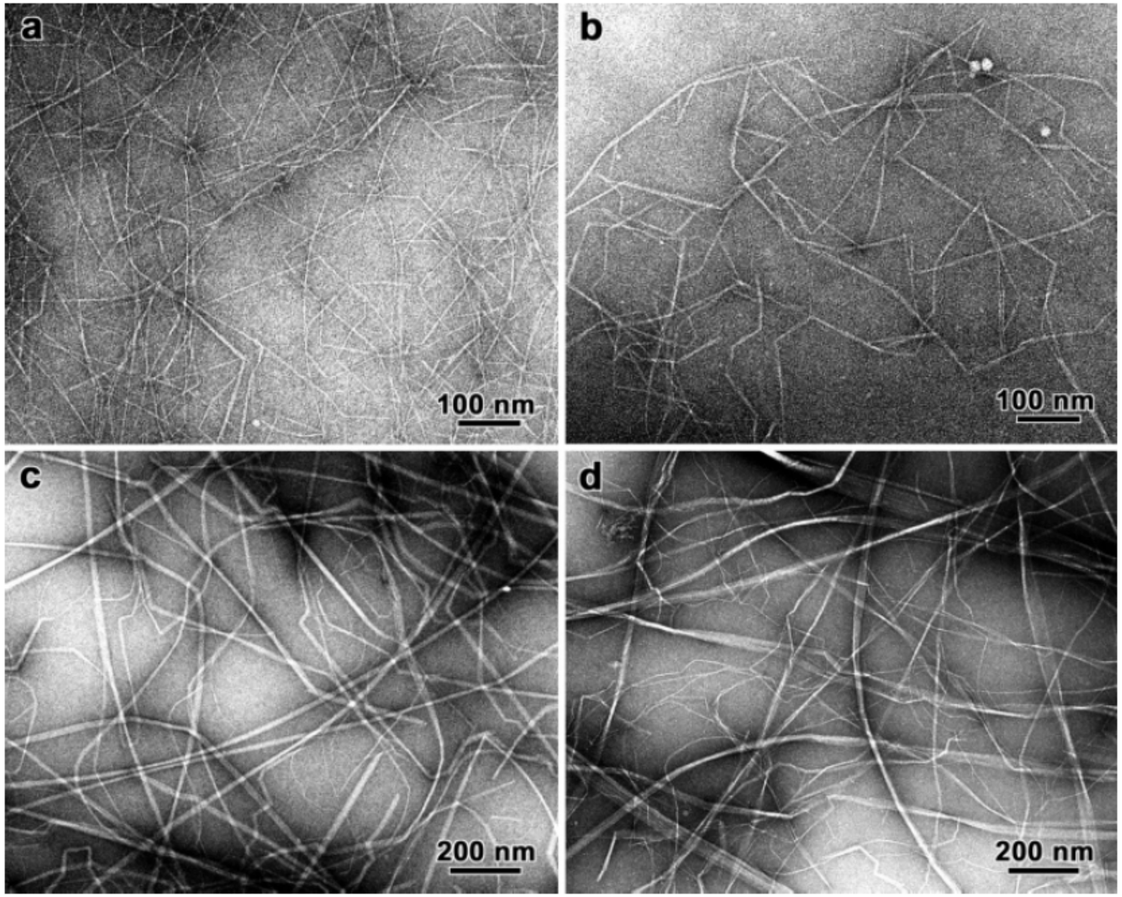
Image from:
Okita et al. *Biomacromolecules* **2010**, *11*, 1696.

Preparation of cellulose nanofibres: chemical isolation

Effect of starting material

wood pulp

cotton



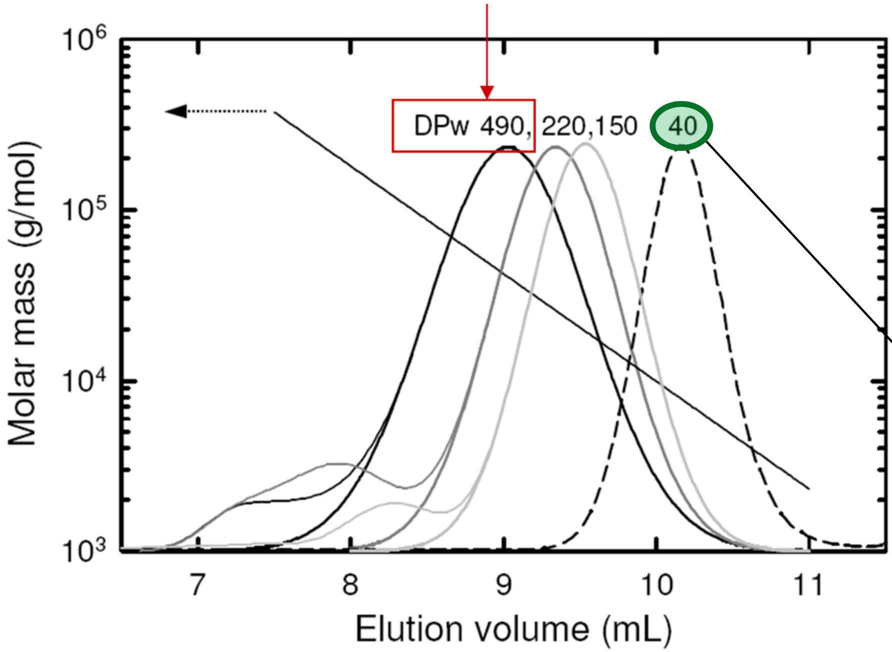
tunicate

bacterial cellulose

Saito et al. *Biomacromolecules* **2006**, *7*, 1687.

Preparation of cellulose nanofibres: chemical isolation

- TEMPO-mediated oxidation of cellulose reduces DP, especially with regenerated cellulose grades
- extensive survey on DP: Isogai et al. *Cellulose* **2009**, *16*, 117.
- however, recent research points out that at neutral conditions in a TEMPO/NaClO/$NaClO_2$ system, the DP reduction is minimized



Original DP: **680**

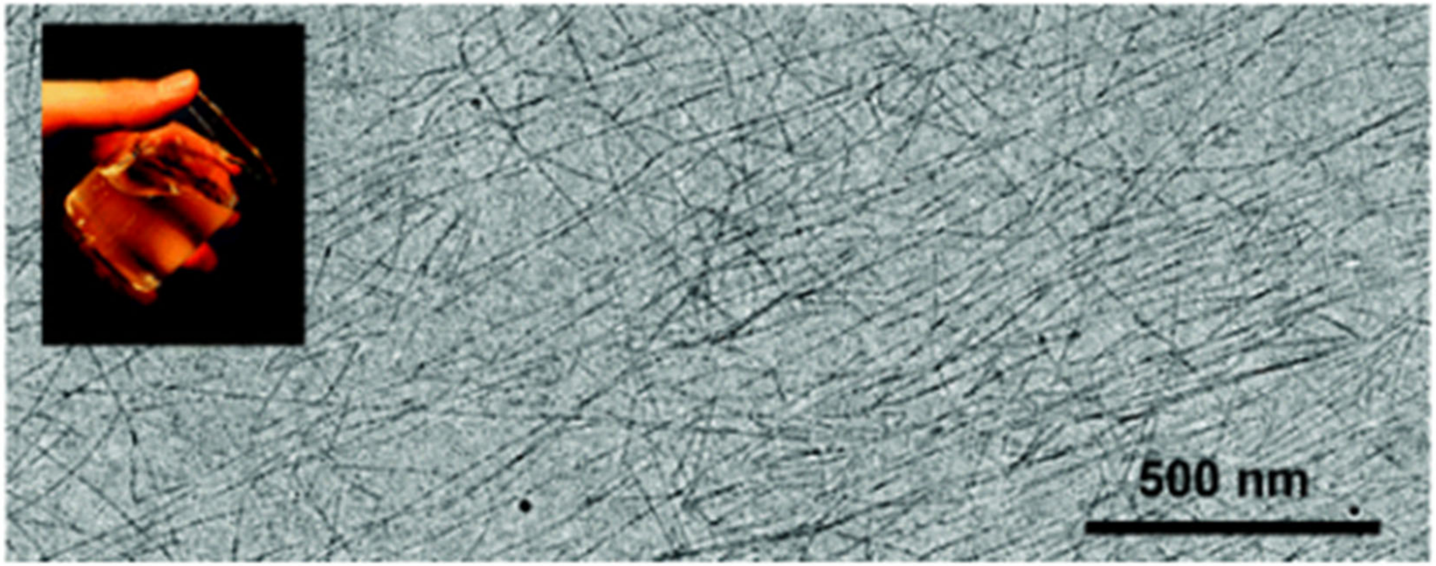
DP after TEMPO/NaClO/$NaClO_2$ (oxidation for 3 days, pH 5.8): **490**

DP after TEMPO/NaBr/NaClO (2 hours, pH 10): **40**

Hirota et al. *Carbohydr. Polym.* **2009**, *78*, 330.

Preparation of cellulose nanofibres: chemical isolation

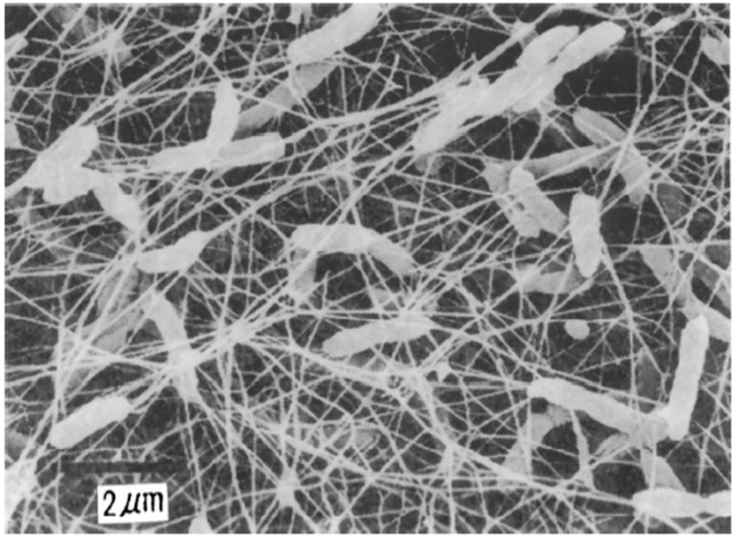
Neutral conditions (TEMPO/NaClO/$NaClO_2$) system result in straighter microfibrils (less defects).



Saito et al. *Biomacromolecules* **2009**, *10*, 1992.

Cellulose nanofibres: bacterial cellulose

- a species of bacteria (*acetobacteria xylinum*) is able to produce pure cellulose microfibrils from sugars
- individual microfibrils are formed on spot
- macroscopically, bacterial cellulose forms a gel like many other types of nanofibrillar cellulose

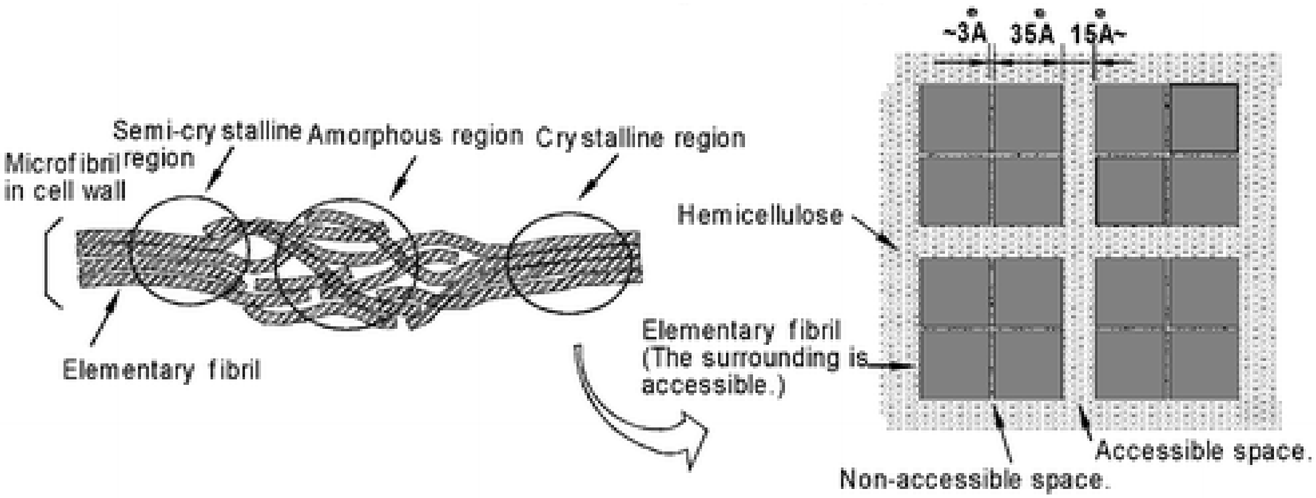


- the microfibrils from bacterial cellulose are larger than in plant cellulose: cross section > 70-140 nm × 7 nm

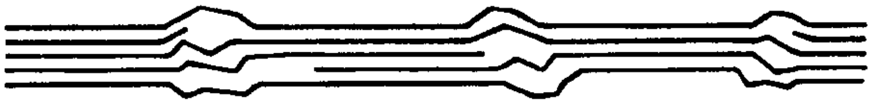
Iguchi et al. *J. Mater. Sci.* **2000**, *35*, 261.

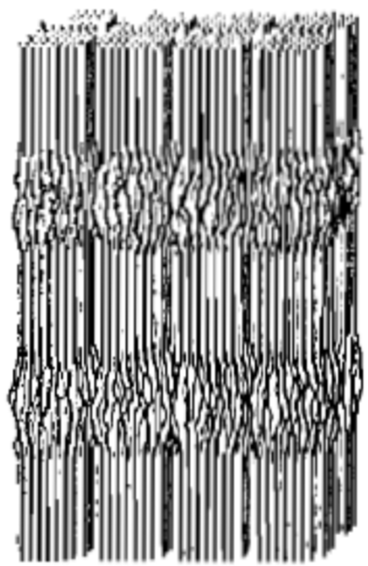
Cellulose nanocrystals: preparation

Structure of cellulose microfibril



Crystallographic data presents evidence that cellulose within microfibrils is not totally crystalline.

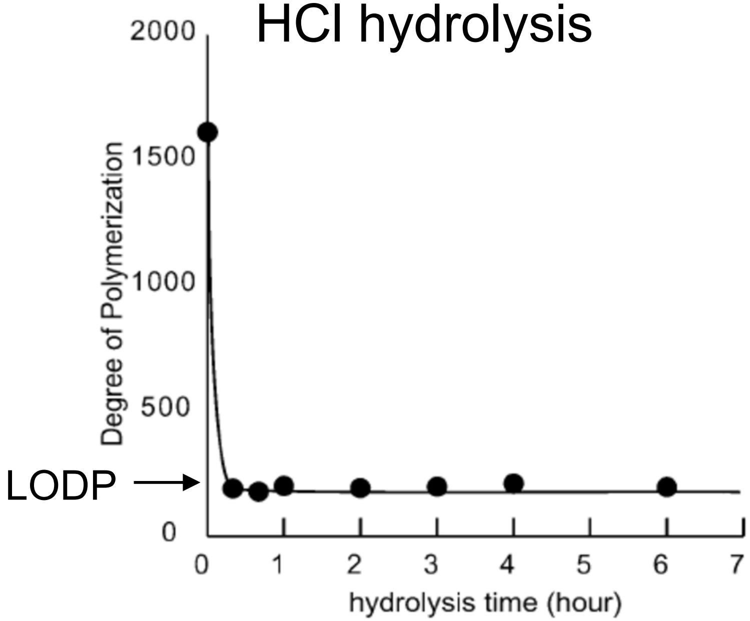




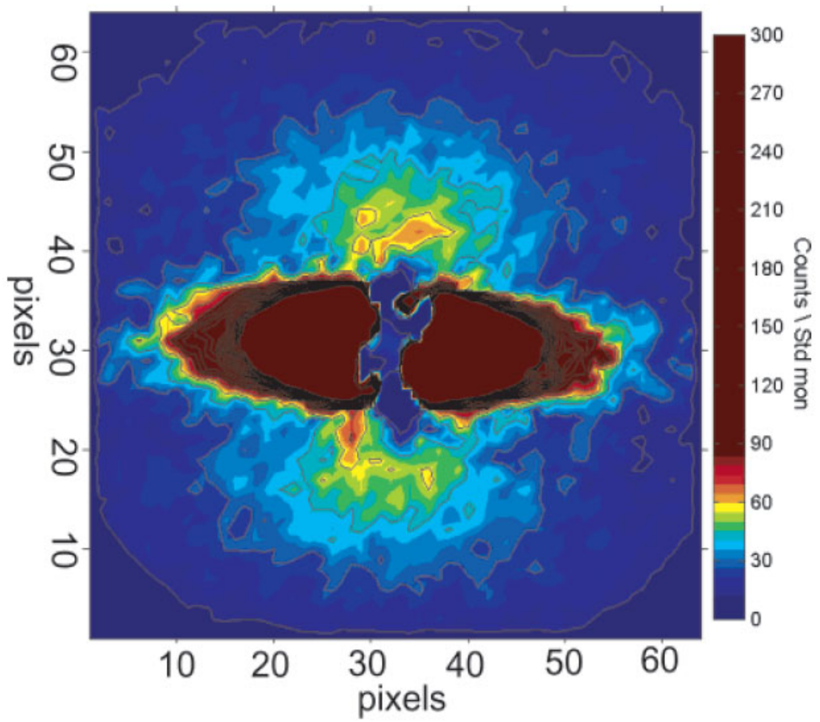
Proposition:
cellulose runs through alternating crystalline and “ amorphous” regions.

Structure of cellulose microfibril

DP of ramie fibres after HCl hydrolysis



SANS* pattern of untreated ramie



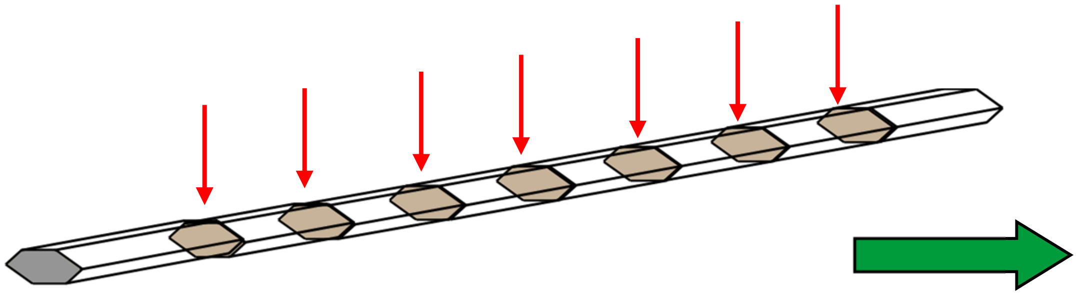
Crystallite length (i.e. length of crystalline domains) by SANS agrees with the level-off degree of polymerization (LODP).

* Small angle neutron scattering

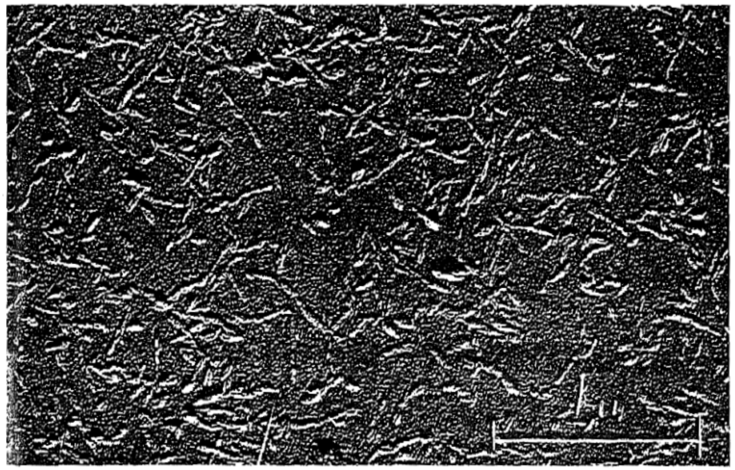
Nishiyama et al. *Biomacromolecules* **2003**, *4*, 1013.

Cellulose nanocrystals

Preparation of cellulose nanocrystals is based on the fringed fibrillar structure of the native cellulose microfibril.



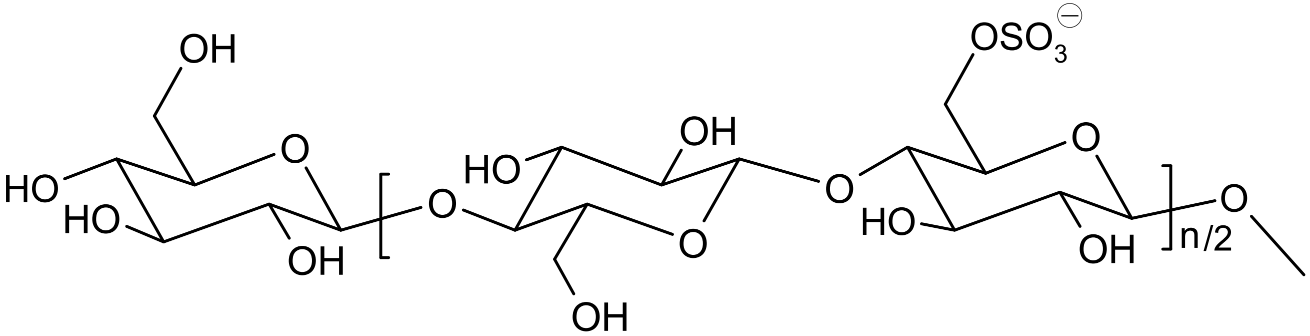
Controlled acid hydrolysis leads to disruption of Disordered domains leaving crystalline cellulose intact.



Result: cellulose nanocrystals

Rånby *Discuss. Faraday Soc.* 1951, *11*, 158.

Cellulose nanocrystals – surface modification during preparation



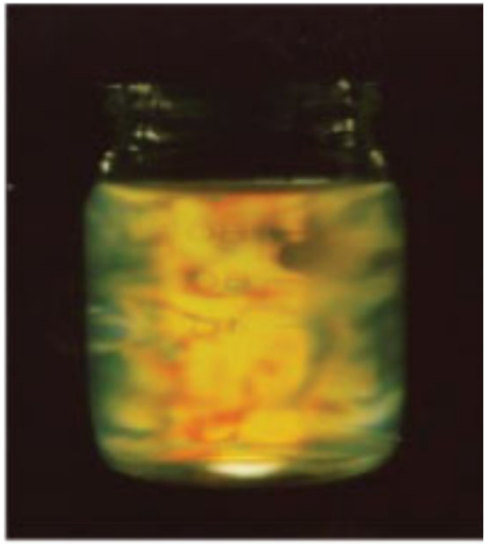
When prepared with sulfuric acid, organic sulphate groups are introduced on the surface of the nanorods.

electrostatic repulsion

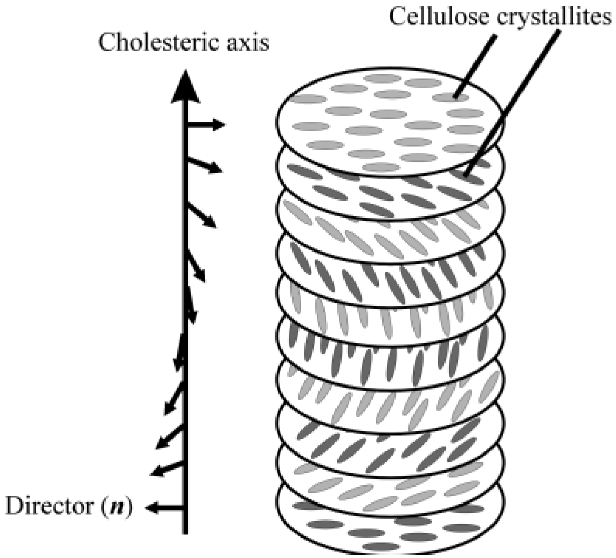
STABLE SUSPENSION IN WATER

Cellulose nanocrystals – liquid crystals

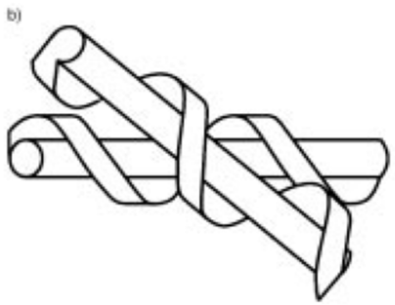
Cellulose nanocrystals spontaneously forms a liquid crystal phase in solution.



Photograph of rodlike nanocrystals in aqueous suspension.
The liquid crystal phase has been formed.



chiral nematic phase formed by cellulose crystallites



tight packing by the chiral interaction of screwlike rods

Revol et al. *Int. J. Biol. Macromol.* **1992**, *14*, 170.
Fleming et al. *Chem. Eur. J.* **2001**, *7*, 1831.
Habibi et al. *Chem. Rev.* **2010**, *110*, 3479.

Cellulose nanocrystals – new preparation method with acid vapour

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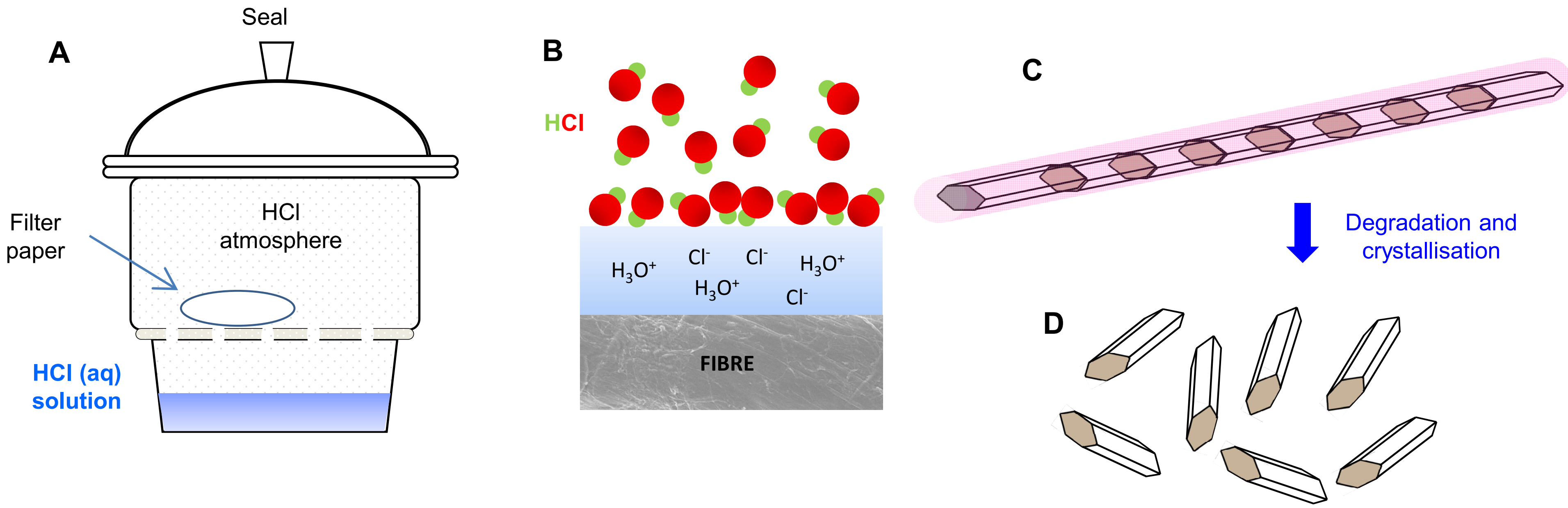
Concept for preparation of cellulose nanocrystals with acid vapor



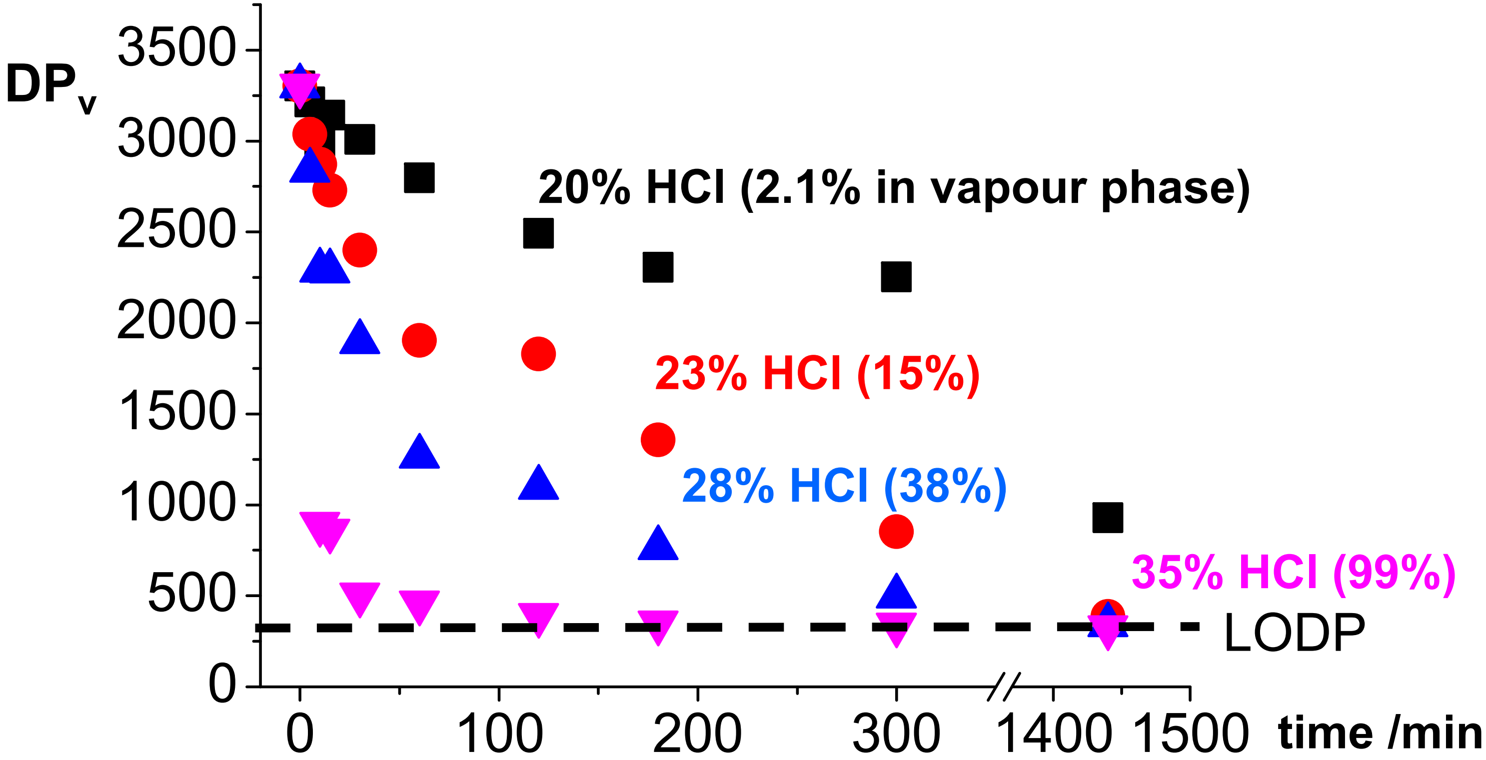
- Hydrogren chloride (HCl) vapor adsorbs on fibre surface
- Fibre surface is always covered by water in ambient conditions

→ HCl dissociates in water, i.e., it becomes an acid
→ Acid and water degrade cellulose until the LODP
→ Nanocrystals can be isolated from the hydrolysed fibres

Angew. Chem. Int. Ed. **2016**, *55*, 14455.

Degradation of cellulose by HCl vapour

Cotton linter fibres (Whatman 1 filter paper)

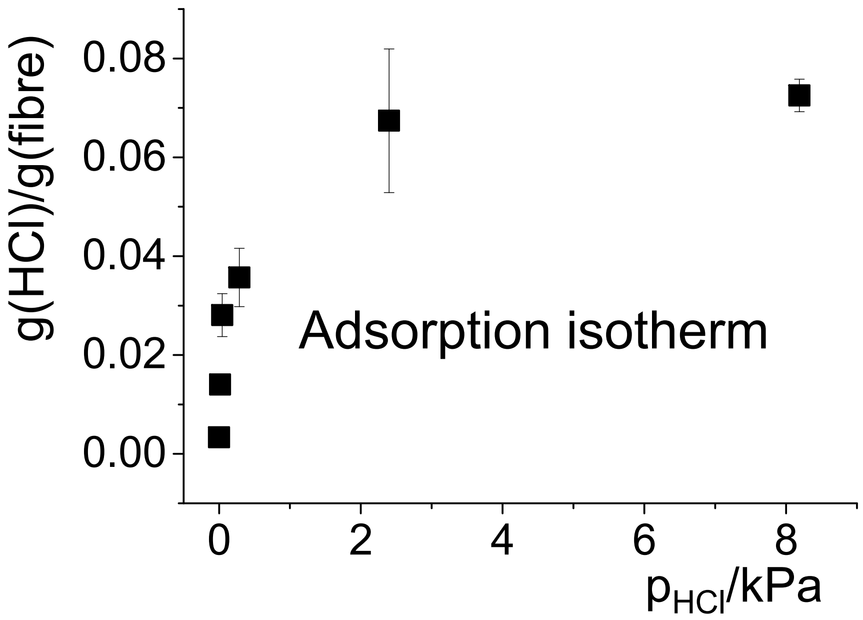


→ Rapid degradation down to LODP level **at room temperature**

HCl accumulation on fibres

Because HCl resides originally in vapour phase, it must reach the fibres by adsorption

Fibres are always covered by a thin layer of water (3-5%)



Practical CNC preparation with HCl vapour

Hydrolysis with HCl vapour:
35% HCl, 4 h, room temperature

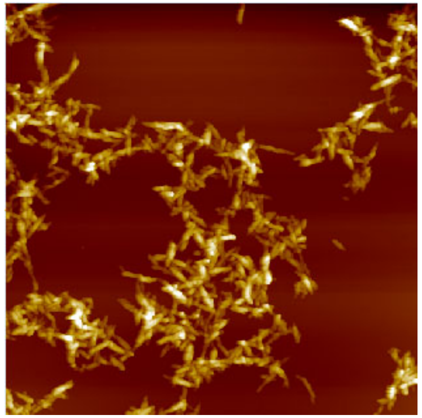
↓

Grinding the hydrolysed substrate in a Wiley mill

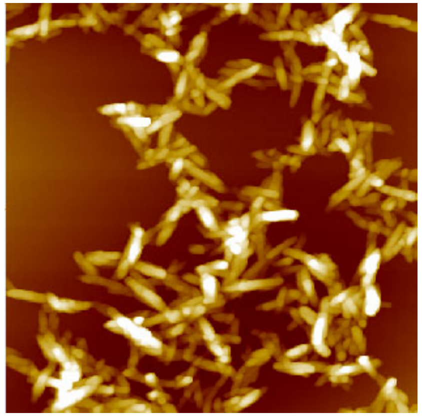
↓

Dispersing the powder in formic acid (heavy sonication)

Note: hydrolysis with HCl(g) is easy, dispersion of CNCs is difficult



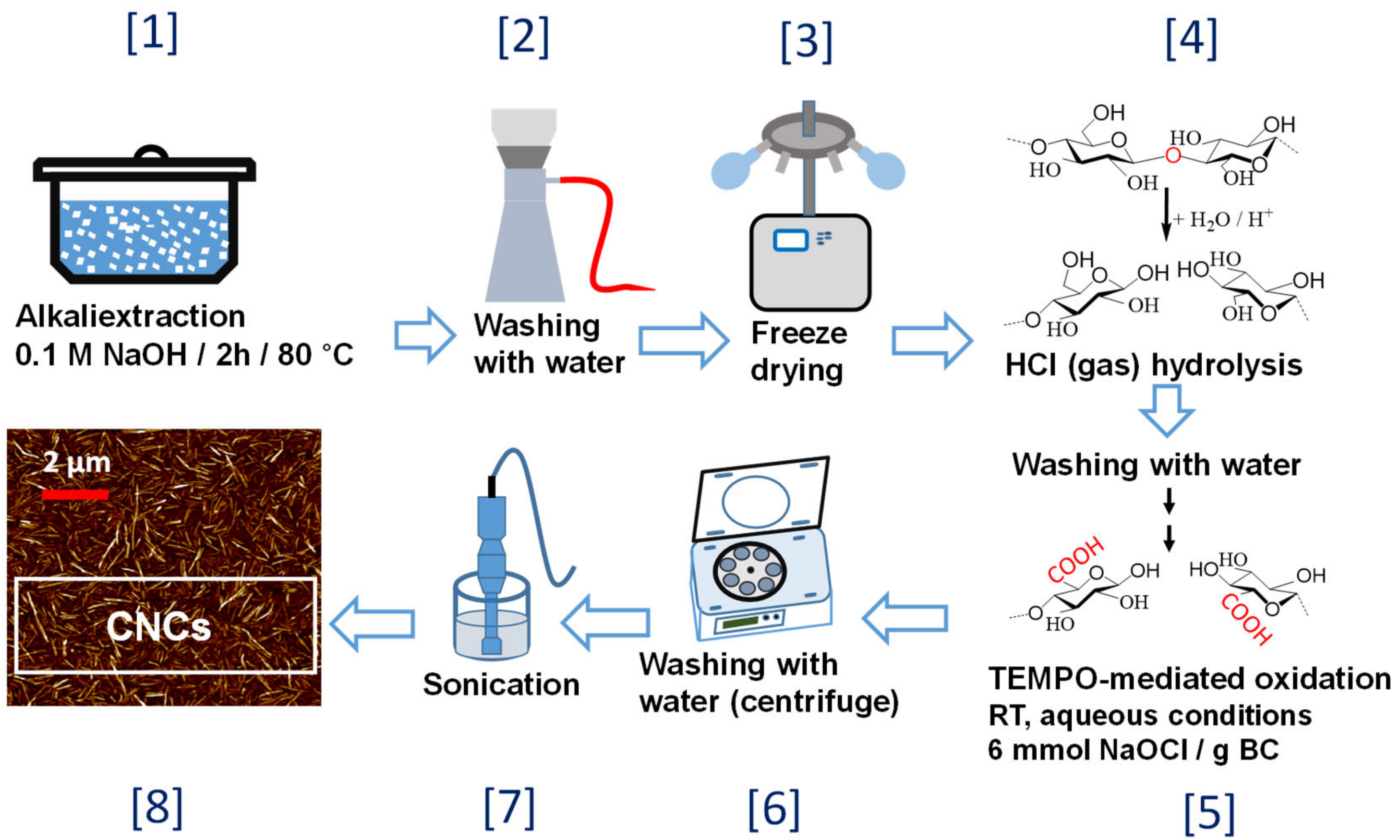
$5 \times 5\ \mu m^2$



$2 \times 2\ \mu m^2$

Angew. Chem. Int. Ed. **2016**, *55*, 14455.

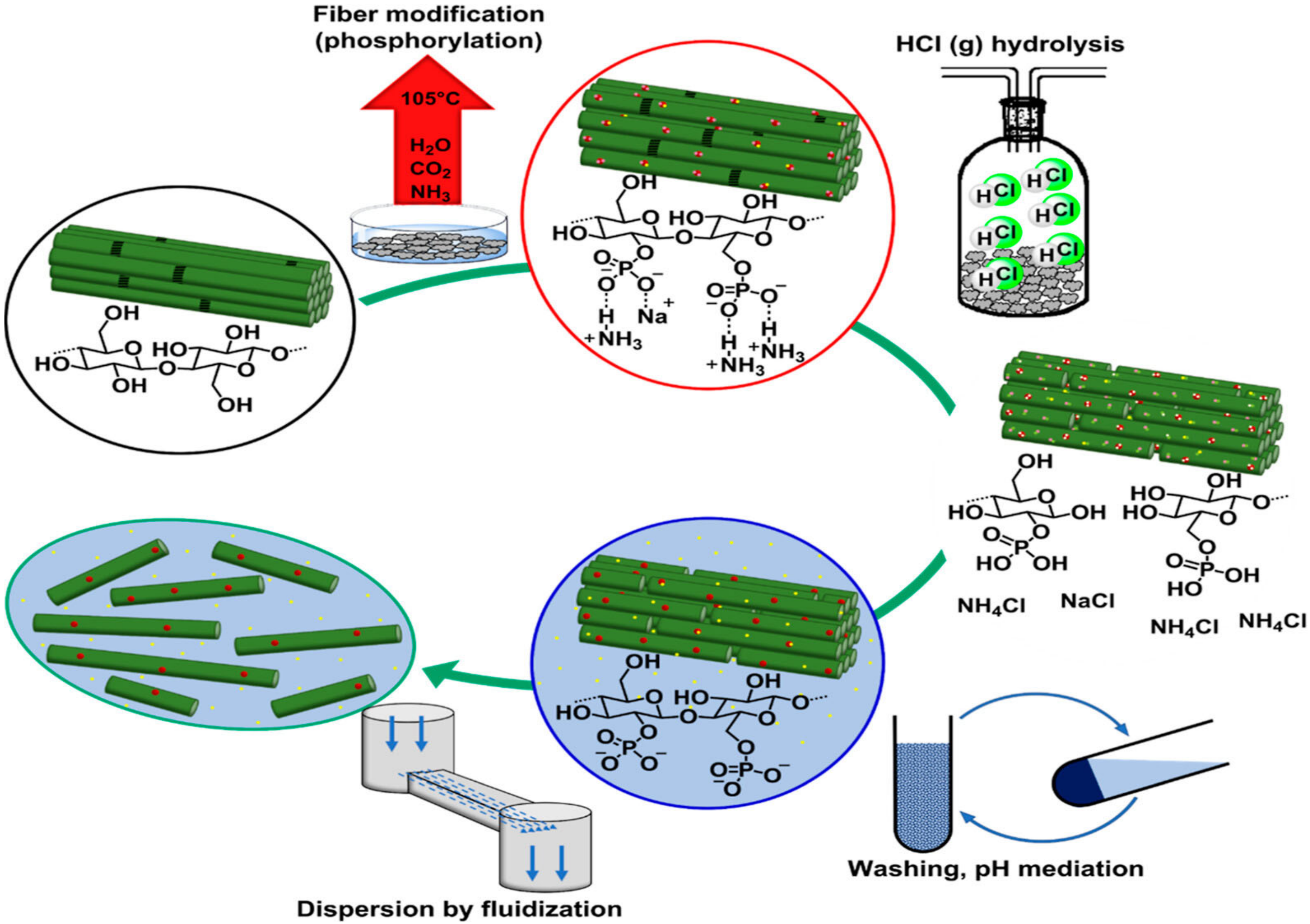
CNCs by acid gas and TEMPO-oxidation



>80% yield!

Pääkkönen et al. *ACS Sustainable Chem. Eng.* **2019**, *7*, 14384.

Phosphorylation of CNCs



Kröger et al. *Biomacromolecules* **2023**, *24*, 1318.

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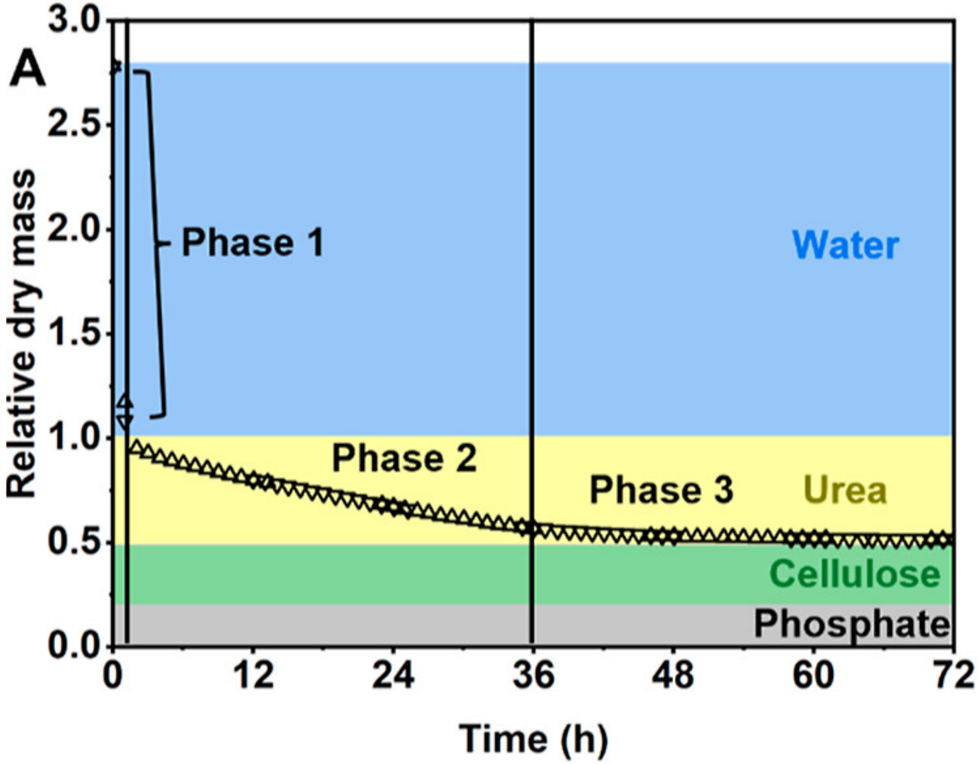
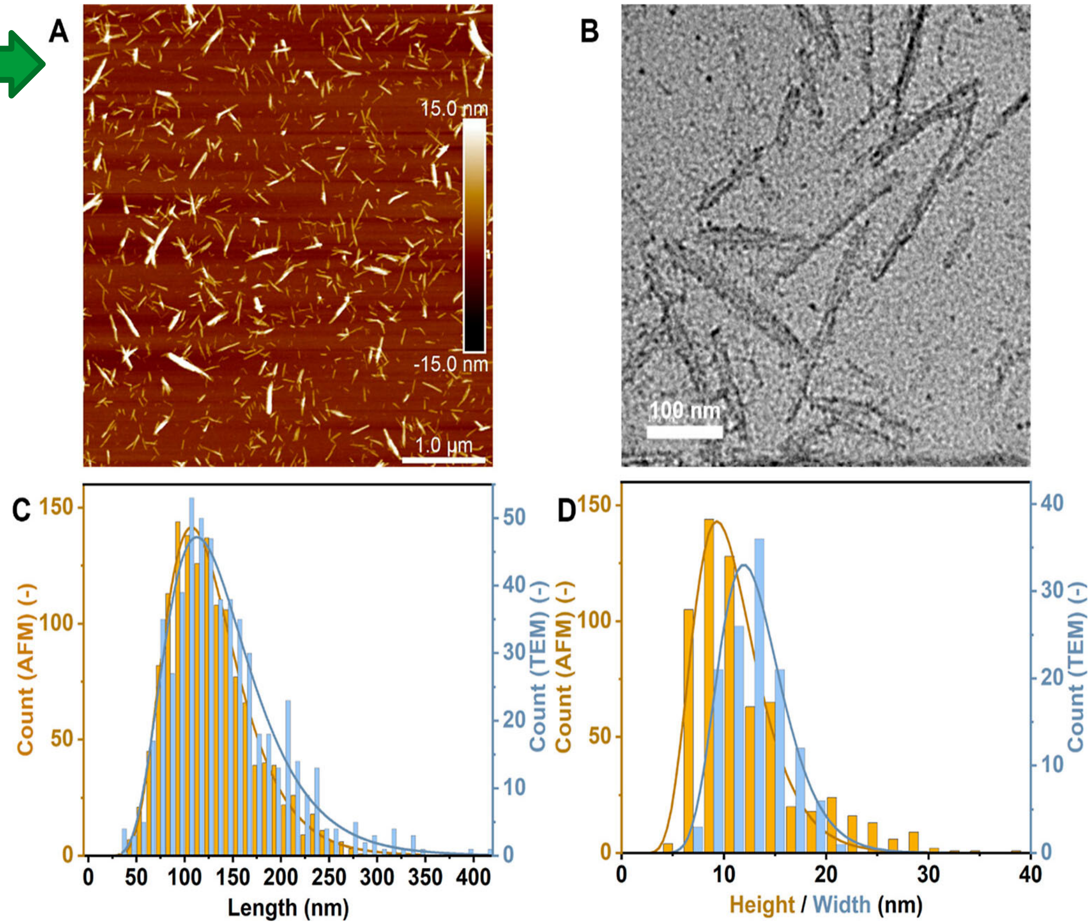
Phosphorylation of CNC





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Kröger et al. *Biomacromolecules* **2023**, *24*, 1318.

Summary

- Preparation / isolation of nanocellulose does make a difference to its surface chemistry