Aalto University
School of Chemical
Technology

# Nanocellulose: preparation and modification

CHEM-E2140

Cellulose-based fibres

Eero Kontturi

29th September 2022

# 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 challenges in CNF and CNC preparation
- Be aware of the main approaches and bottlenecks in chemical modification of CNFs and CNCs

# 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
(5) Summary: comparison between CNF and 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).

# Why do we want nanocellulose?

**Alternatives to non-renewable materials**

- Reduce the use of, e.g., fossil-based components for materials
- Ultimate goal: renewable, biodegradable materials with unique properties

**Why nanocellulose?**

- High strength
- Low density
- Renewable and abundant
- Very high aspect ratio (length/width especially in the case of nanofibrils)
- Can be chemically modified for functional properties
- Specific response to water

# Why do we want nanocellulose?

**Example**
Nanocomposite made of poly(lactic acid) as a continuous matrix and nanofibrillar cellulose as the reinforcing phase
→ Fully bio-based and biodegradable alternative to plastics

**Other potential applications**

- Viscosity modifiers
- Hydrogels for tissue growth
- Hydrogels for wound healing
- Drug release matrices
- Sensor materials
- Paper-based electronics
- Templates for chiral materials
- Platforms for asymmetric catalysis
- Security papers (liquid crystal phases)

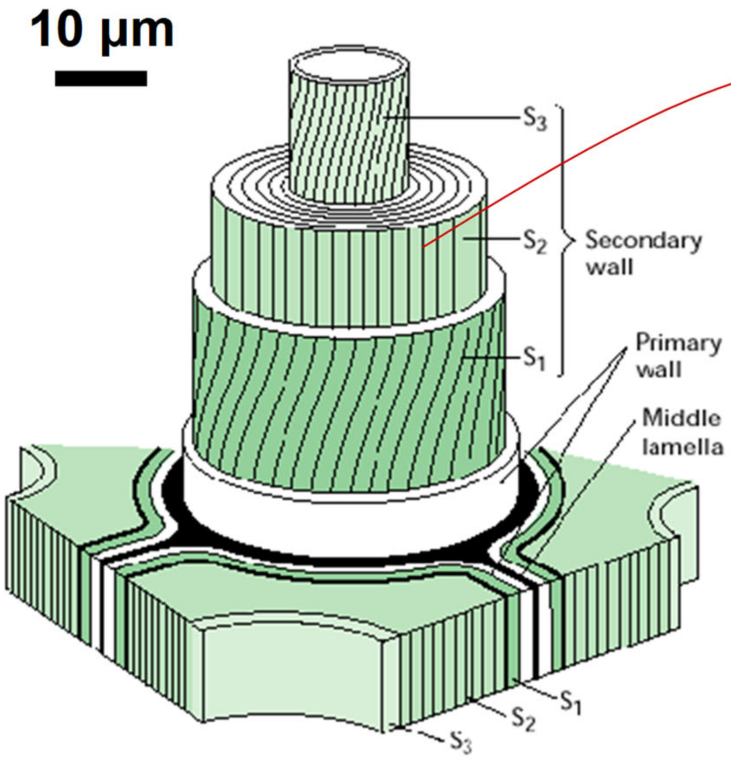
# Cellulose nanofibres: preparation

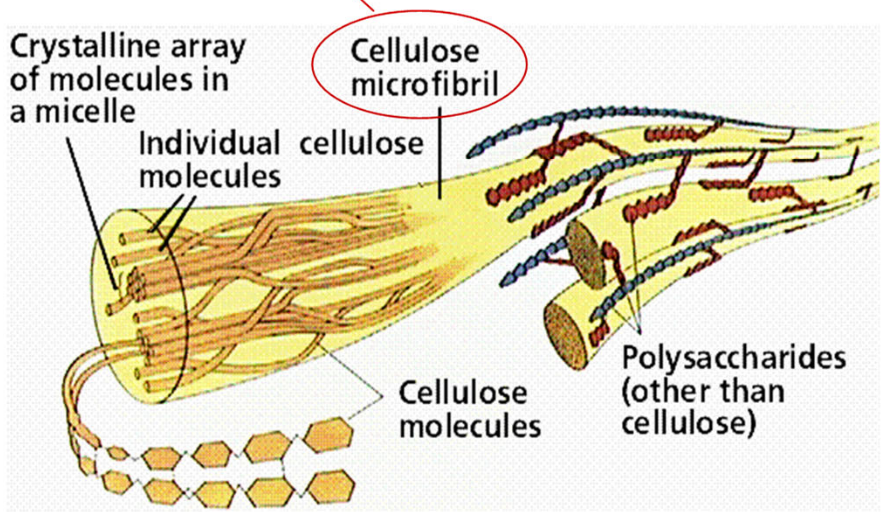
# Ultrastructure of native cellulose

Individual fibre

Cellulose microfibril

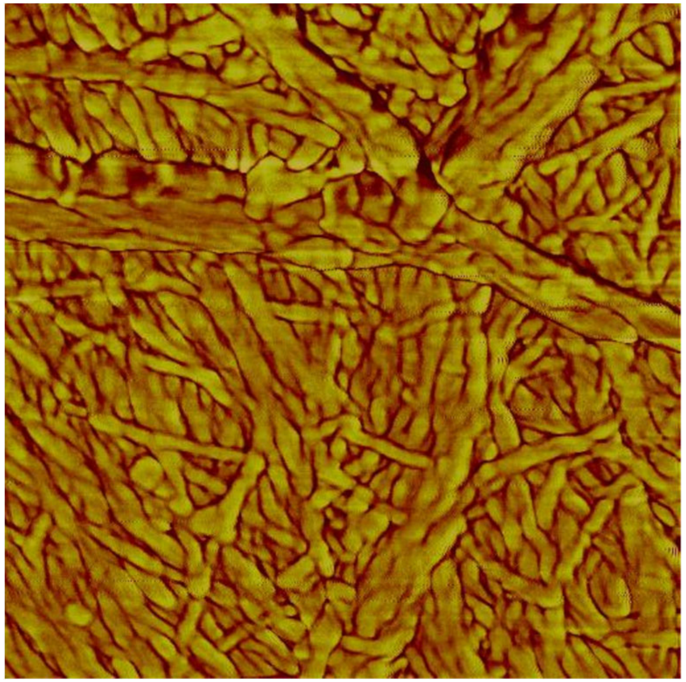
Diameter: 2-20 nm
(In wood: 3-4 nm)



# 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.

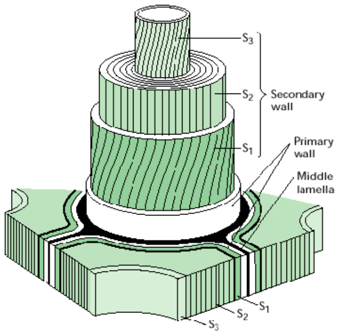
A. Heyn *J. Ultrastructure Res.* **1969**, *26*, 52.

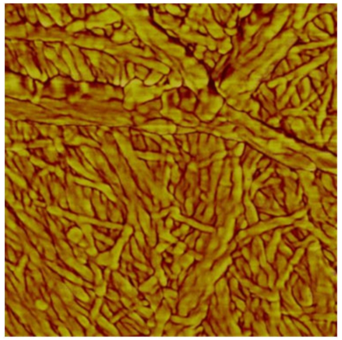
# Cellulose nanofibres

**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**



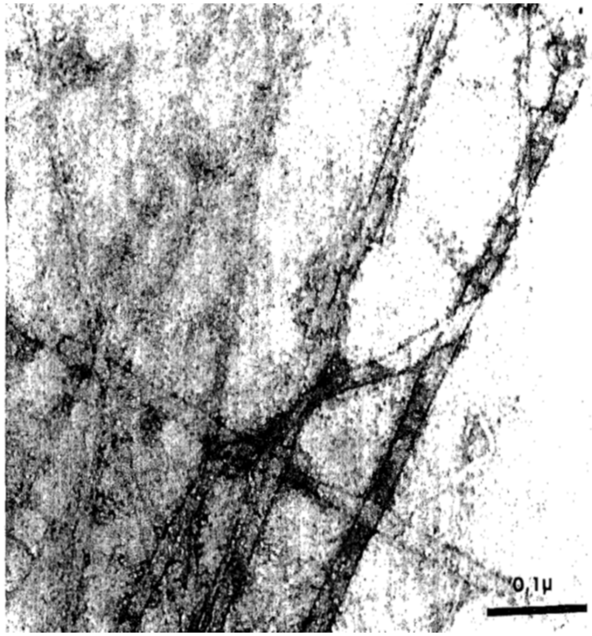
# Preparation of cellulose nanofibres: mechanical disintegration

EARLY EXAMPLES OF INDIVIDUALIZATION OF MICROFIBRILS

METHOD: ULTRASONICATION

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

From aspen holocellulose

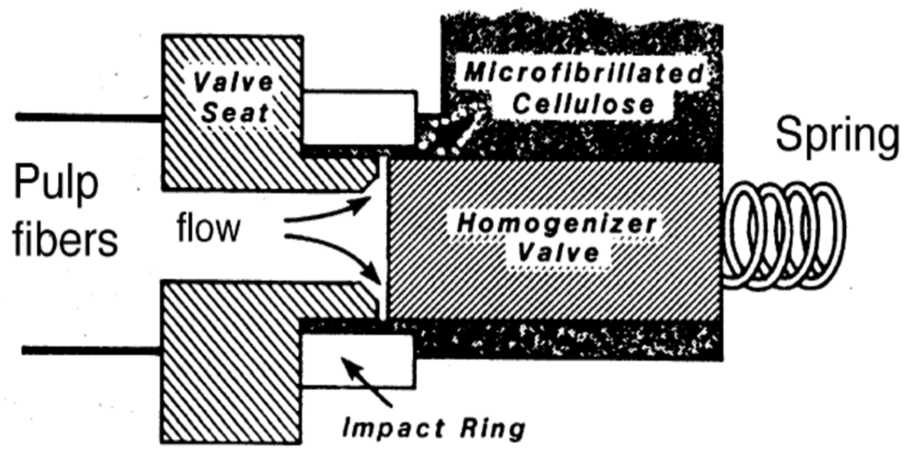


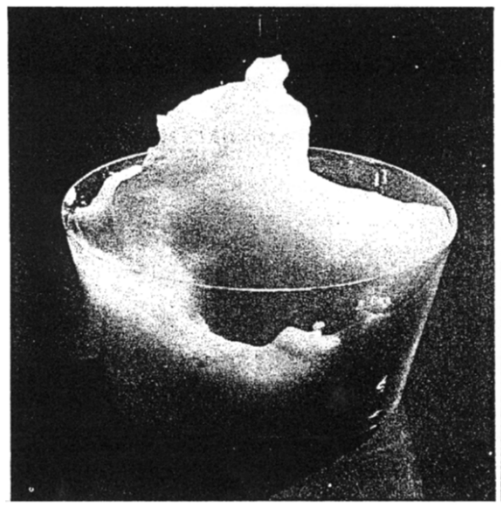
From valonia alga

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

# Preparation of cellulose nanofibres: mechanical disintegration

First attempt to isolate microfibrils for materials science purposes.



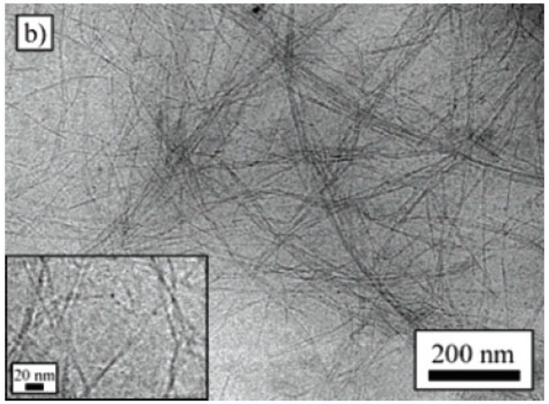



Turbak et al. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1983**, *37*, 815.

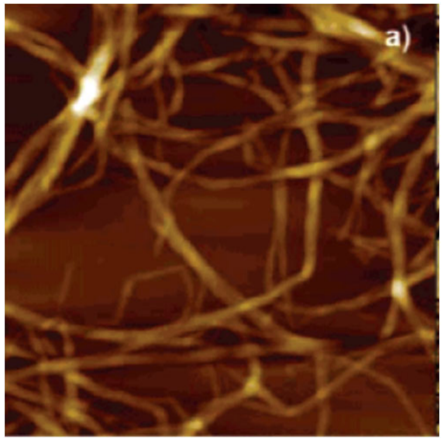
# Preparation of cellulose nanofibres: mechanical disintegration

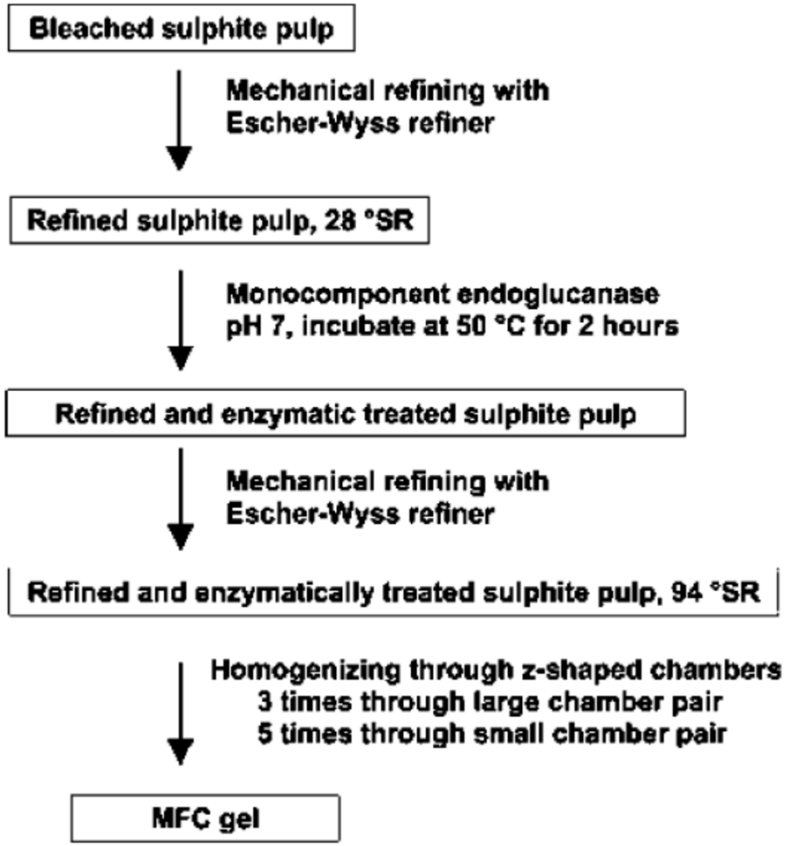
Enzymatic pretreatment to bleached sulphite pulp.

TEM




AFM



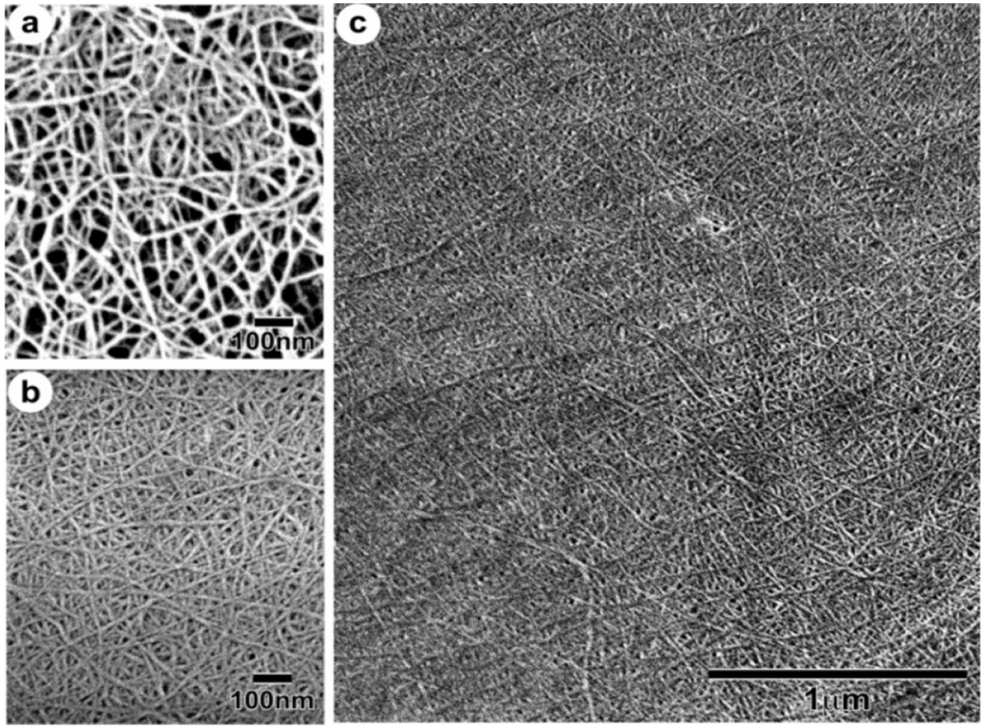




Microfibrils and microfibril aggregates, ca. 5-10 nm in size.

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.

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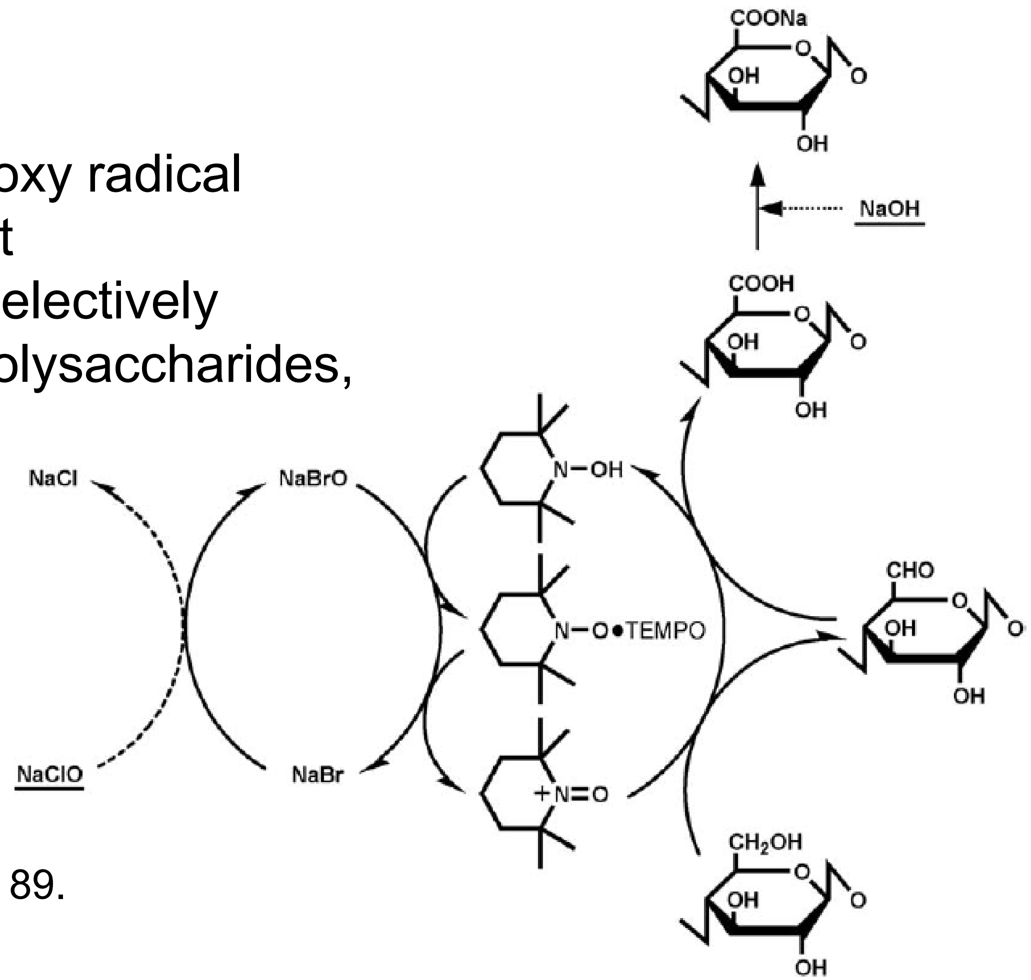
# Preparation of cellulose nanofibres: chemical isolation

## 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



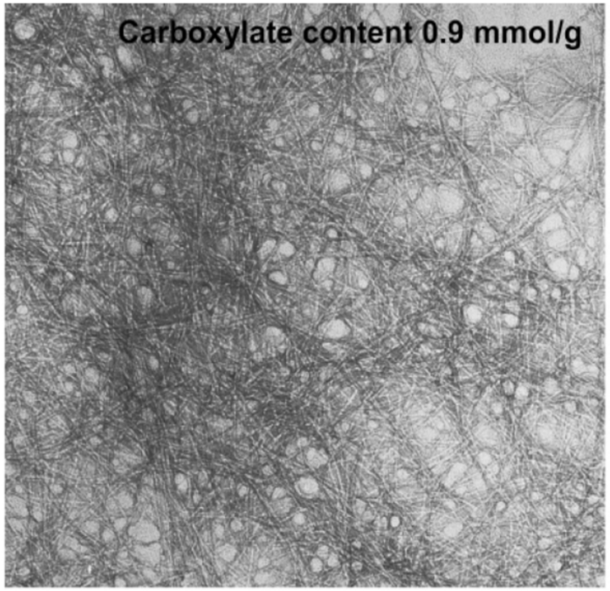

Pioneered for polysaccharides:
de Nooy et al. *Carbohydr. Res.* **1995**, *269*, 89.

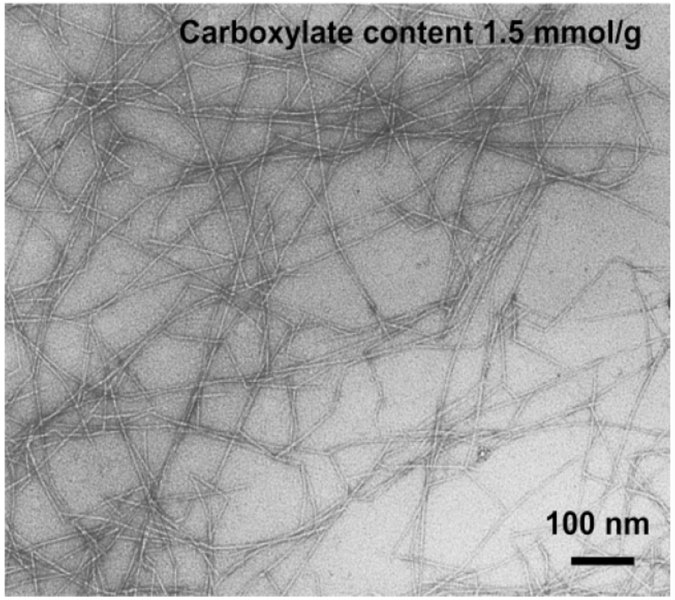
Pioneered for cellulose:
Isogai and Kato *Cellulose* **1998**, *5*, 153.

# Preparation of cellulose nanofibres: chemical isolation

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

↓ **supernatant**



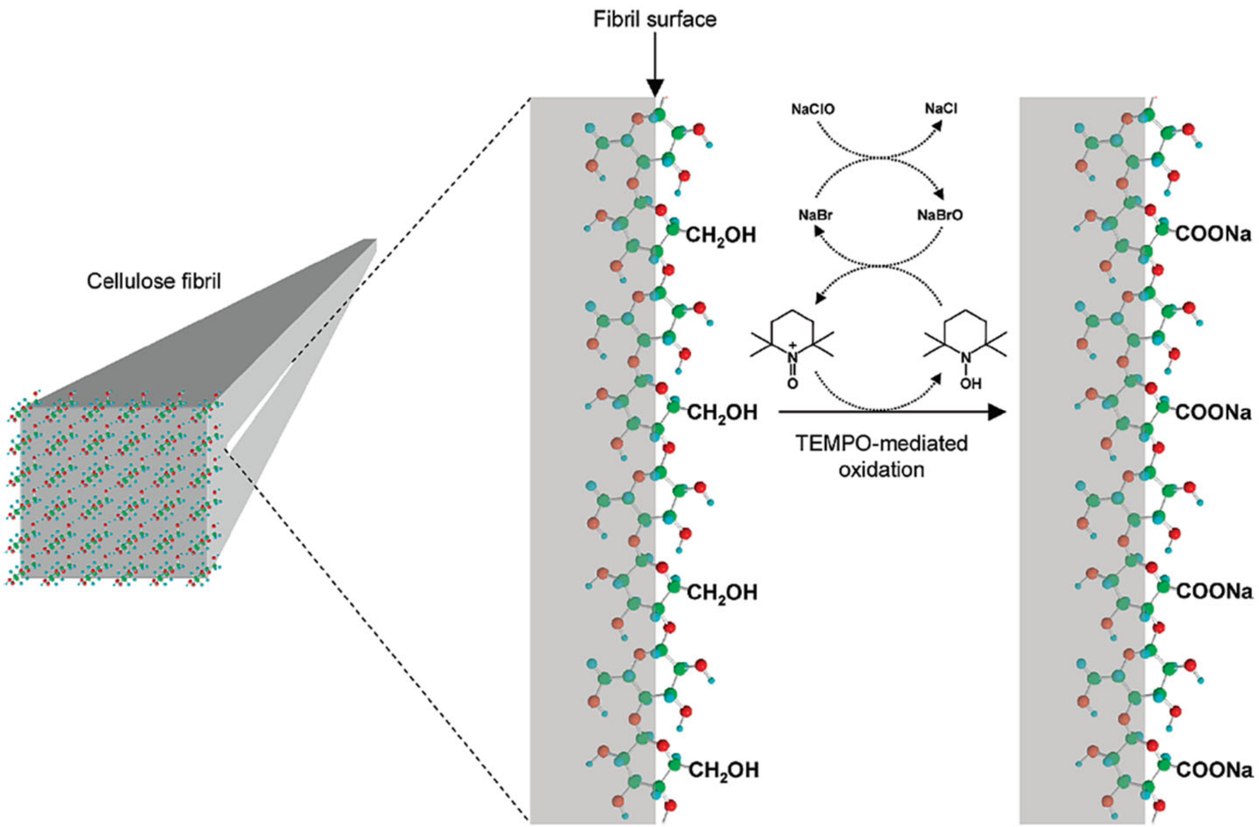

**RESULT: highly monodisperse microfibrils (3-4 nm width)**



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.



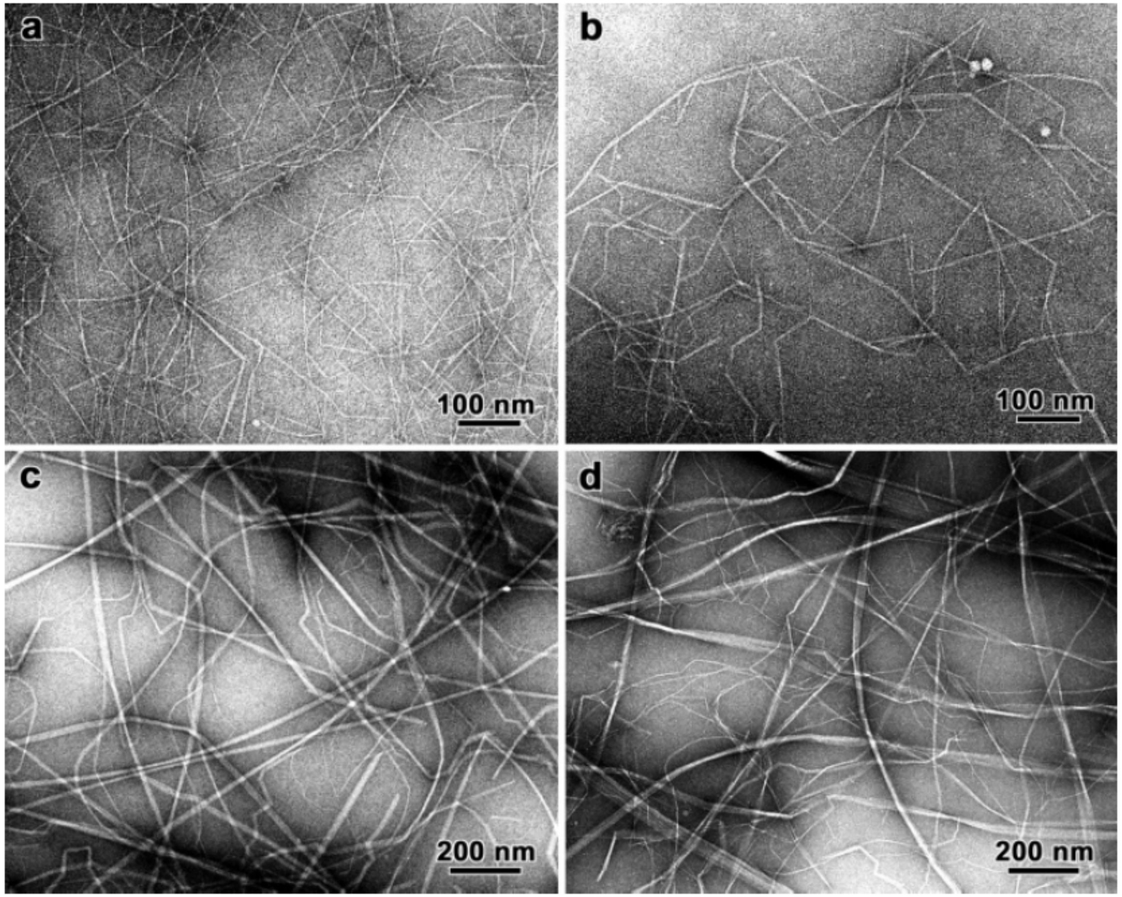
Image from:
Okita et al. *Biomacromolecules* **2010**, *11*, 1696.

# Preparation of cellulose nanofibres: chemical isolation

**Effect of starting material**

wood pulp

cotton



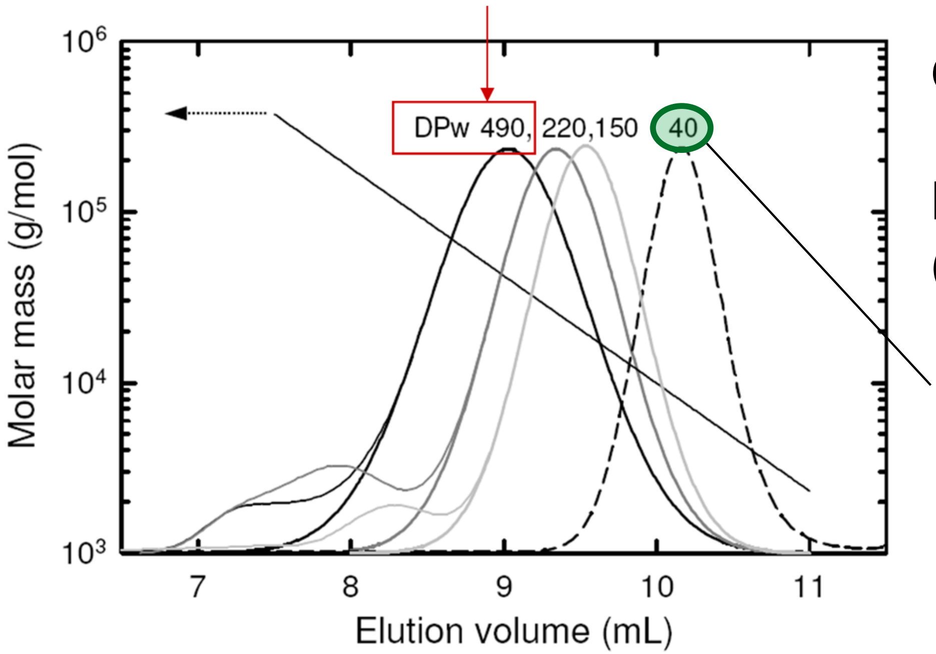

tunicate

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.

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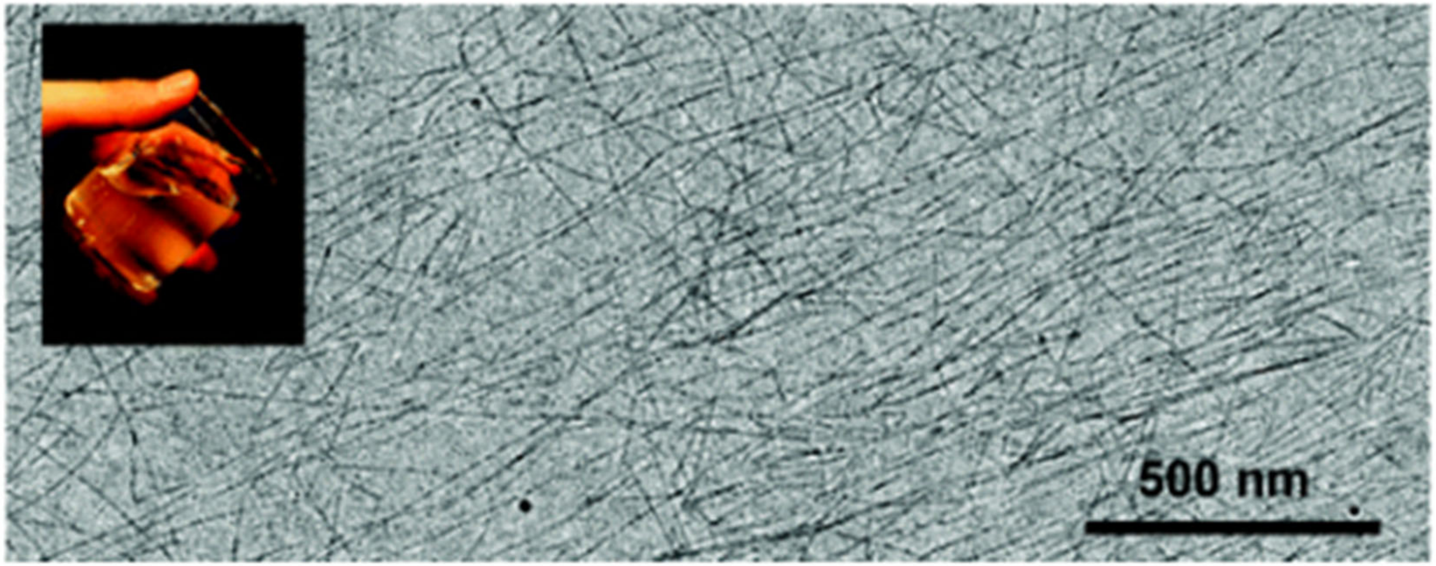
# Preparation of cellulose nanofibres: chemical isolation

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

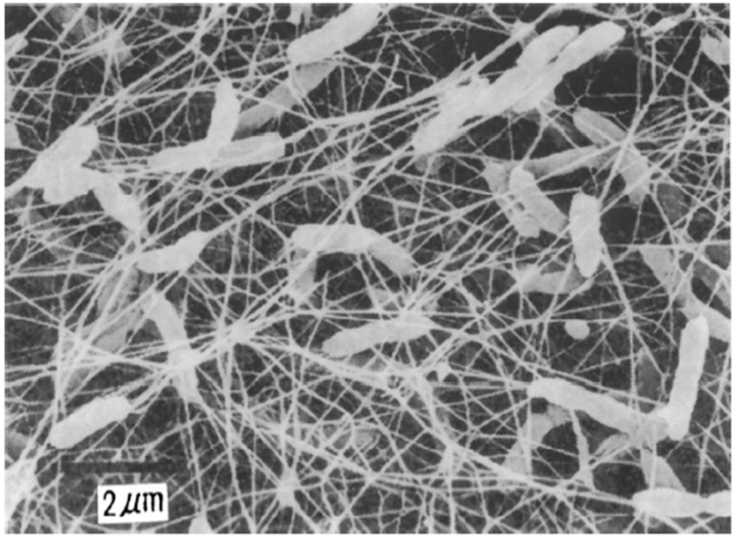





Saito et al. *Biomacromolecules* **2009**, *10*, 1992.

# 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

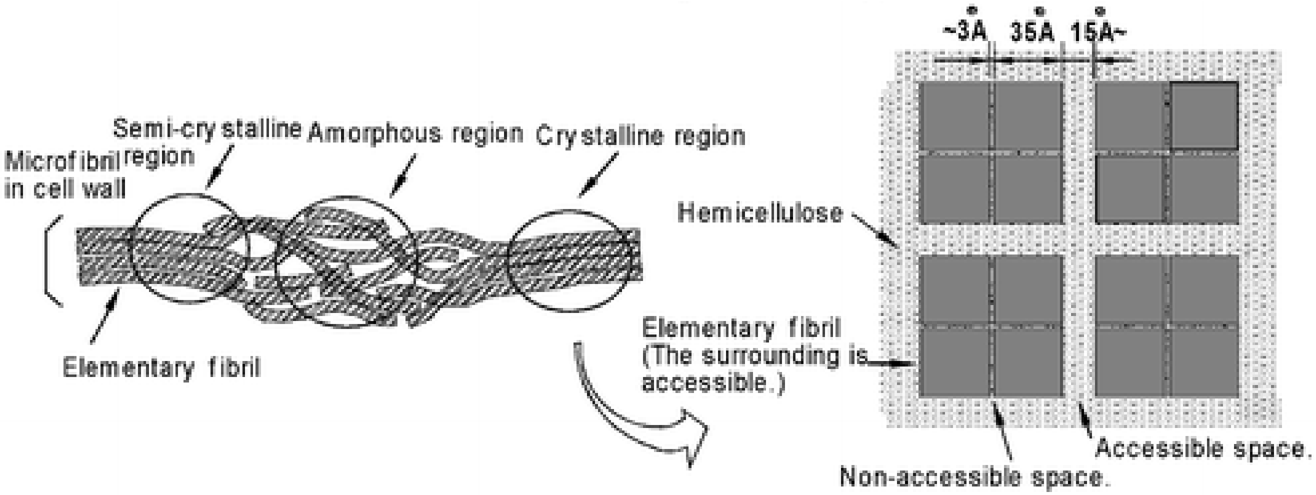



- the microfibrils from bacterial cellulose are larger than in plant cellulose: cross section > 70-140 nm × 7 nm

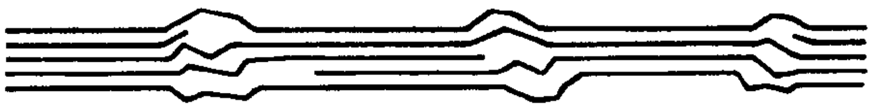
Iguchi et al. *J. Mater. Sci.* **2000**, *35*, 261.

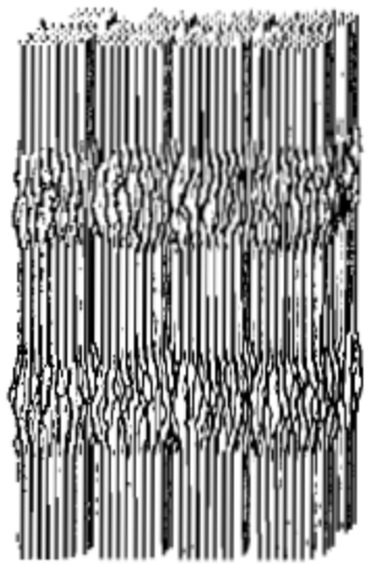
# Cellulose nanocrystals: preparation

# Structure of cellulose microfibril




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

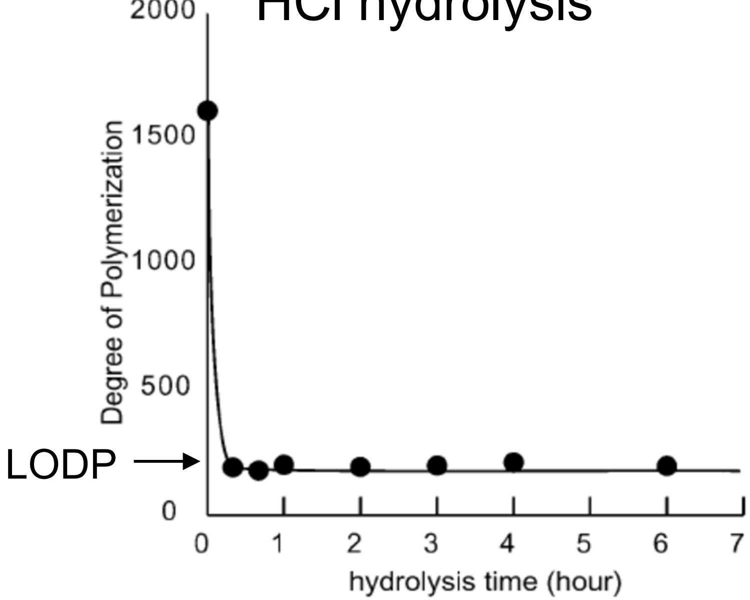




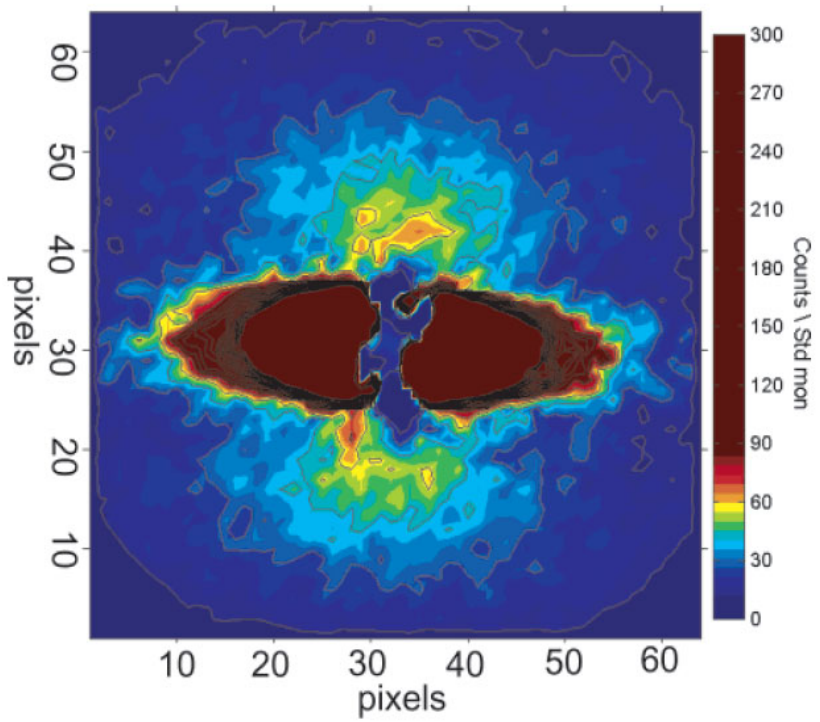
Proposition:
cellulose runs through alternating crystalline and “ amorphous” regions.

# Structure of cellulose microfibril

DP of ramie fibres after HCl hydrolysis




SANS* pattern of untreated ramie



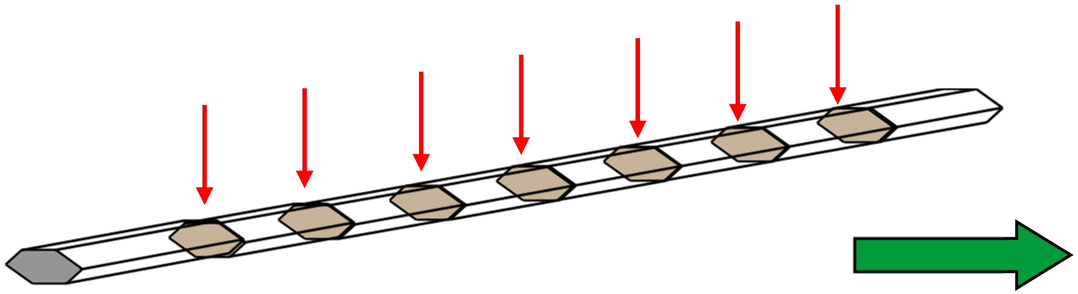

Crystallite length (i.e. length of crystalline domains) by SANS agrees with the level-off degree of polymerization (LODP).

* Small angle neutron scattering

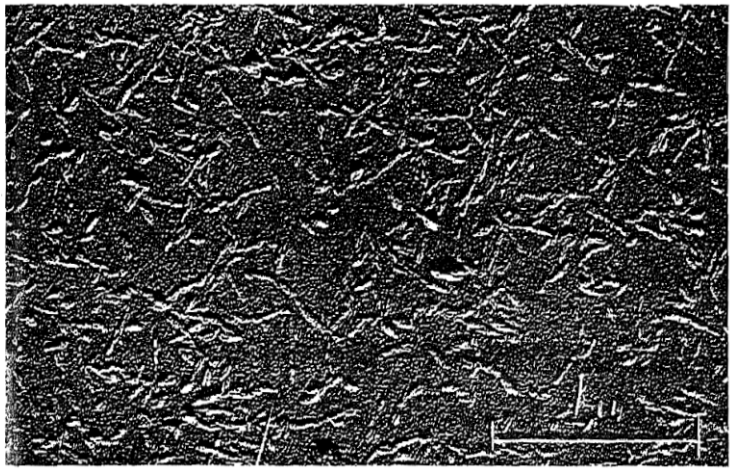
Nishiyama et al. *Biomacromolecules* **2003**, *4*, 1013.

# 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.



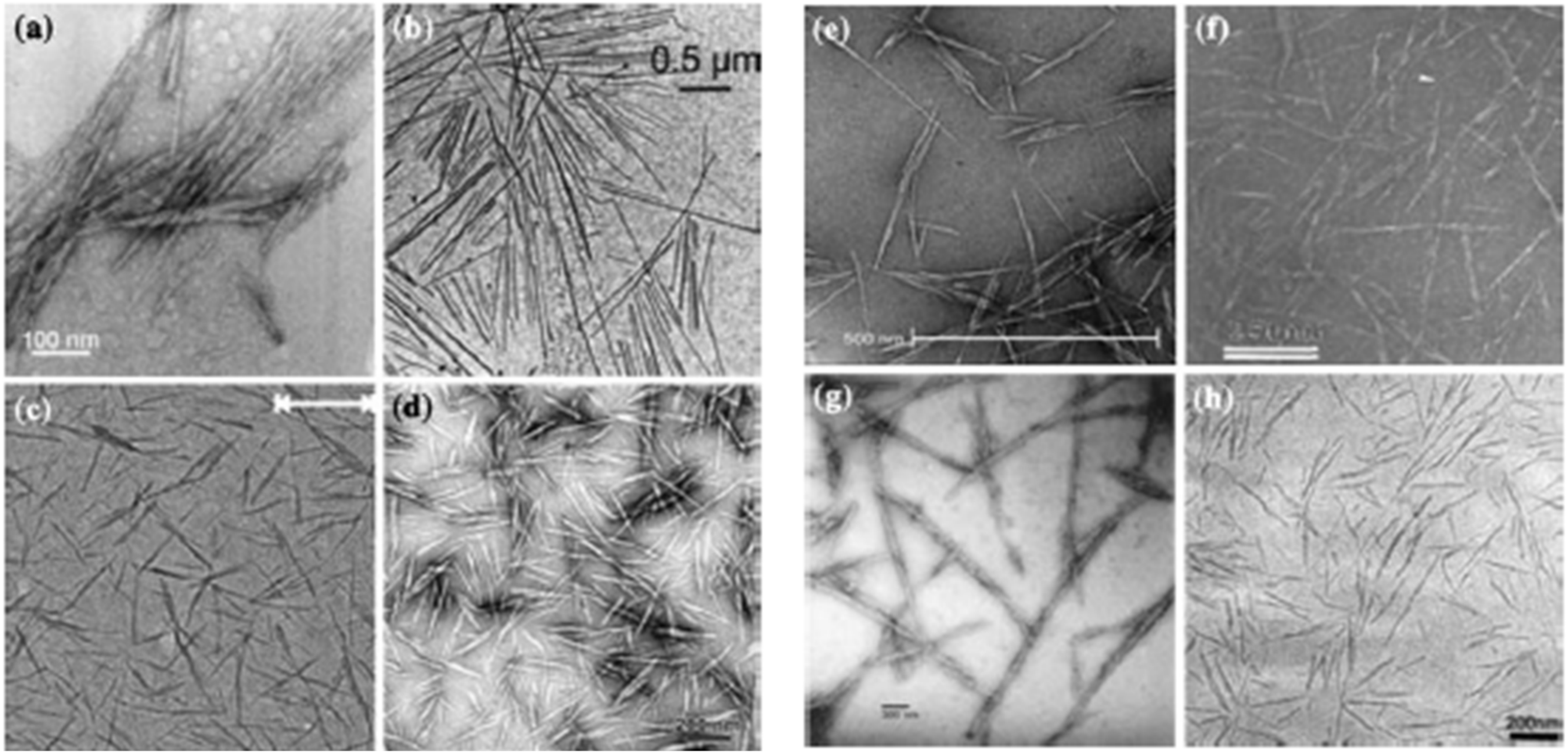
Result: cellulose nanocrystals

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

# Cellulose nanocrystals - dimensions

Nanocrystal dimensions depend on the starting material (botanical source).

Microcrystalline cellulose | Tunicate | Sisal | Straw

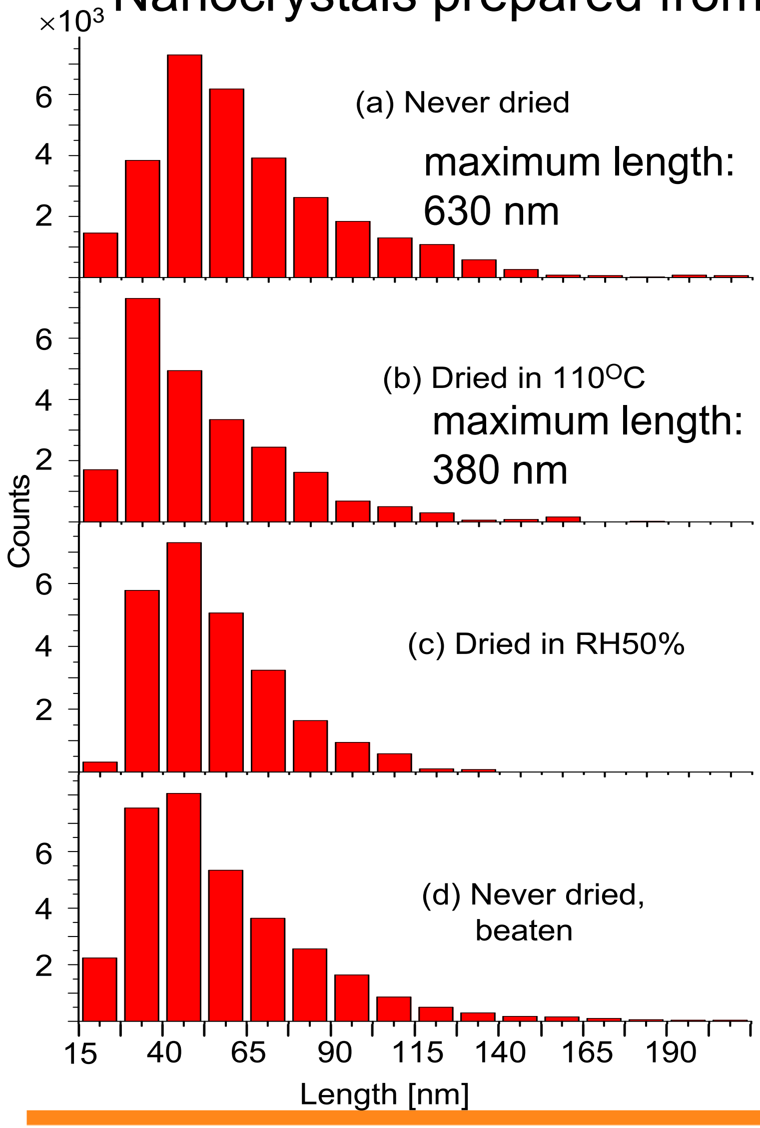



Cotton | Ramie | Bacterial cellulose | Sugarbeet

Eichhorn et al. *J. Mater. Sci.* **2010**, *45*, 1.

# Cellulose nanocrystals - dimensions

Nanocrystals prepared from kraft pulp




Average length is roughly similar in all samples (~60 nm)
→ corresponds to LODP of kraft pulp

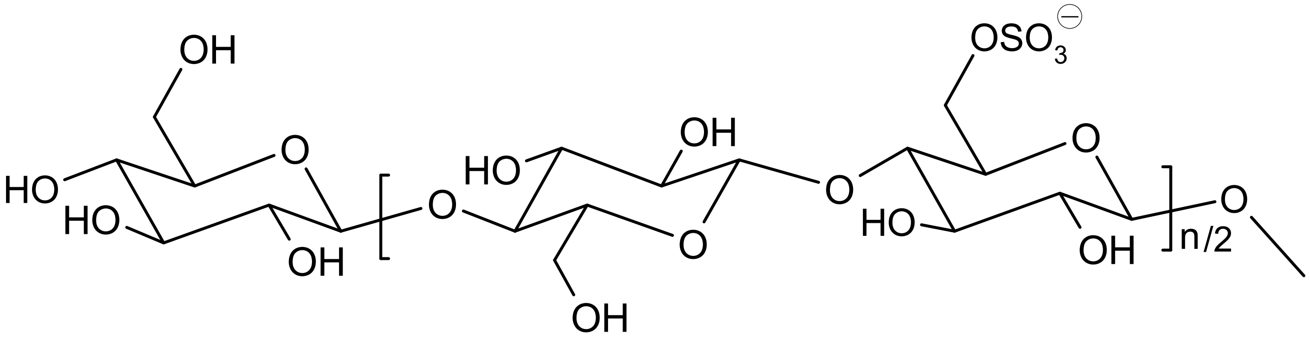
- higher number of longer nanocrystals in never dried samples

- higher amount of shorter nanocrystals in dried samples

ACID HYDROLYSIS IS MORE EFFECTIVE ON DRIED FIBRES.

Kontturi and Vuorinen
*Cellulose* **2009**, *16*, 65.

# Cellulose nanocrystals – surface charge



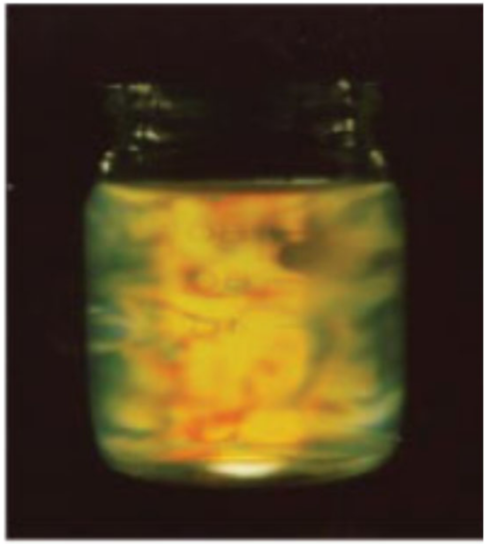

When prepared with sulfuric acid, organic sulphate groups are introduced on the surface of the nanorods.

electrostatic repulsion

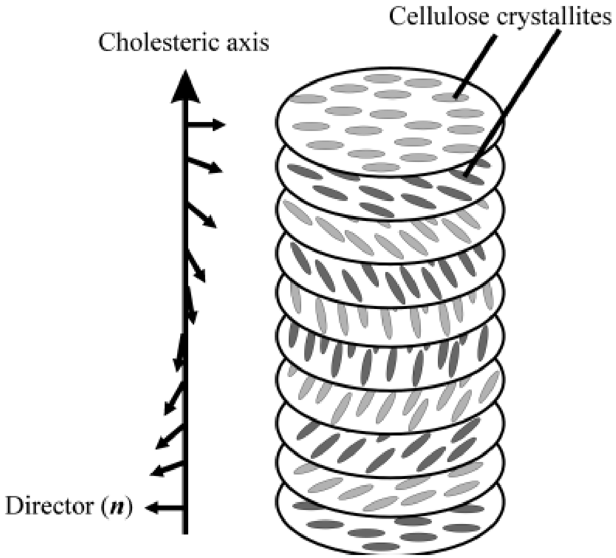
**STABLE SUSPENSION IN WATER**

# Cellulose nanocrystals – liquid crystals

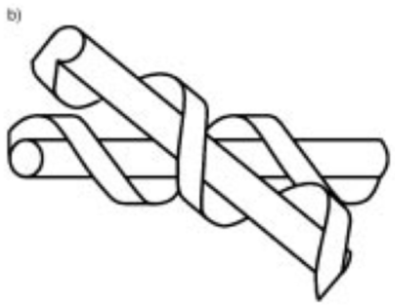
Cellulose nanocrystals spontaneously forms a liquid crystal phase in solution.



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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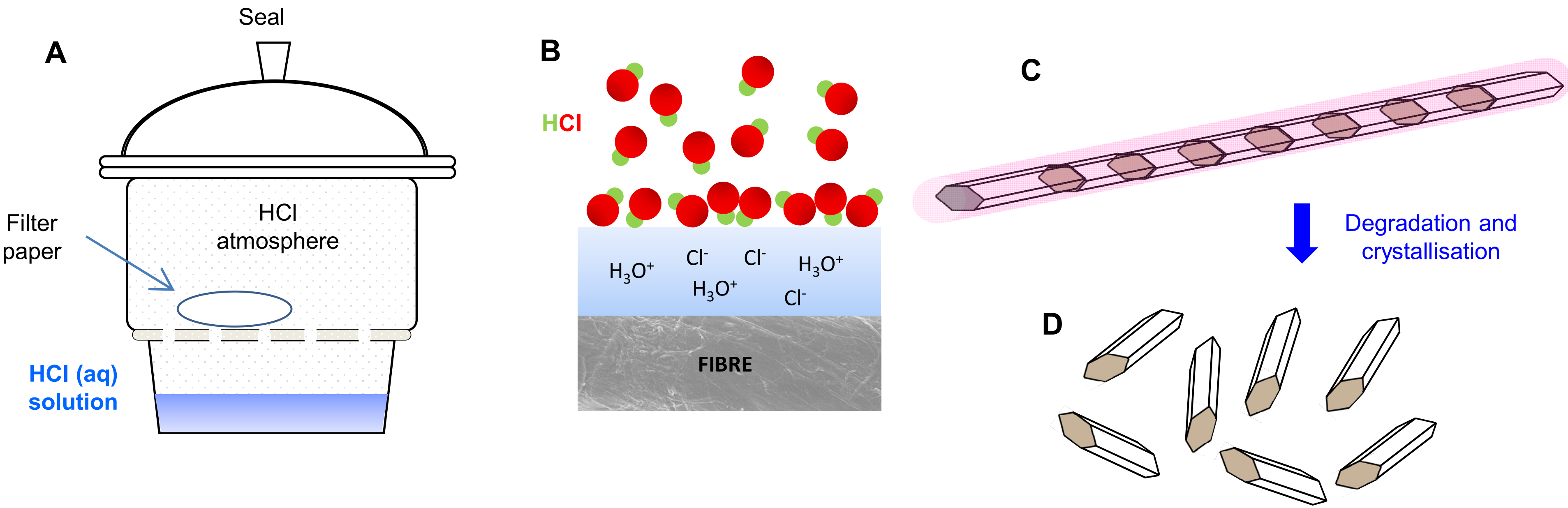
# Concept for preparation of cellulose nanocrystals with acid vapor




- 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

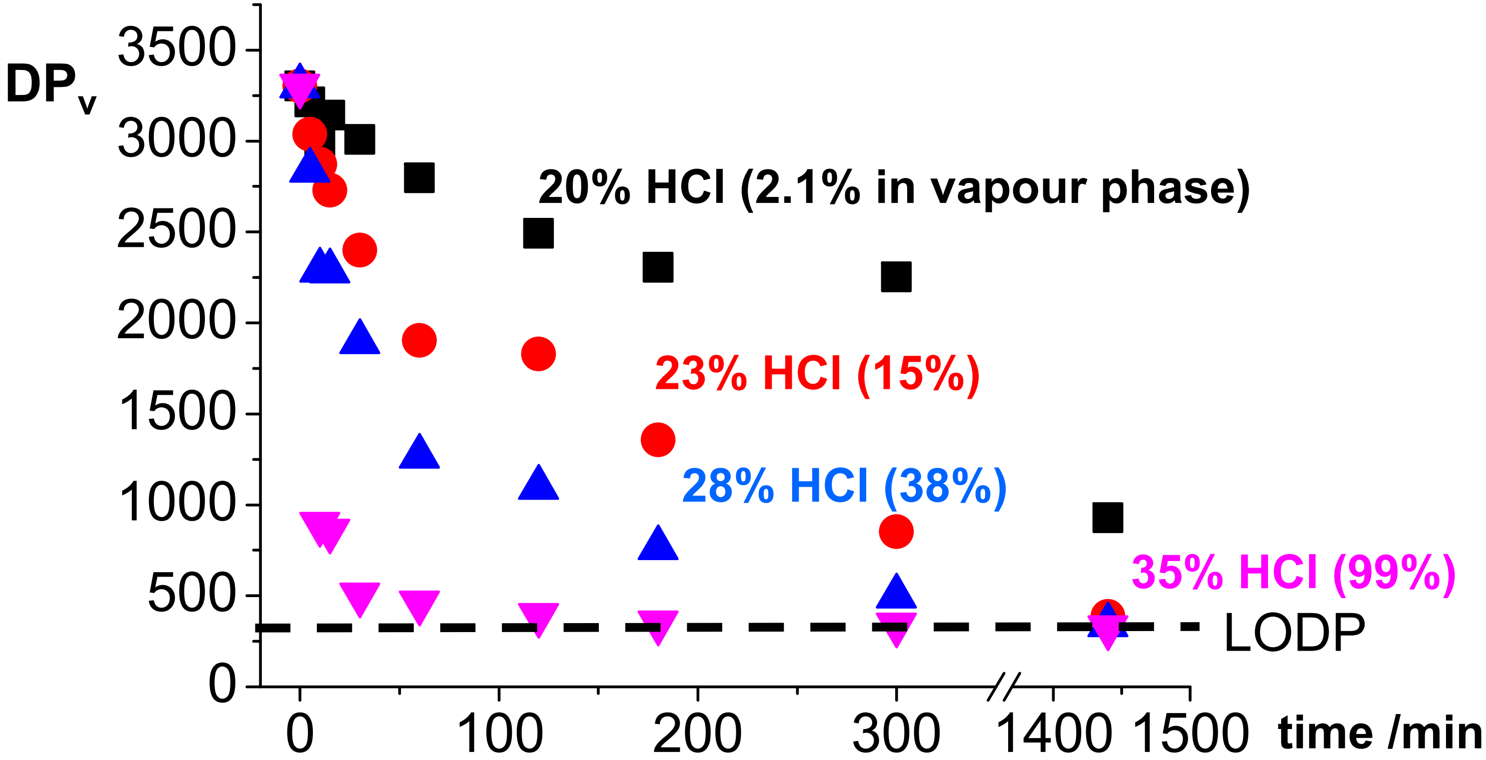
→ Acid and water degrade cellulose until the LODP

→ 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)

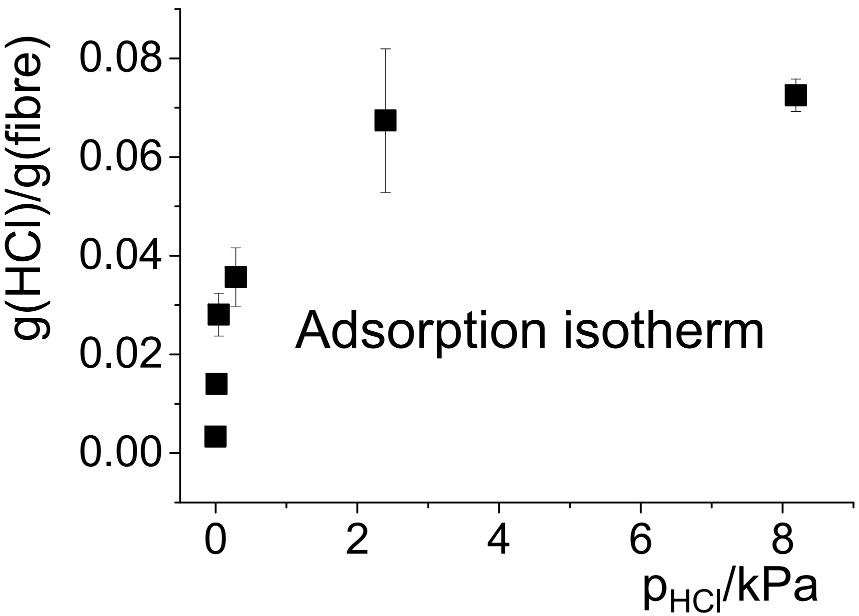



→ Rapid degradation down to LODP level **at room temperature**

# 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

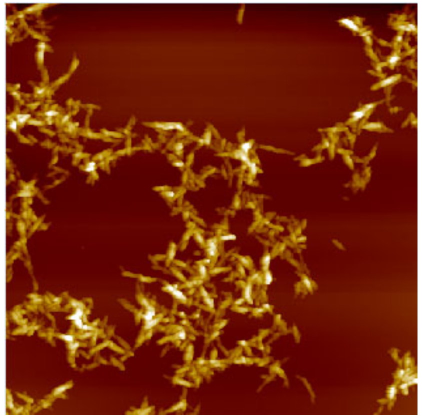
↓

Grinding the hydrolysed substrate in a Wiley mill

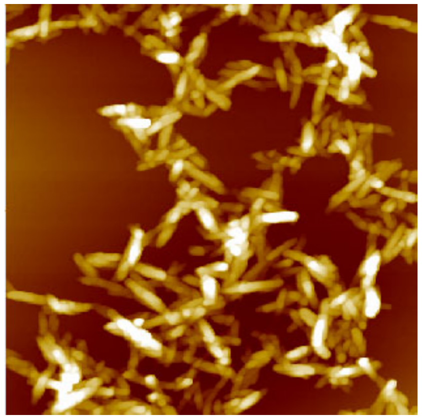
↓

Dispersing the powder in formic acid (heavy sonication)

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



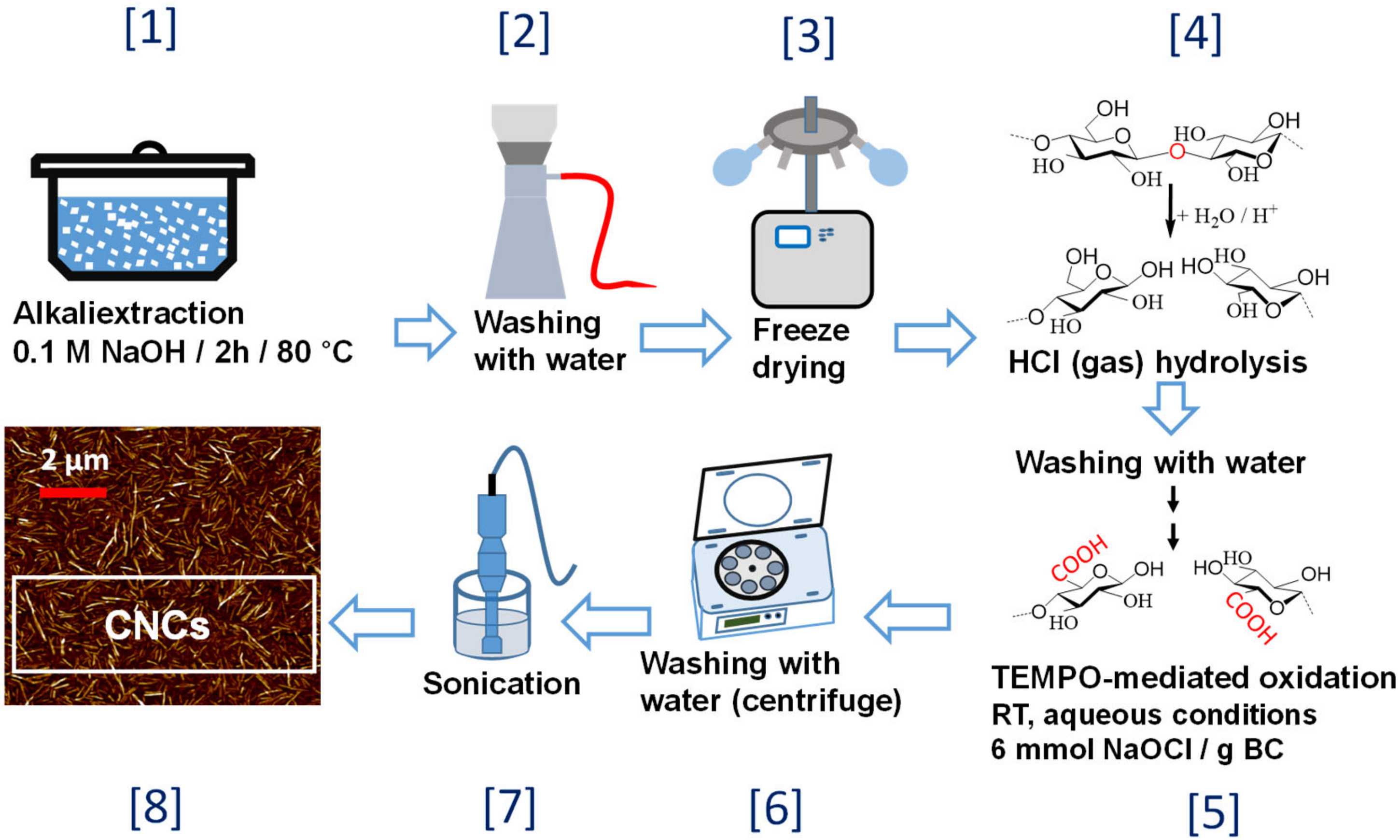
5×5 μm²



2×2 μm²

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

# CNCs by acid gas and TEMPO-oxidation




**>80% yield!**

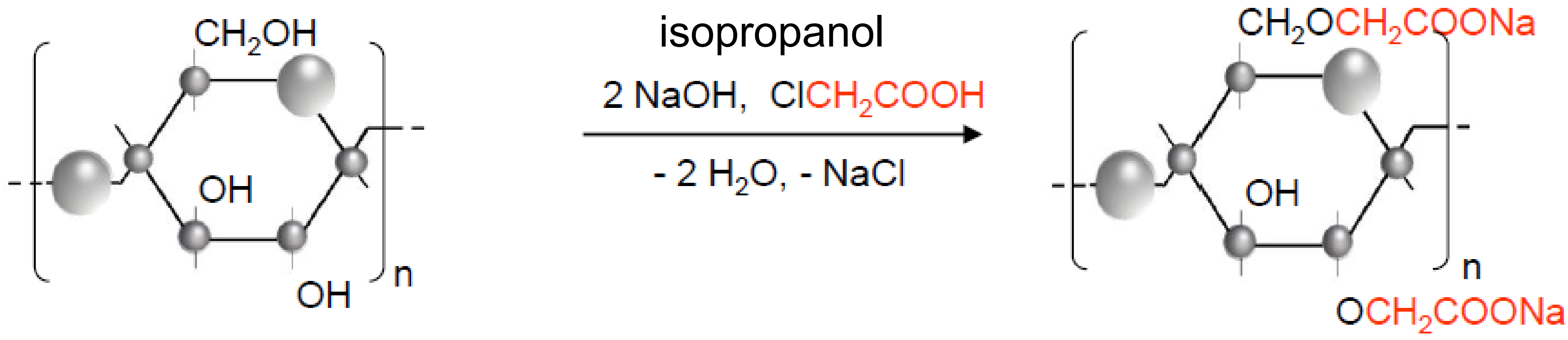
Pääkkönen et al. *ACS Sustainable Chem. Eng.* **2019**, *7*, 14384.

# Cellulose nanofibres: modifications

# Strategies for CNF modification

- CNF modification is *always* surface modification
- Functional groups are attached on the surface of CNF and the interior semi-crystalline microfibril remains intact
- CNF modification can be performed either before CNF preparation (pre-treatment) or after the CNF has been isolated
- Often aims at better water dispersion (by increasing charge) or decreasing hydrophilic / hygroscopic nature (by introducing hydrophobic functional groups)

# Carboxymethylation of CNF

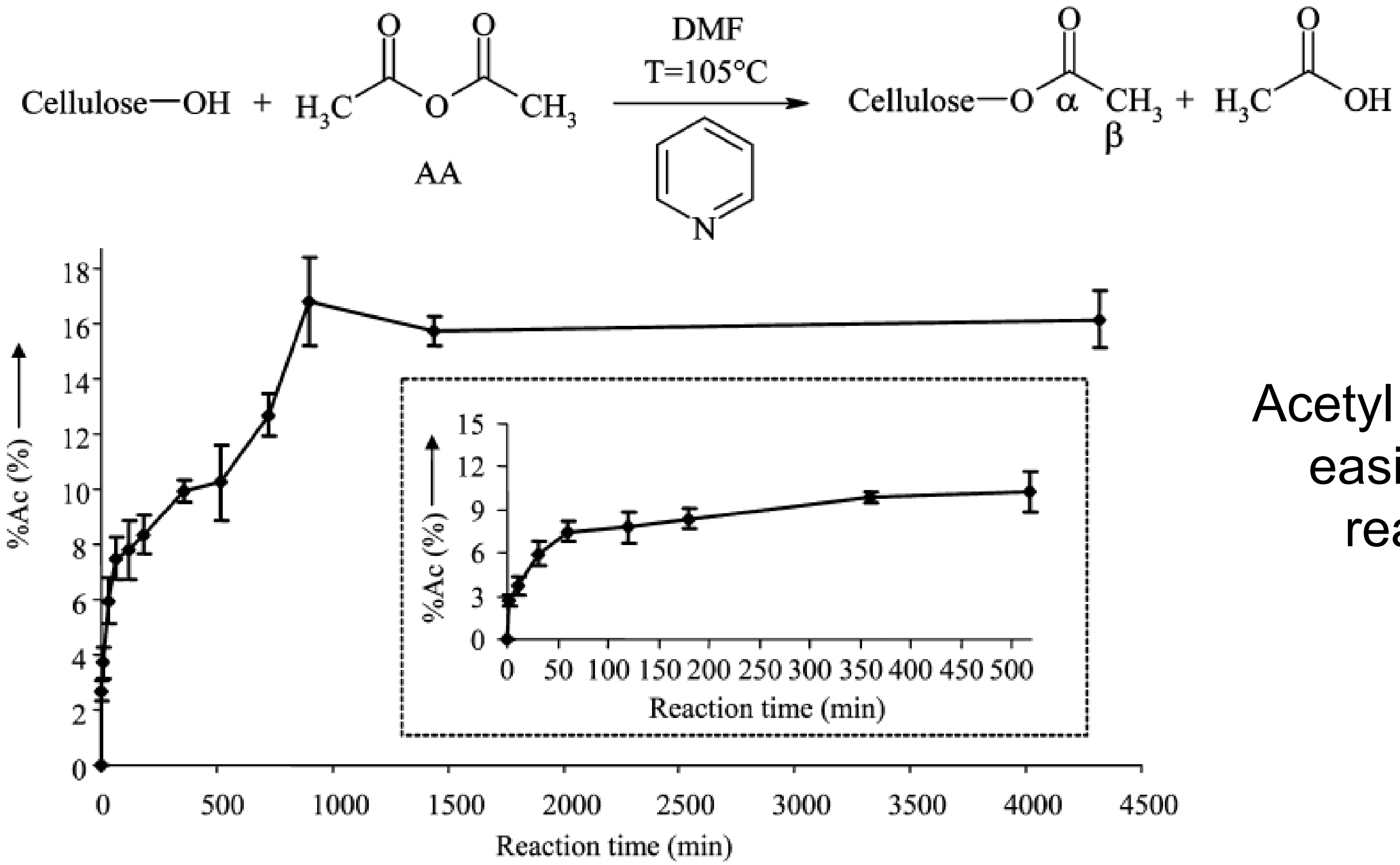



- Carboxymethylation is performed on dissolving pulp prior to CNF preparation (mechanical isolation of CNF)
- Additional carboxymethyl units on CNF surface result in highly charged CNF

Wågberg et al. *Langmuir* **2008**, *24*, 784.

# Acetylation of CNF

CNF is acetylated in dimethyl formamide (DMF) with a pyridine catalyst

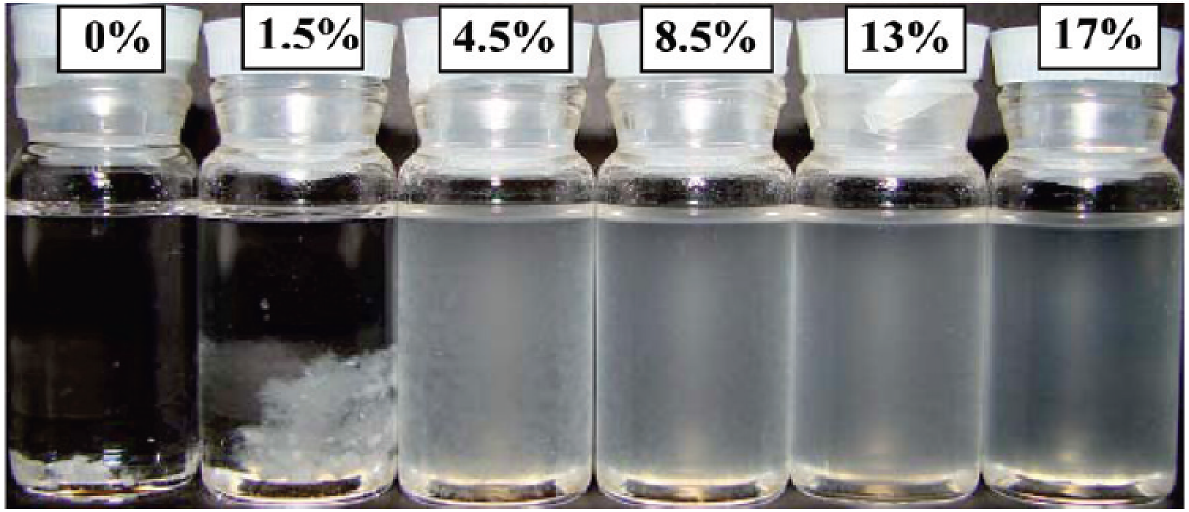



Acetyl content can be easily tuned with reaction time.

Tingaut et al. *Biomacromolecules* **2010**, *11*, 454.

# Acetylation of CNF

Acetyl content




- Acetylation dramatically improves the dispersibility of NFC in chloroform

Tingaut et al. *Biomacromolecules* **2010**, *11*, 454.

# Cellulose nanocrystals: modification

# General issues on CNC modifications

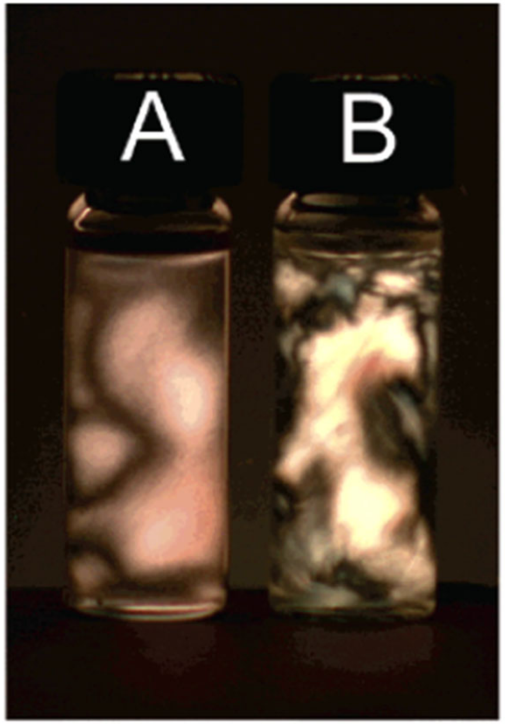
- Like NFC, CNC modification aims at surface functionalization, leaving the crystalline core intact
- Because of the sulphate groups on the CNC surface, they disperse extremely well in water
- However, water is a tricky medium for organic synthesis: most reactions will not work
- Nearly all CNC modification methods are designed to occur after the CNC preparation (no pre-treatments because of harsh preparation conditions)
- Grafting of polymer chains on CNC surface is particularly popular at present

# Cellulose nanocrystals – dispersions

Problem with cellulose nanocrystals:

- they disperse almost only in water (if charged with sulphate groups)
- they do not disperse in nearly anything if they are not charged

→ the use in hydrophobic composite matrix is difficult (aggregation)



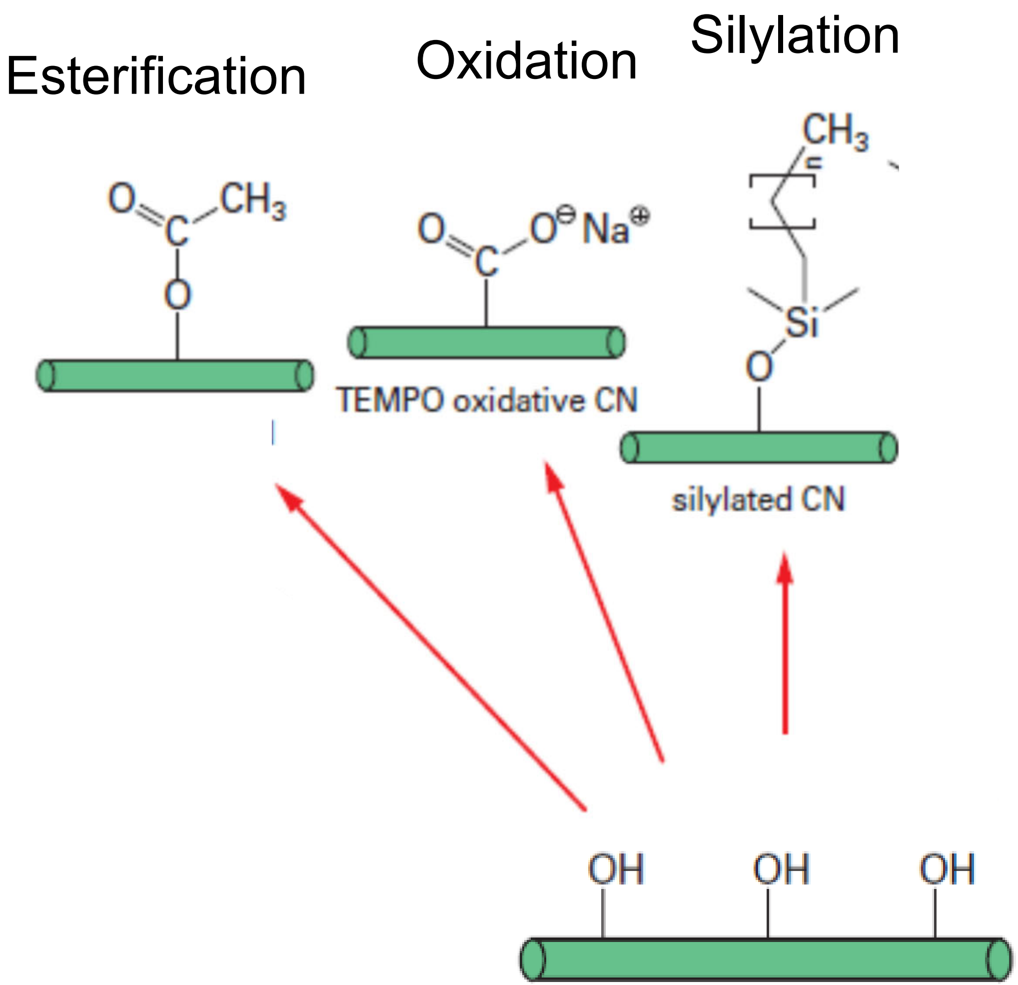

Notable exceptions with dispersing solvents:

- m-cresol (A)
- formic acid (B)

Otherwise, there are intensive research efforts to chemically modify CNCs to improve their dispersion in various media.

van den Berg et al. *Biomacromolecules* **2007**, *8*, 1353.

# CNC modification routes




Note:
Etherification is not generally considered for already isolated CNCs

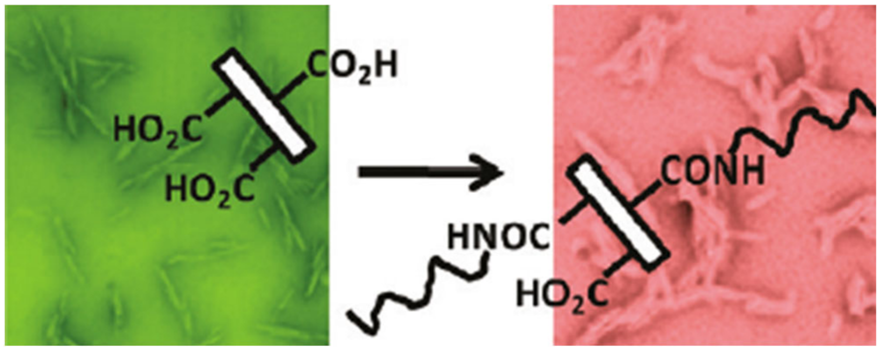
# Polymer grafting on CNCs

**Polymer grafting onto nanocrystal surface is particularly trendy.**

TEMPO-oxidation on whisker surface

↓

Attachment of poly(styrene) or poly(tert-butyl acrylate) on whisker surface (*grafting-to*)

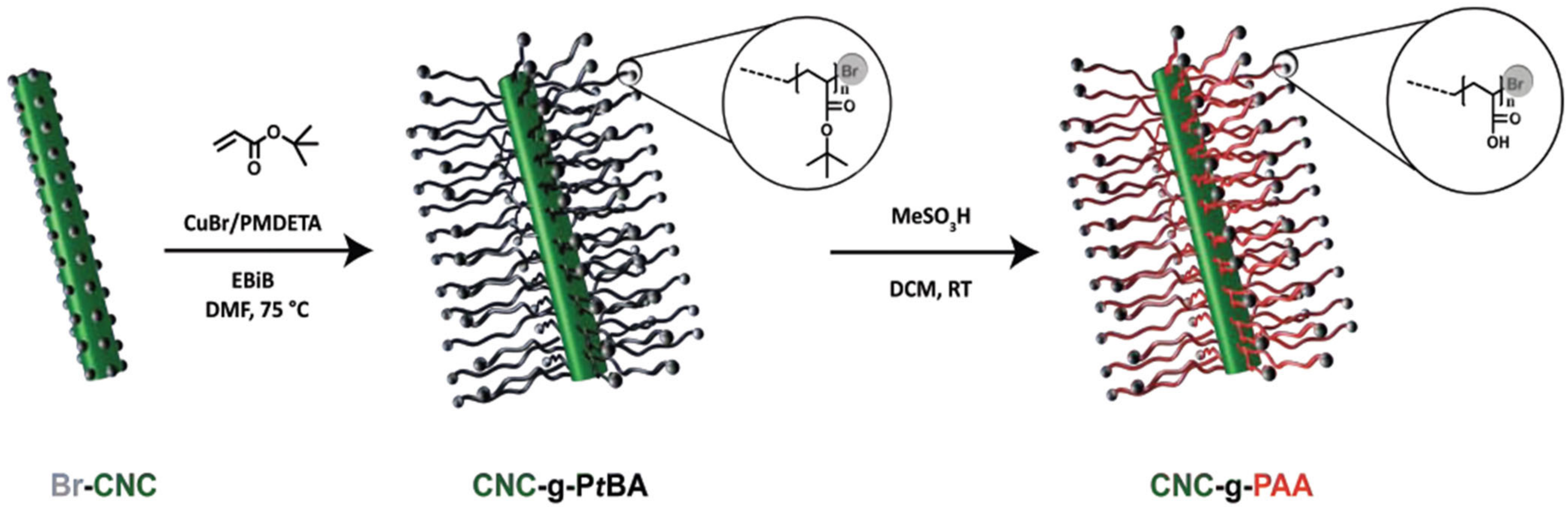



Harrison et al. *Biomacromolecules* **2011**, *12*, 1214.

# Polymer grafting on CNCs

**Polymer grafting onto nanocrystal surface is particularly trendy.**

Activation of nanocrystal surface with an initiator
→ atom transfer radical polymerization (ATRP) of poly(*tert*-butyl acrylate) (*grafting-from*)
→ acid hydrolysis to polyacrylic acid




Majoinen et al. *Biomacromolecules* **2011**, *12*, 2997.

# Summary:
# Nanofibrillar vs. nanocrystalline
# (CNF vs. CNC)

# Different types of nanocellulose – a comparison

Mechanically produced CNFs

- Cheap(ish) (after suitable pretreatments)
- Polydisperse width, mostly higher than in native microfibrils
- Not very stable in dispersion
- Always present with hemicellulose (anything between 3-25%) and traces of lignin

Chemically produced CNFs (TEMPO-oxidized)

- Sodium hypochlorite is expensive
- Monodisperse width that corresponds to the native microfibril
- Stable dispersion because of the charged COOH-groups on the surface
- Not pure cellulose but uronic acid groups on the nanofibril surface
- Includes also hemicellulose which is difficult to quantify because these CNFs resist acid hydrolysis

# Different types of nanocellulose – a comparison

**Cellulose nanofibres**

- **Gels at low concentrations (0.5-1.5 w%)**
- Very high aspect ratio (l/d can be ~1000)
- Flexible, spaghetti-like shape
- Behaviour not always well defined
- Intensive research from 2007 onwards
- Promising in especially composites applications (reinforcing phase)

**Cellulose nanocrystals**

- **Fluid dispersion at low concentrations**
- Not very high aspect ratio
- Rod-like: always straight shape
- Intensive research from 1992 onwards (although a surge after 2005 occurred)
- Promising as filler material, viscosity controller etc.
- Many high end applications have been proposed (incl. liquid crystal utilization)

# Recommended review articles

On all kinds of nanocellulose :
Klemm et al. *Angew. Chem. Int. Ed.* **2011**, *50*, 5438.
Kontturi et al. *Adv. Mater.* **2018**, *30*, 1703779.
Ajdary et al. *Adv. Mater.* **2021**, *33*, 2001085.
Heise et al. *Adv. Mater.* **2021**, *33*, 2004349.

On cellulose nanofibres:
Nechyporchuk et al. *Ind. Crops Prod.* **2016**, *93*, 2.
Wang et al. *Biomacromolecules* **2021**, *22*, 4037.

On cellulose nanocrystals:
Mariano et al. *J. Polym. Sci., Part B* **2014**, *52*, 791.
Trache et al. *Nanoscale* **2017**, *9*, 1763.

On bacterial cellulose:
Wang et al. *Carbohydr. Polym.* **2019**, *219*, 63.

On nanocellulose modification:
Habibi *Chem. Soc. Rev.* **2014**, *43*, 1519.
Eyley and Thielemans *Nanoscale* **2014**, *6*, 7764.