Hydrolysis With Hydrogen Chloride Gas as A Modular Step in Cellulose Nanocrystal Isolation

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TAPPI NANO DIVISION

Research questions

Can we treat acid hydrolysis as a separate procedure in the preparation of cellulose nanocrystals?

Can we better control the yield, morphology and surface chemistry if hydrolysis is a separate step?

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Outline

(1) Isolation of cellulose nanocrystals: background on acid hydrolysis

(2) Liquid/solid *vs.* gas/solid system

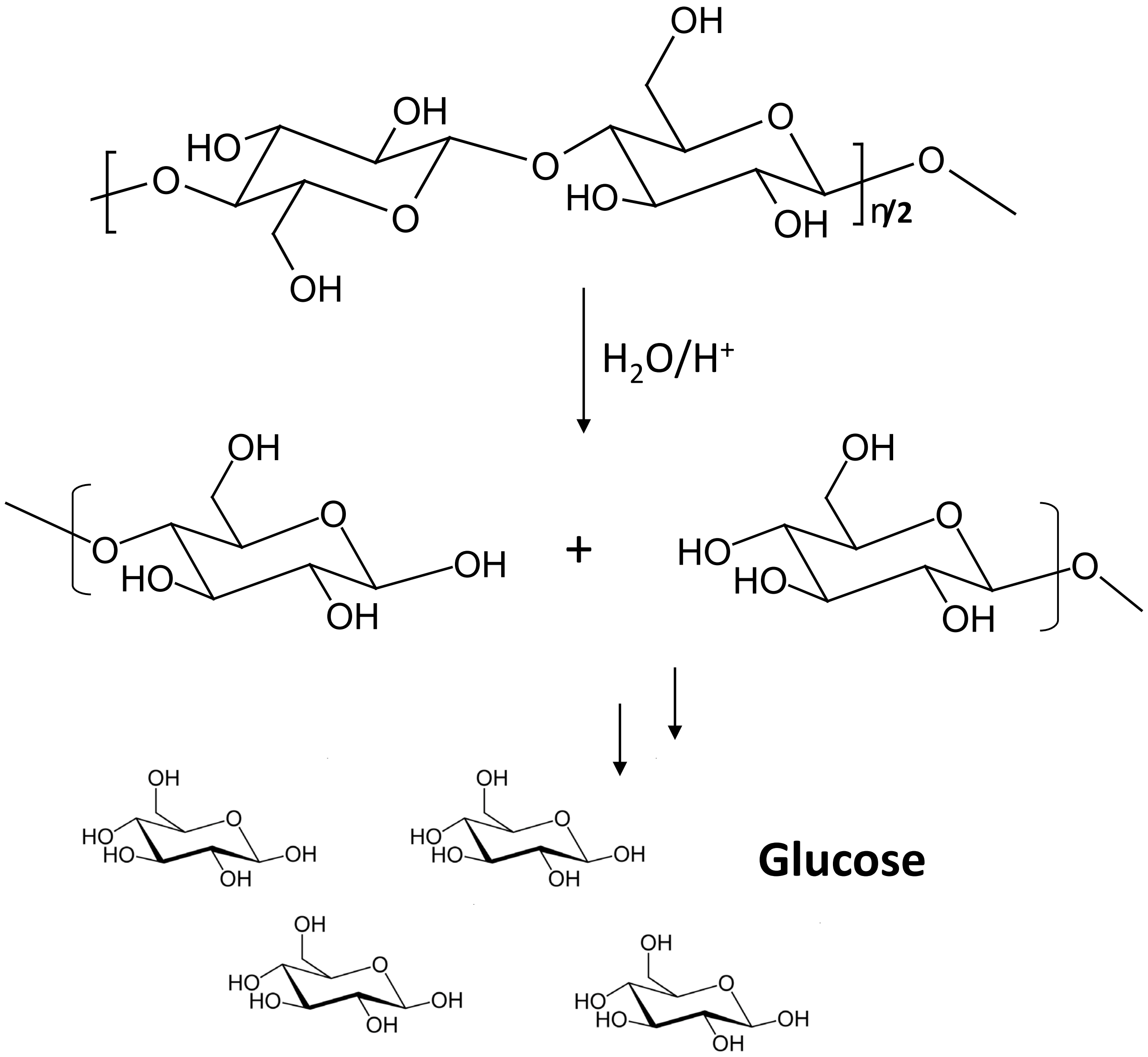
(3) Acid hydrolysis of cellulosic fibers by HCl (g)

(4) Dispersion of CNCs from hydrolysed fibres

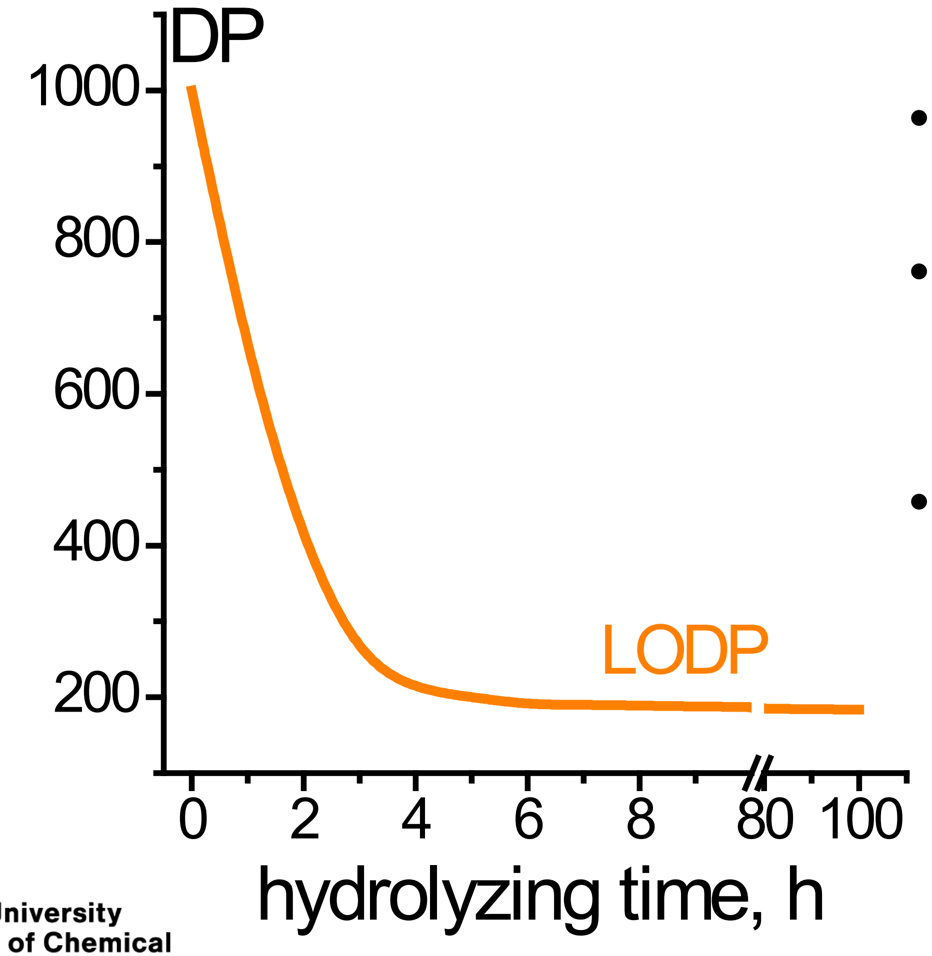
Acid hydrolysis

Degradation to glucose

- Extreme concentrations are required for complete degradation; e.g., 72% (w/w) H_2SO_4



Leveling-off degree of polymerization (LODP)



- When "extreme concentrations" are not used
- Levelling-off degree of polymerization: acid hydrolysis nearly halts at a certain point of degradation
- Common explanation for LODP: "amorphous" regions are hydrolysed and crystallites are left intact

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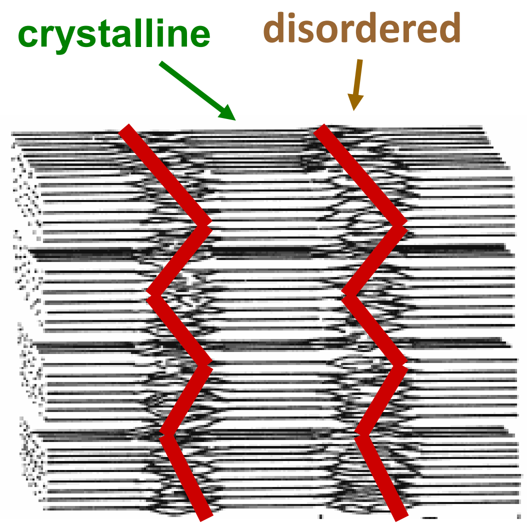
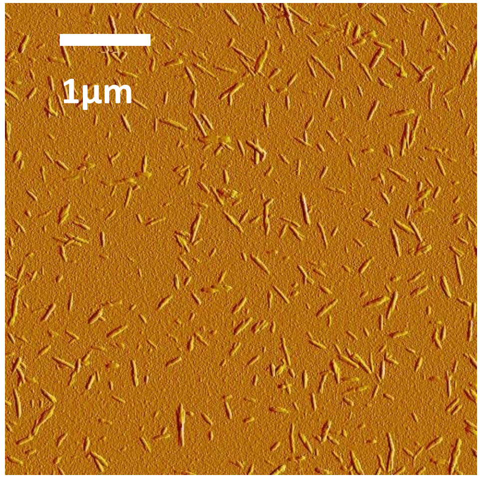
Principle behind Cellulose Nanocrystal isolation

Cellulose microfibril



Strong acid hydrolysis →

Cellulose nanocrystals



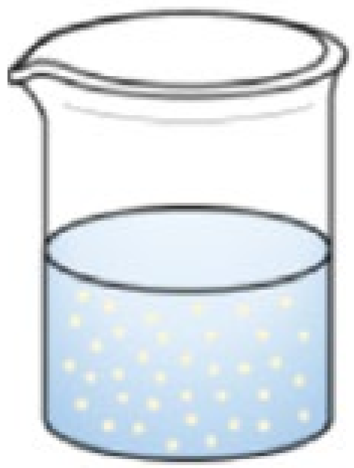
Result:
Cellulose Nanocrystals

Acid hydrolysis targets the disordered regions in a cellulose microfibril.

Gas/solid system *vs.* liquid/solid system

Liquid/solid system

- Solid fibers / liquid (aqueous) acid (or other catalyst)
- The most common system for cellulose hydrolysis
- Usually under elevated temperatures (~80-100°C)
- Purification of the products is not straightforward



Gas/solid system

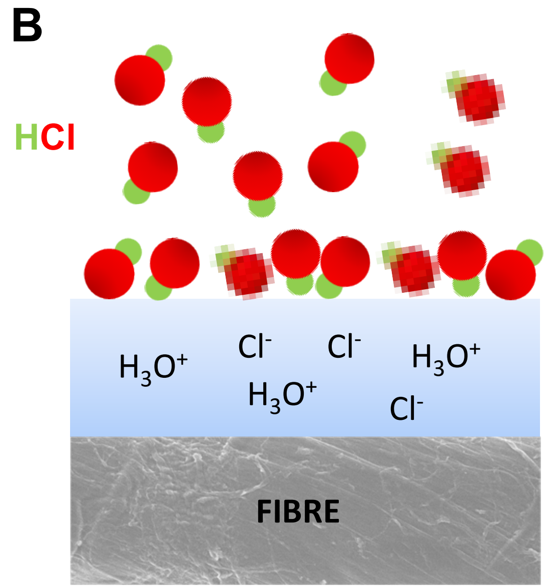
- Gaseous acid adsorbs on the fiber surface
- Fibers are covered by a thin layer of water

→ Acid dissociates

→ Hydrolysis proceeds

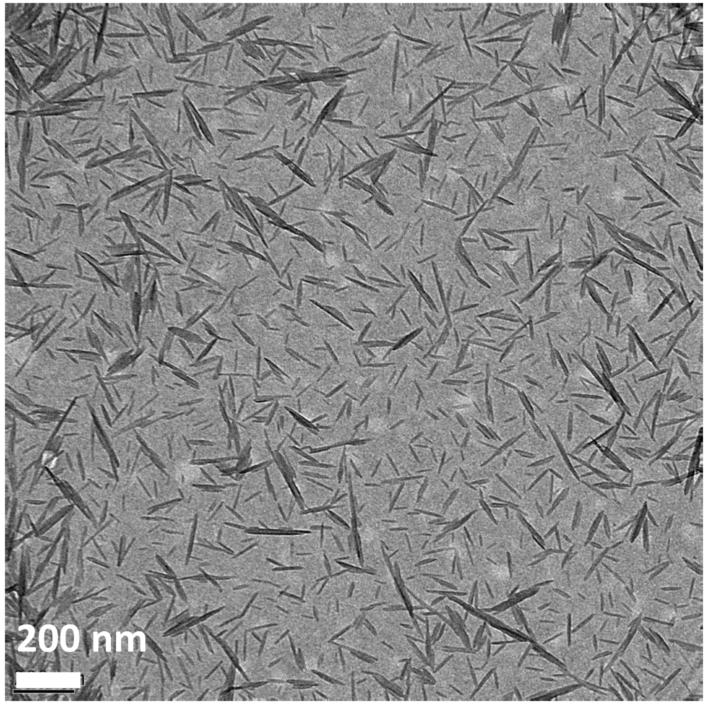
→ After hydrolysis, the acid desorbs

→ Purification of the products is simple



Isolation of cellulose nanocrystals (CNCs) by gaseous acid

CNC preparation – state of the art



- Source: Whatman 1 (from cotton linters)
- Temperature: 45ºC
- Acid concentration: 64% (w/w) H_2SO_4 (aq)
- Time: 45 min

Purification steps:

- Centrifugation
- Dialysis (~7 days)
- Filtering

- Yields are generally low: 20-50%
- Water consumption is huge

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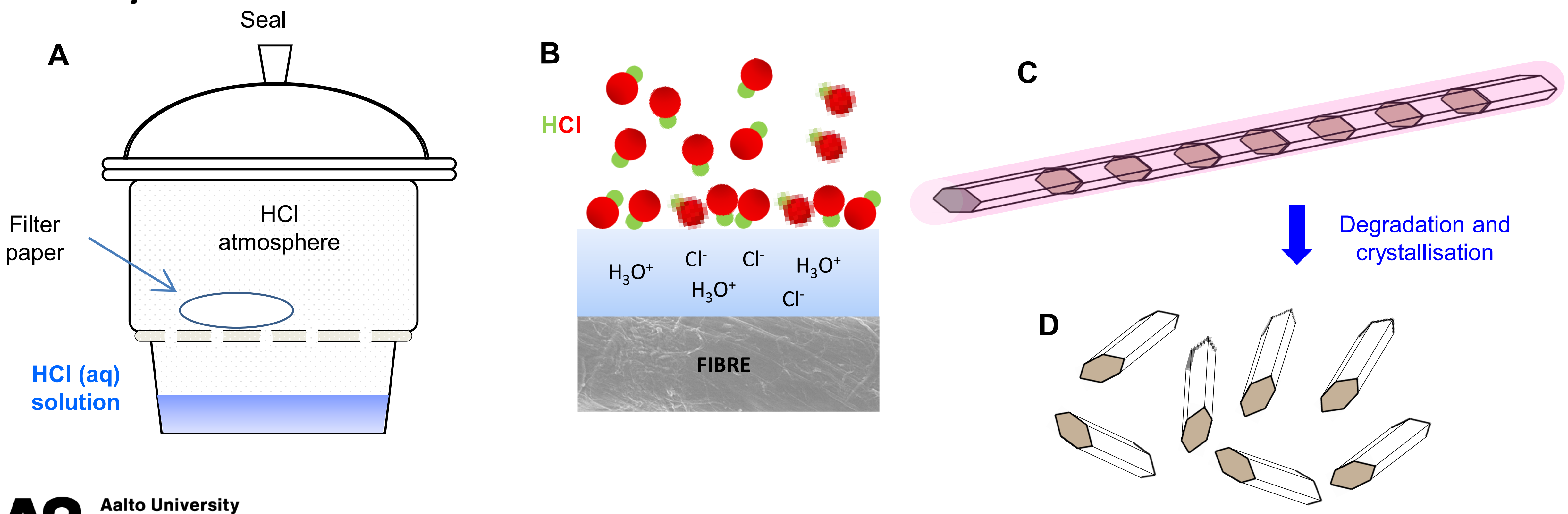
CNC isolation by HCl vapor

- Gaseous HCl molecules adsorb on water-covered fibers
- Adsorbed HCl dissociates and catalyzes cellulose hydrolysis to LODP
- CNCs can be dispersed from hydrolyzed fibres in formic acid

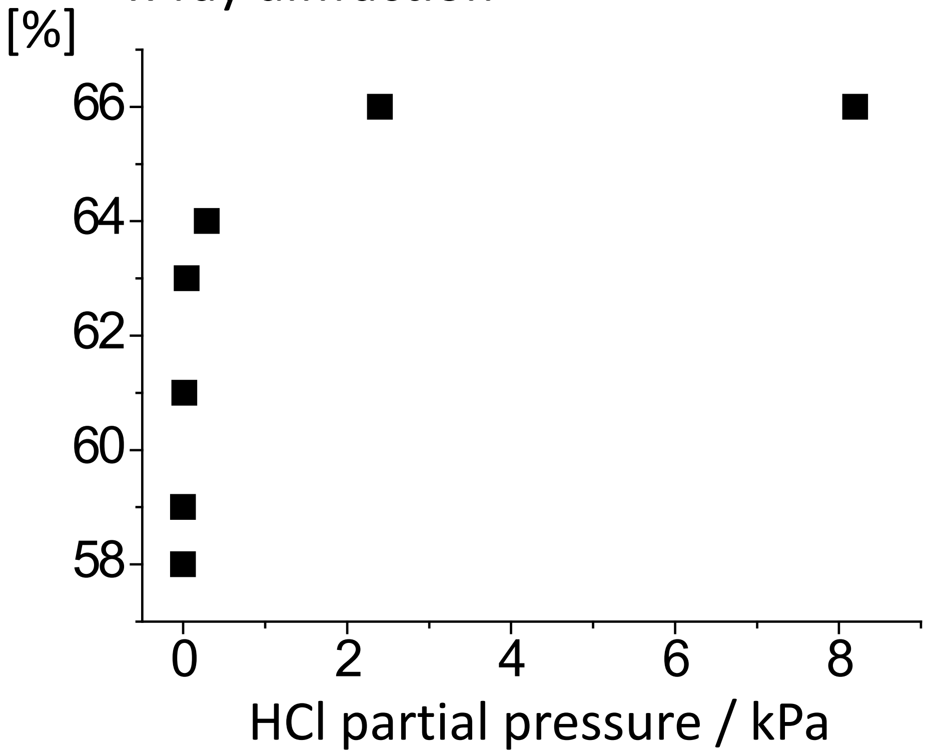
→ 97% yield



Kontturi et al. *Angew. Chem. Int. Ed.* **2016**, *54*, 14455.

Crystallinity in HCl (g) hydrolysis

Degree of crystallinity as determined by x-ray diffraction



NOTE: No change in morphology of the fibres

NOTE: No mass transfer out of the fibres

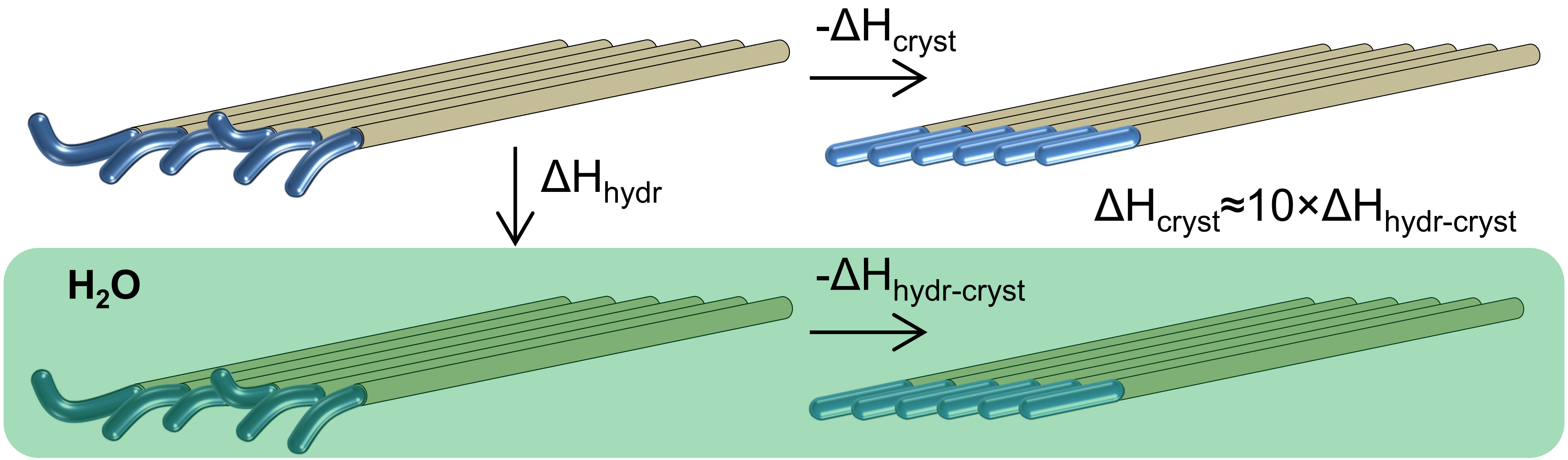
- Acid hydrolysis of cellulose usually results in formation of extractable sugars
- Hot water extraction of the hydrolyzed filter paper failed to extract virtually *anything*

REASON: vapour phase acid causes crystallization of cellulose simultaneously with its degradation.

Kontturi et al. *Angew. Chem. Int. Ed.* **2016**, *54*, 14455.

Crystallinity in HCl (g) hydrolysis

Why does the crystallinity increase?



Under water, the energy required for crystallization is 10-fold to compared with the energy required in air.

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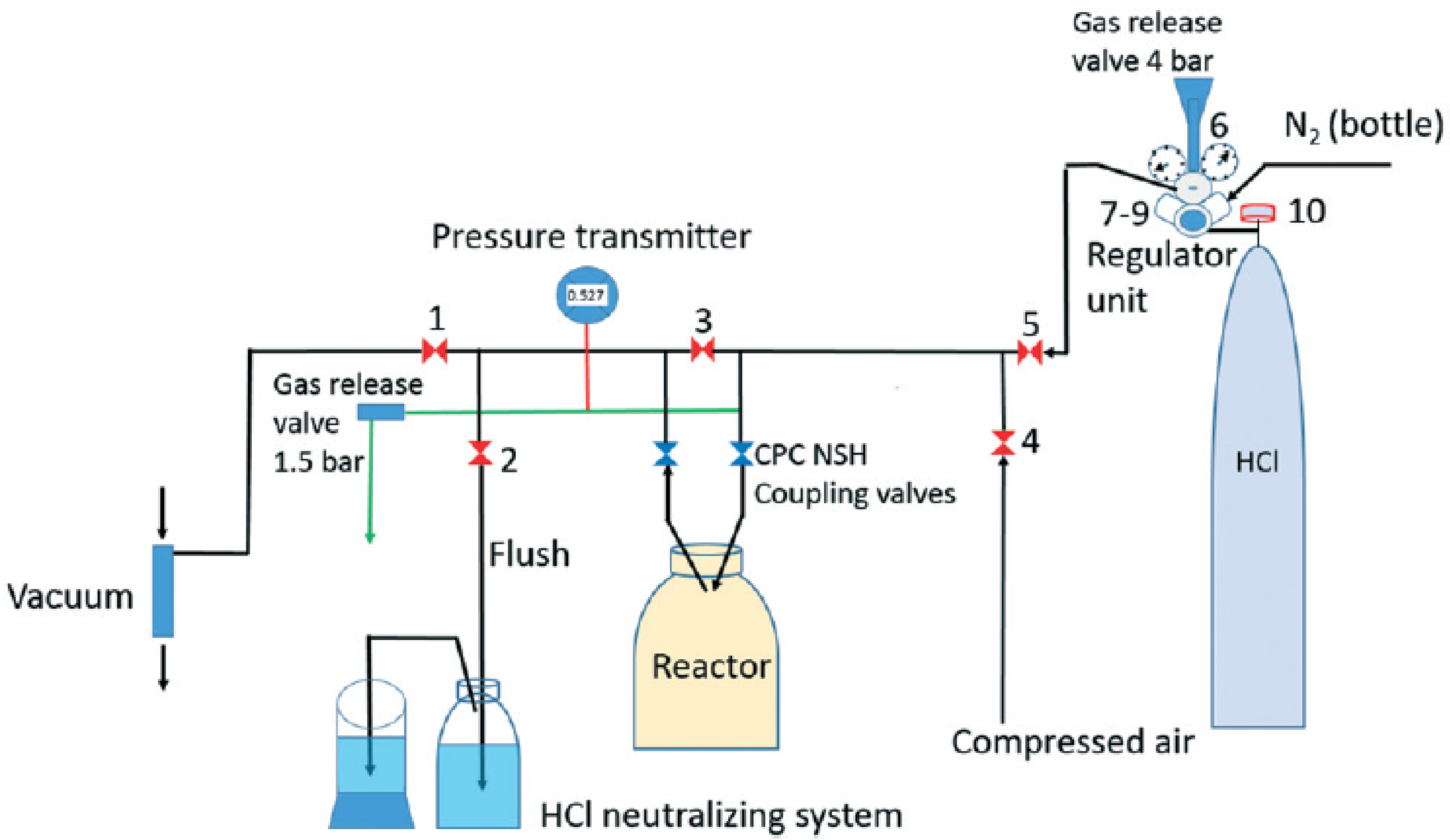
Kontturi et al. *Angew. Chem. Int. Ed.* **2016**, *54*, 14455.

Upscaled reactor for HCl (g)



- Custom built reactor enables upscaling from gram scale to hundreds of grams
- HCl (g) pressure can be rised to several bars instead of vapor pressure (<0.1 bar at most)

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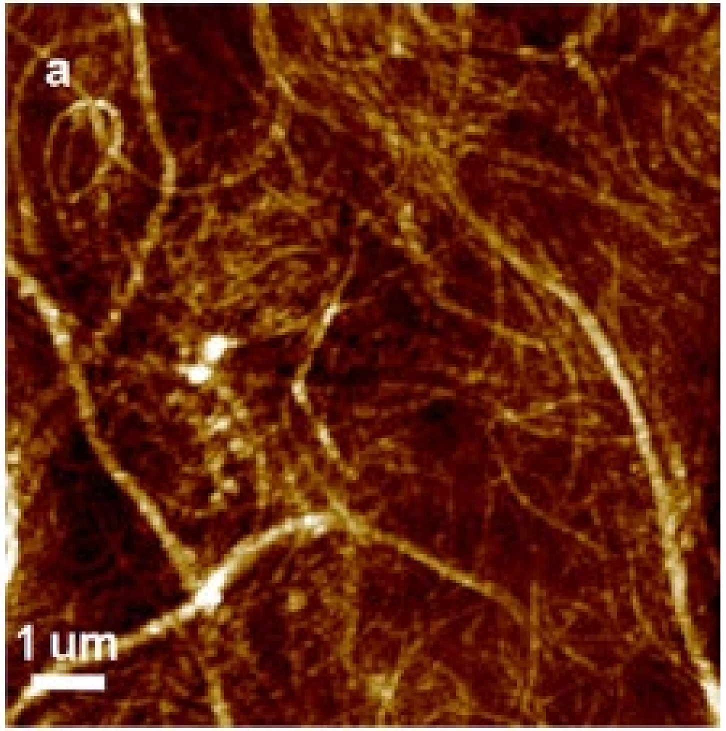
Pääkkönen et al. *React. Chem. Eng.* **2018**, *3*, 312.

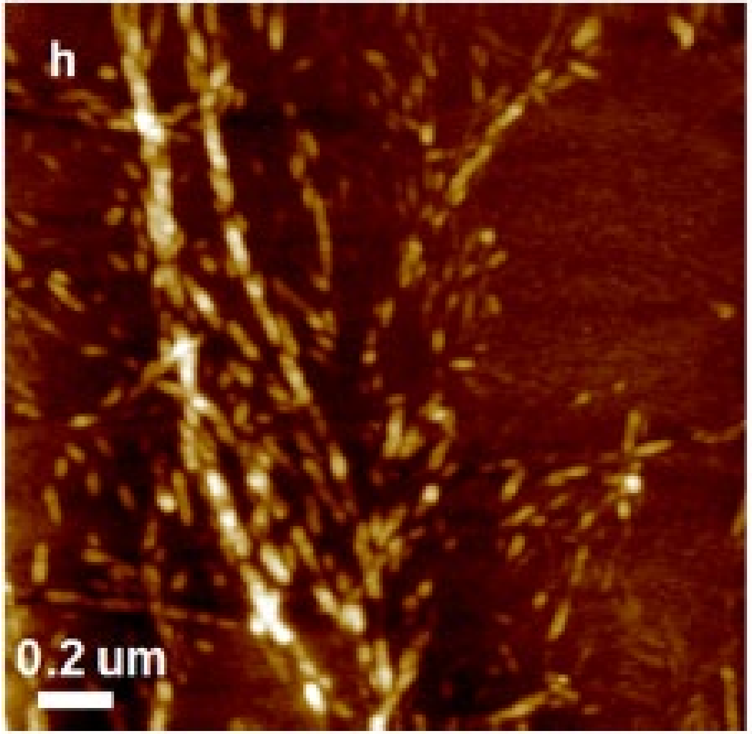
Analytical detour

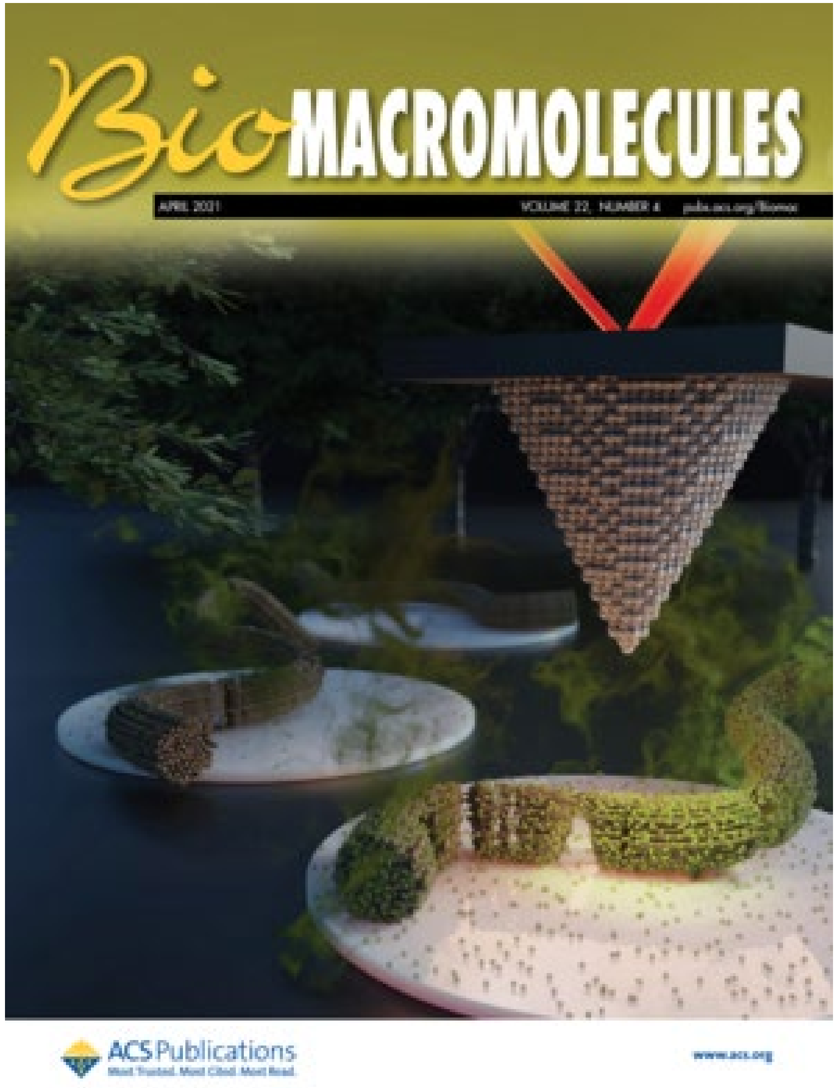
Crystalline/disorder transition in cellulose microfibrils visualized by HCl (g) hydrolysis

Pristine isolated microfibrils



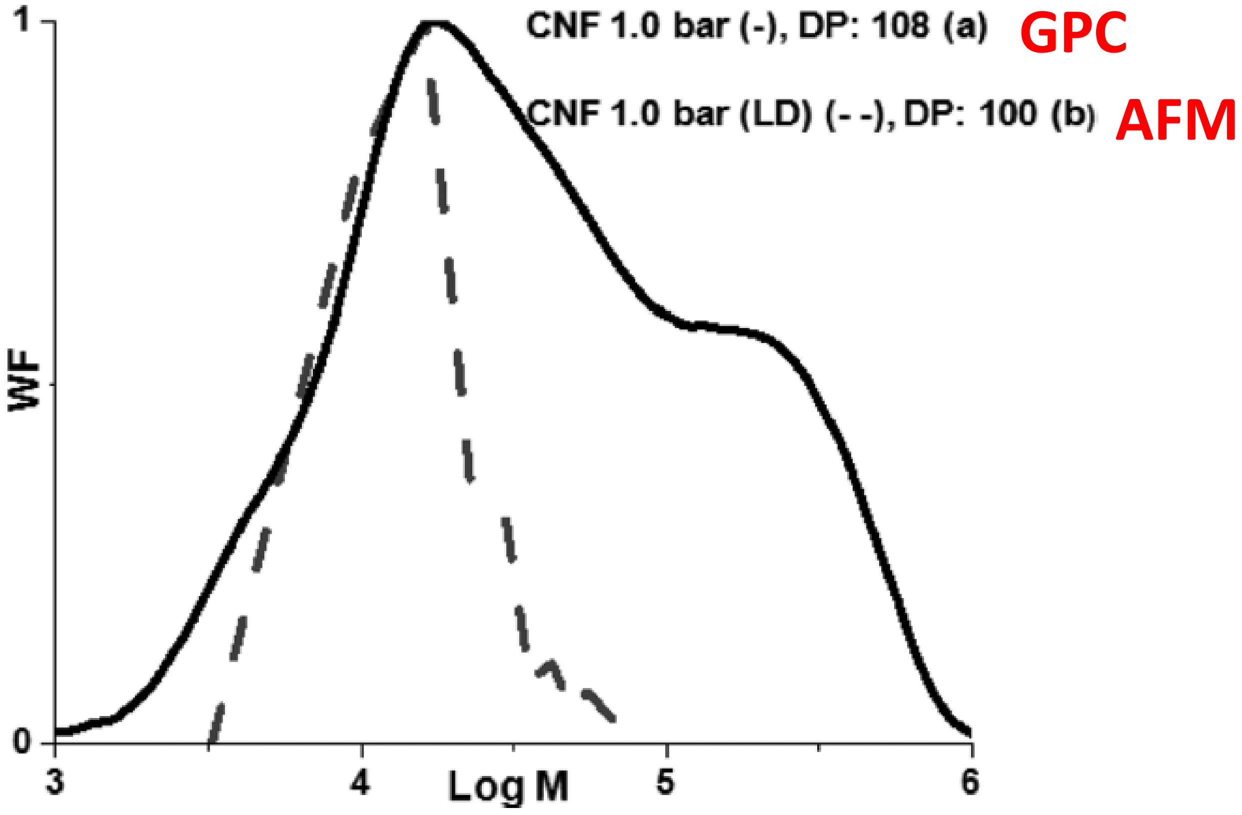
Hydrolyzed microfibrils

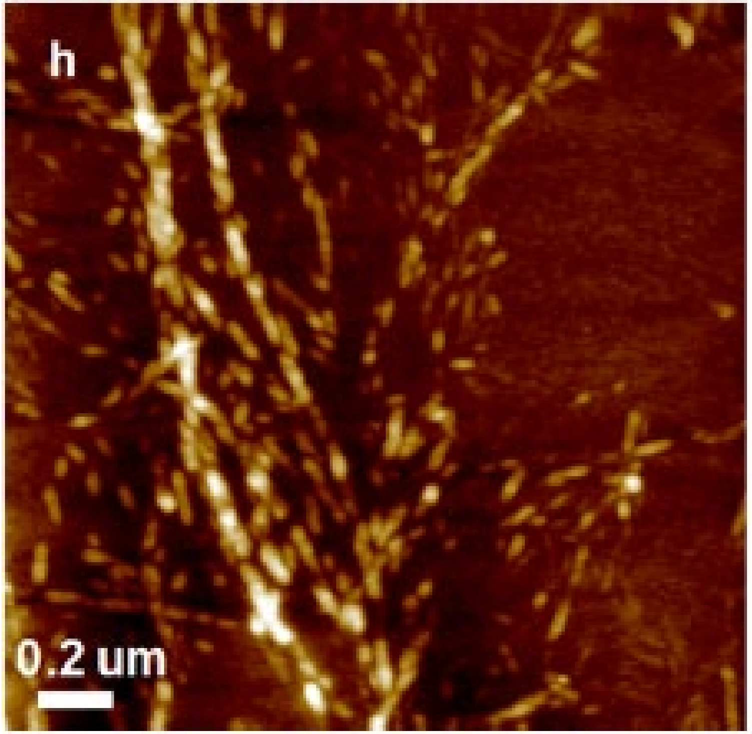




Spiliopoulos et al. *Biomacromolecules* **2021**, *22*, 1399.

Analytical detour: LODP visualized





Gas hydrolysis maintains morphology
→ Enables visualization

Spiliopoulos et al. *Biomacromolecules* **2021**, *22*, 1399.

Summary: CNCs by HCl (g)

- Hydrolysis down to LODP with HCl (g) proceeds rapidly at room temperature
- Crystallinity of cellulose is slightly increase during hydrolysis
- Reactor with HCl (g) is more efficient and more reproducible than HCl the use of vapor
- CNCs can be produced isolated from hydrolyzed fibers by prolonged sonication in formic acid

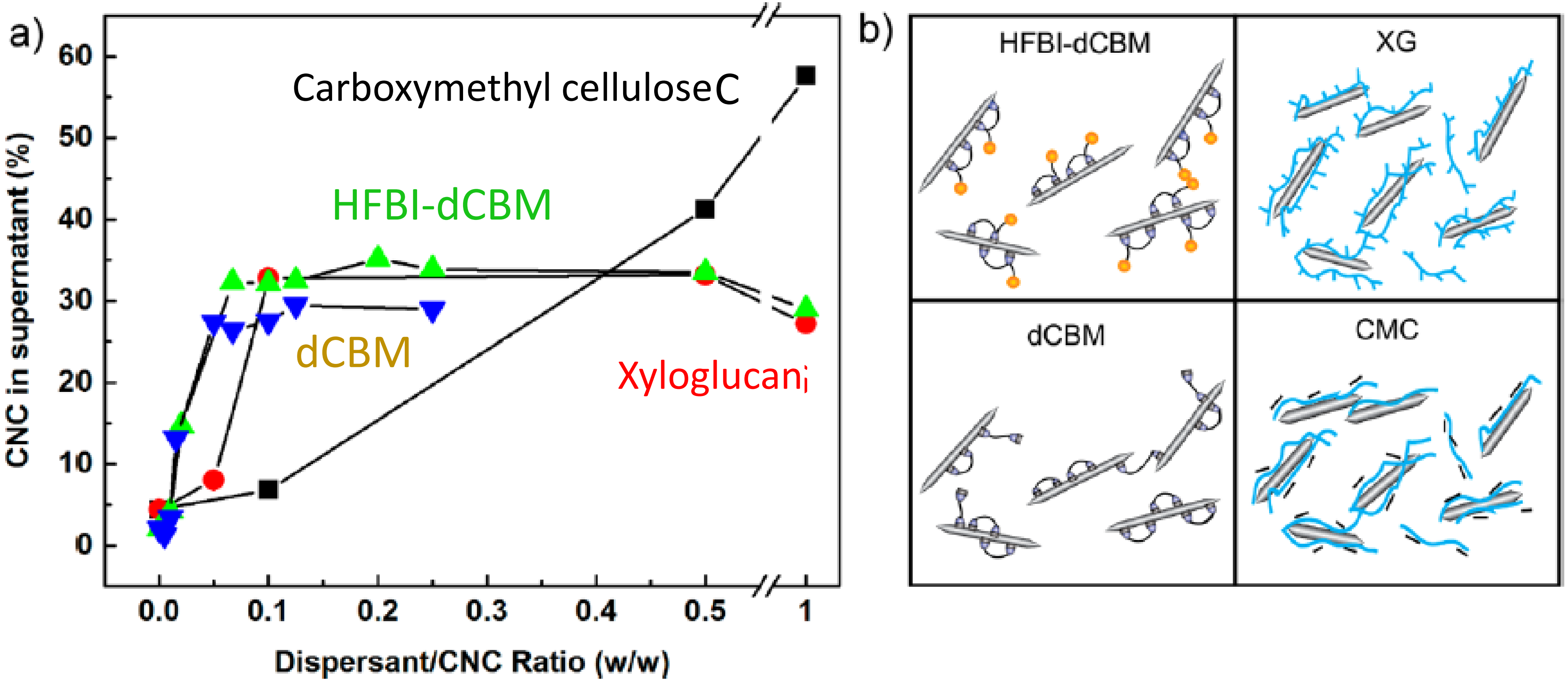
Dispersion methods for fibers hydrolyzed by HCl vapor

Dispersion problem

- After hydrolysis by HCl (g), the fibers are still intact, albeit brittle
- Washing is easy
- Dispersion into CNCs is difficult
- Proof-of-concept dispersion in formic acid is not realistic

Dispersion by polysaccharides

- Dispersion by carboxymethyl cellulose, xyloglucan or modified proteins



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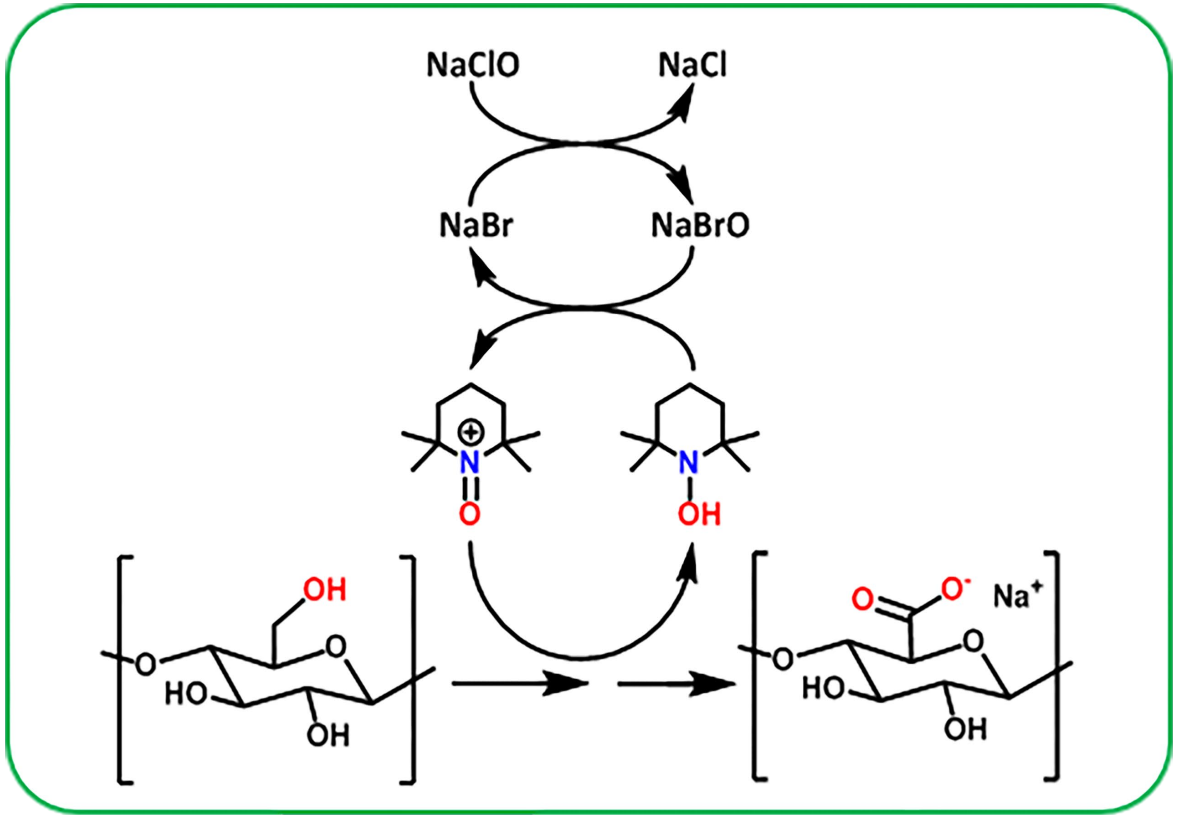
Fang et al. *Biomacromolecules* **2016**, *17*, 1458.

TEMPO-oxidation after hydrolysis



Basic idea:

- Introduce charge on the surface facilitates dispersion of CNCs

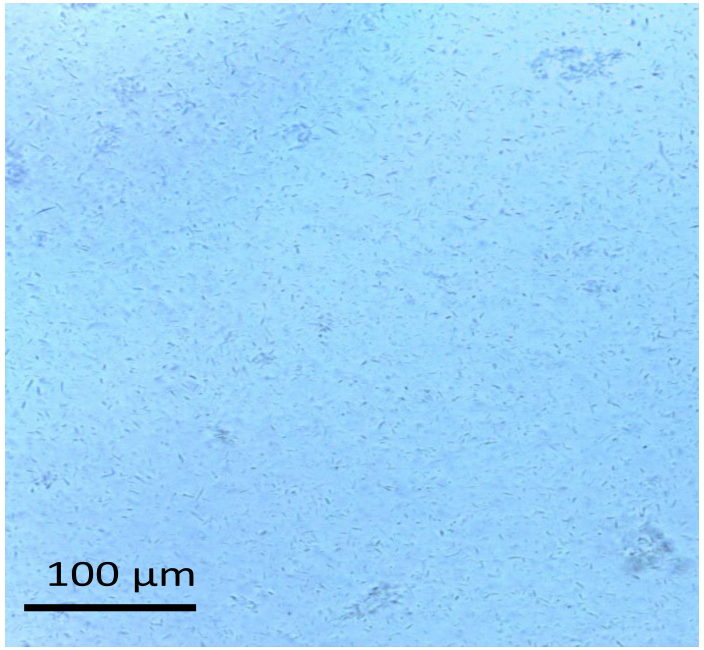
TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl radical

- Used commonly to isolate cellulose nanofibres

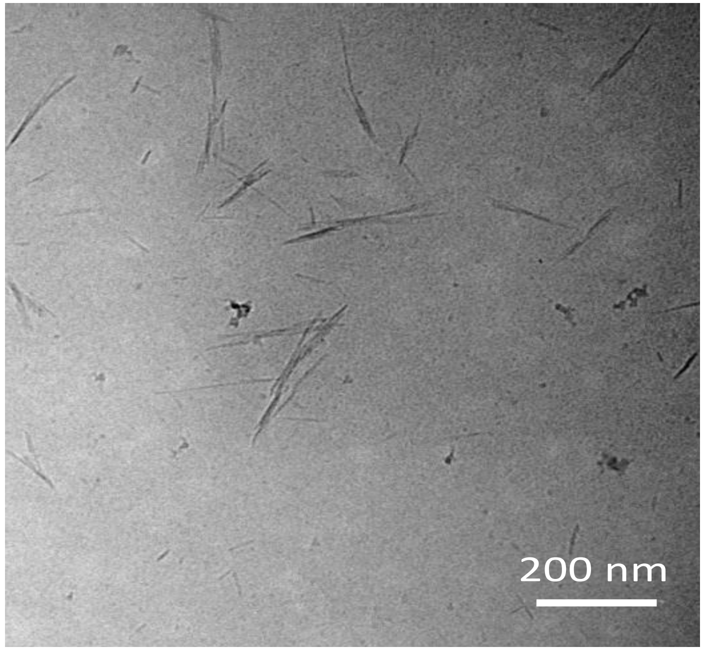
Early attempt: TEMPO-oxidation of microcrystalline cellulose

Fine fraction: cellulose nanocrystals

Optical micrograph



Cryo TEM



- Narrow particle size distribution
- Individual particles are clearly rod-like cellulose nanocrystals
- Yield only ~4%

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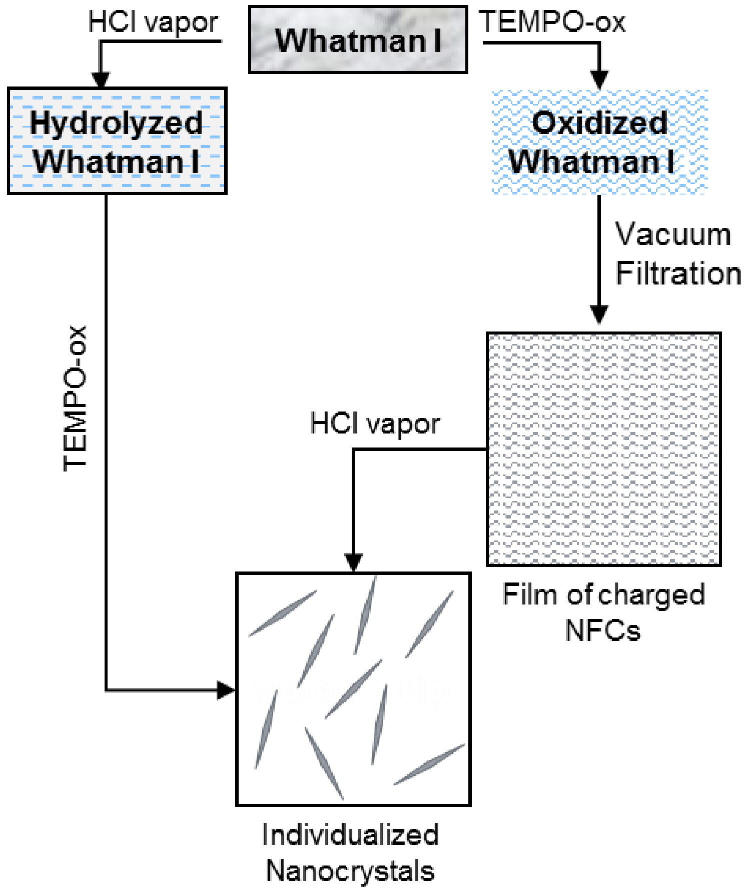
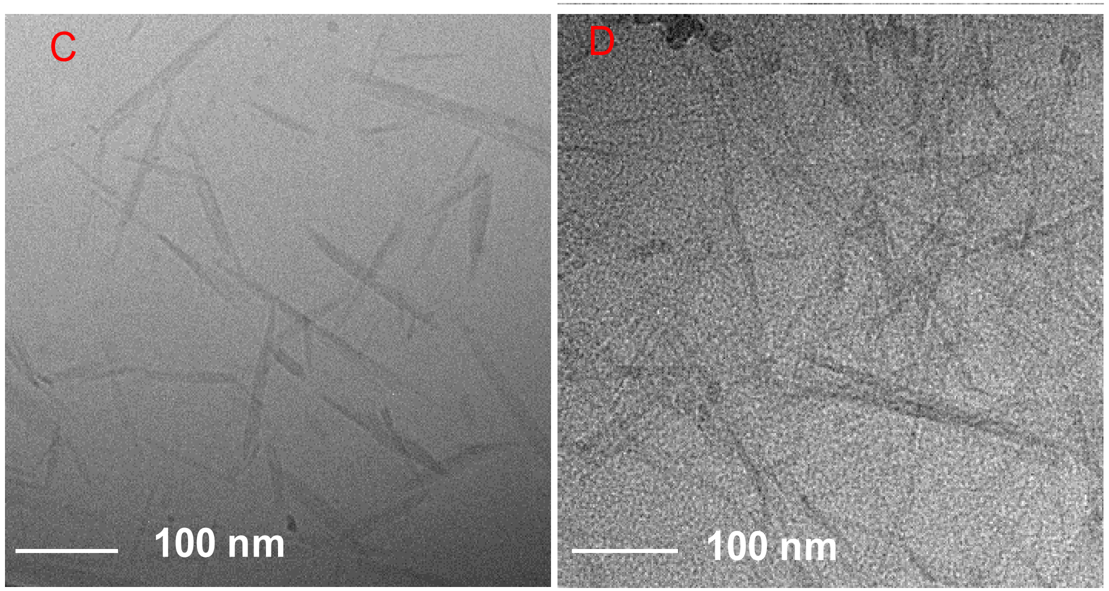
Peyre et al. *Green Chem.* **2015**,*17*, 808.

TEMPO-oxidation after hydrolysis



HCl (g) + TEMPO　　TEMPO + HCl (g)



Yield 40%　　Yield 55%

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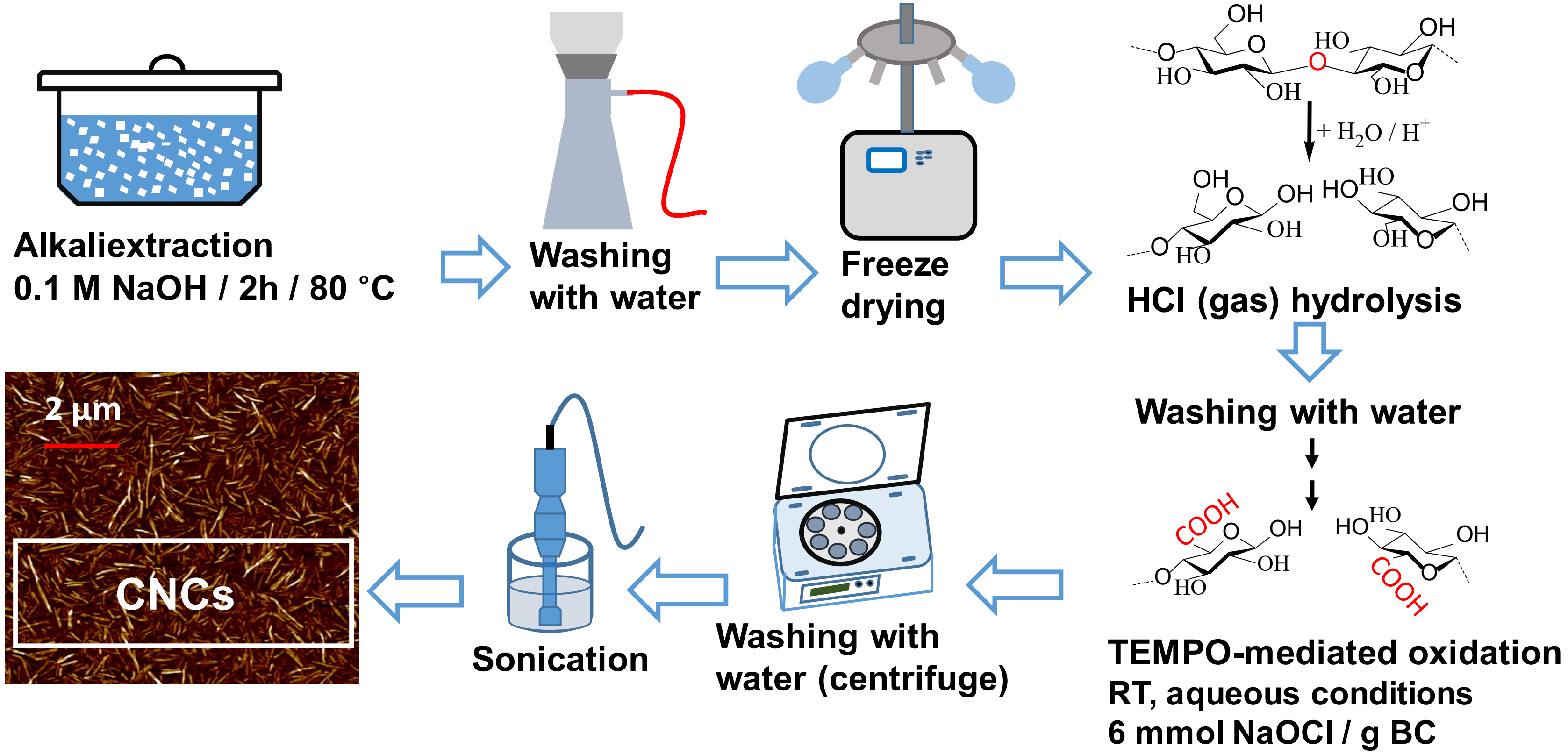
Lorenz et al. *Faraday Discuss.* **2017**, *202*, 315.

TEMPO-oxidation for a more accessible substrate



- Xerogel of bacterial cellulose was used

→ High porosity

→ High accessibility

80% yield of CNCs

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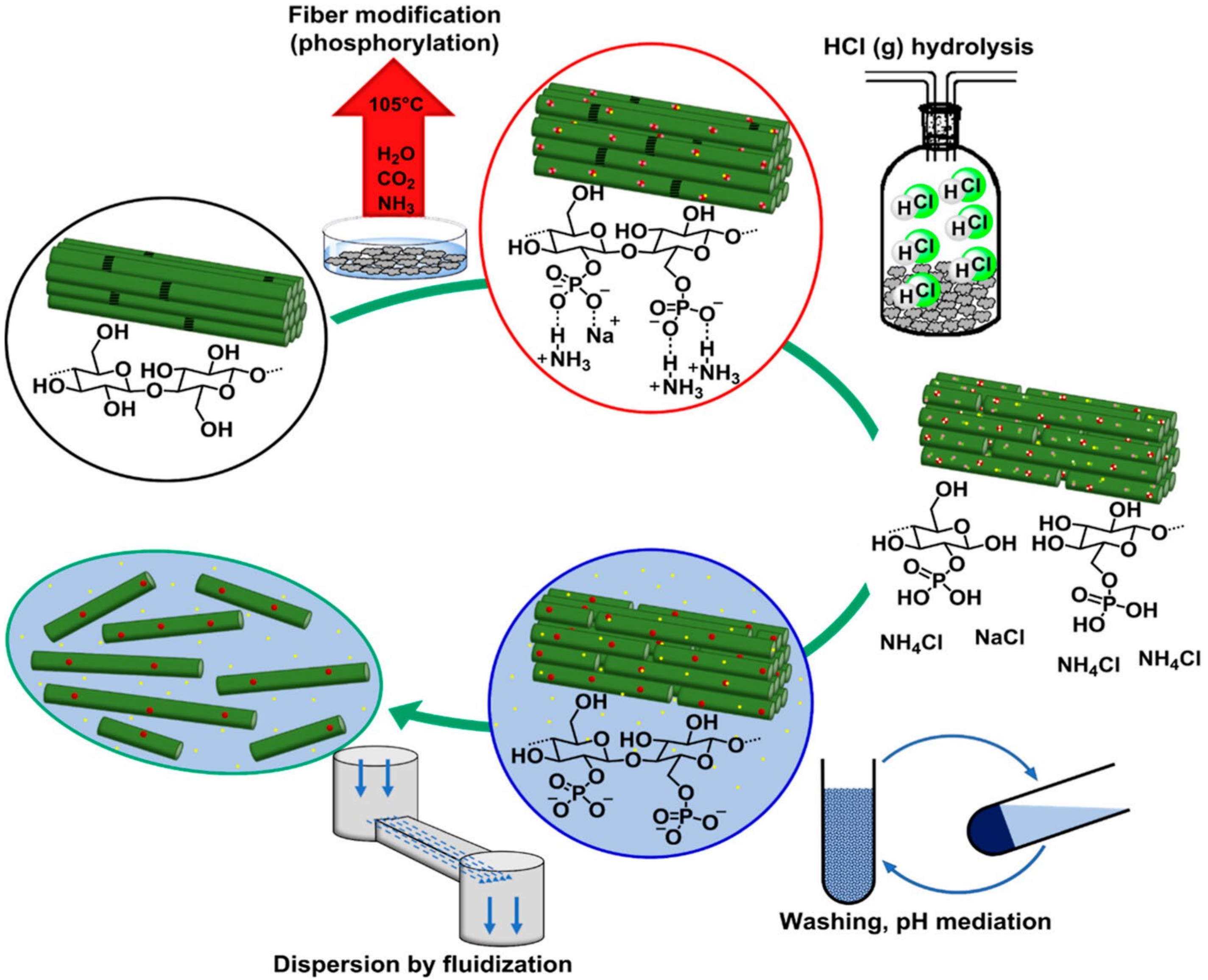
Pääkkönen et al. *ACS Sustainable Chem. Eng.* **2019**, *7*, 14384.

Phosphorylation of CNCs



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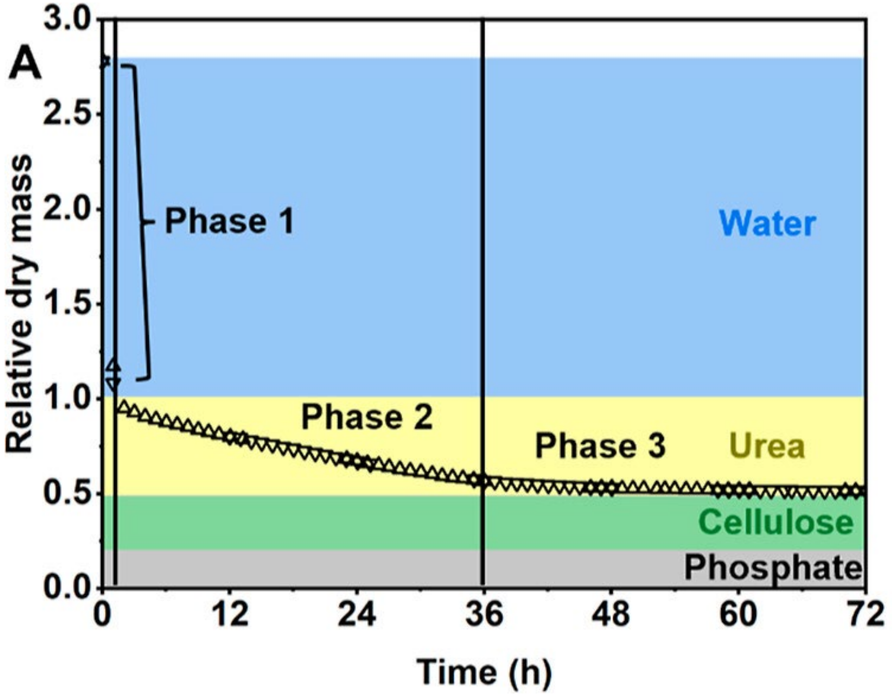
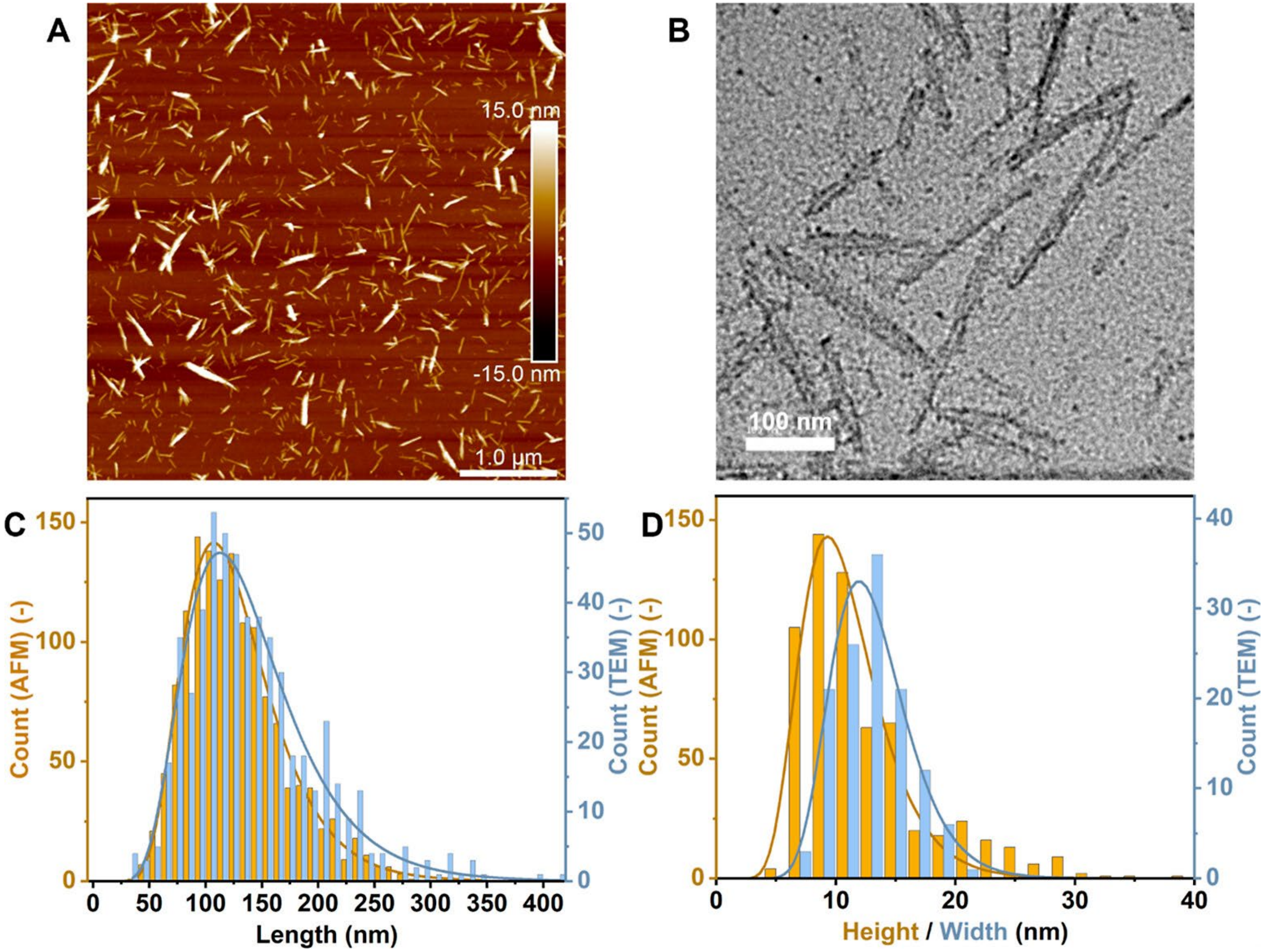
Kröger et al. *Biomacromolecules* **2023**, *24*, 1318.

Following phosphorylation





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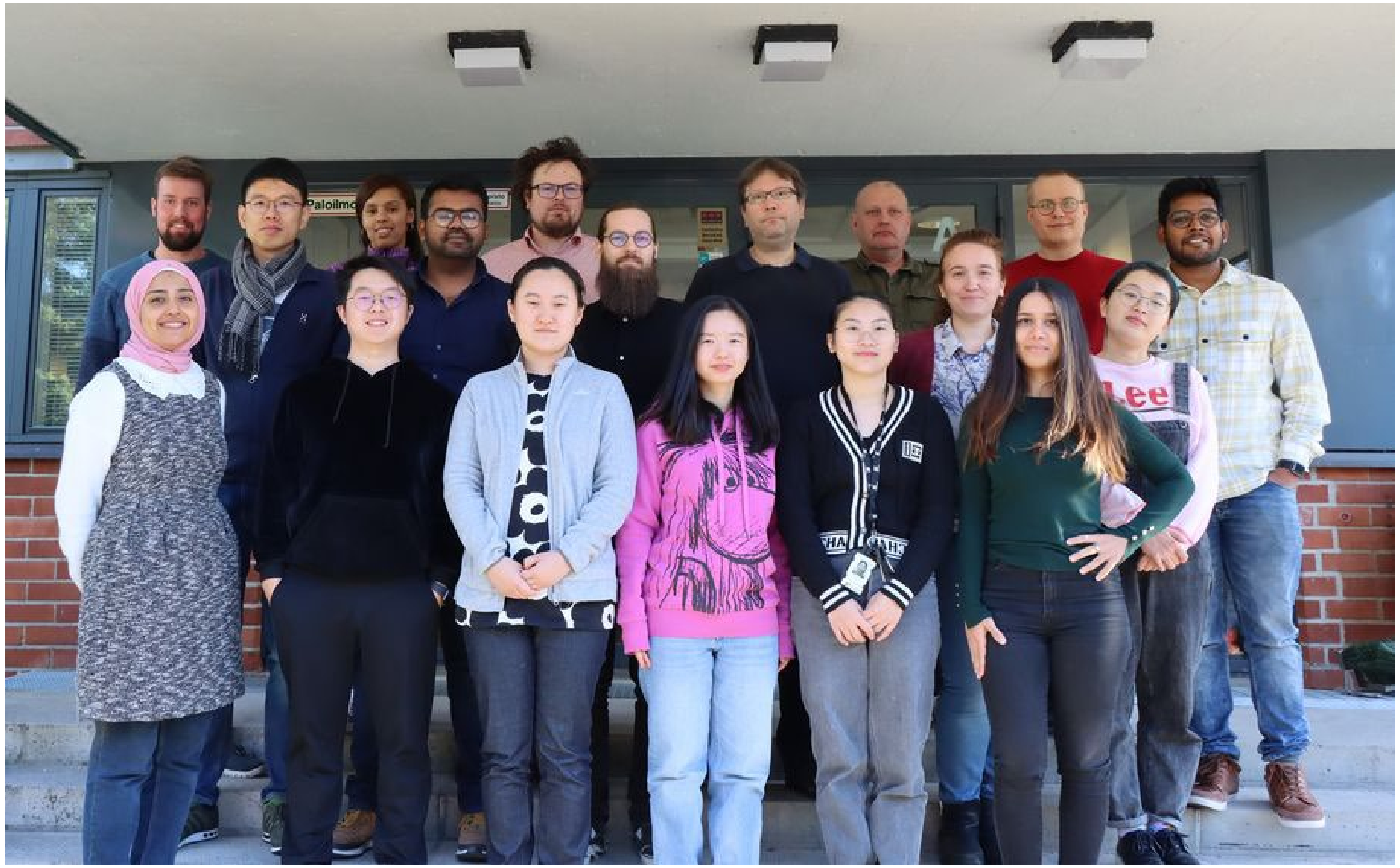
Kröger et al. *Biomacromolecules* **2023**, *24*, 1318.

Conclusion

- **CNCs are easy to purify after hydrolysis in gas/solid system**
- **Yields are high**
- **Dispersion is a bottleneck**
- **Dispersion methods from fibers hydrolyzed HCl (g):**
  - Water-soluble polysaccharides as dispersion agents
  - TEMPO-oxidation
  - Phosphorylation

Acknowledgements

Research group: Materials Chemistry of Cellulose



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