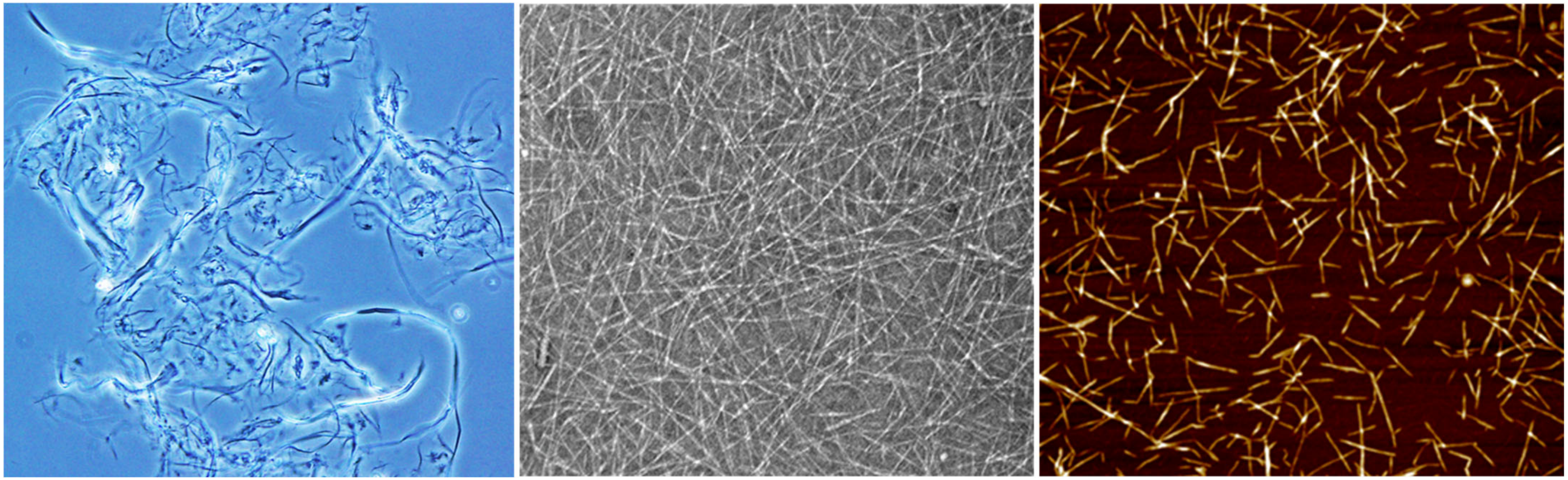
Wood cellulose nanomaterials

Chemistry of diverse and unique structures, morphologies, and characteristics



INTERNATIONAL ACADEMY OF WOOD SCIENCE
1966

IAWS 60th Anniversary Conference

June 1-4, 2026, ETH Zürich

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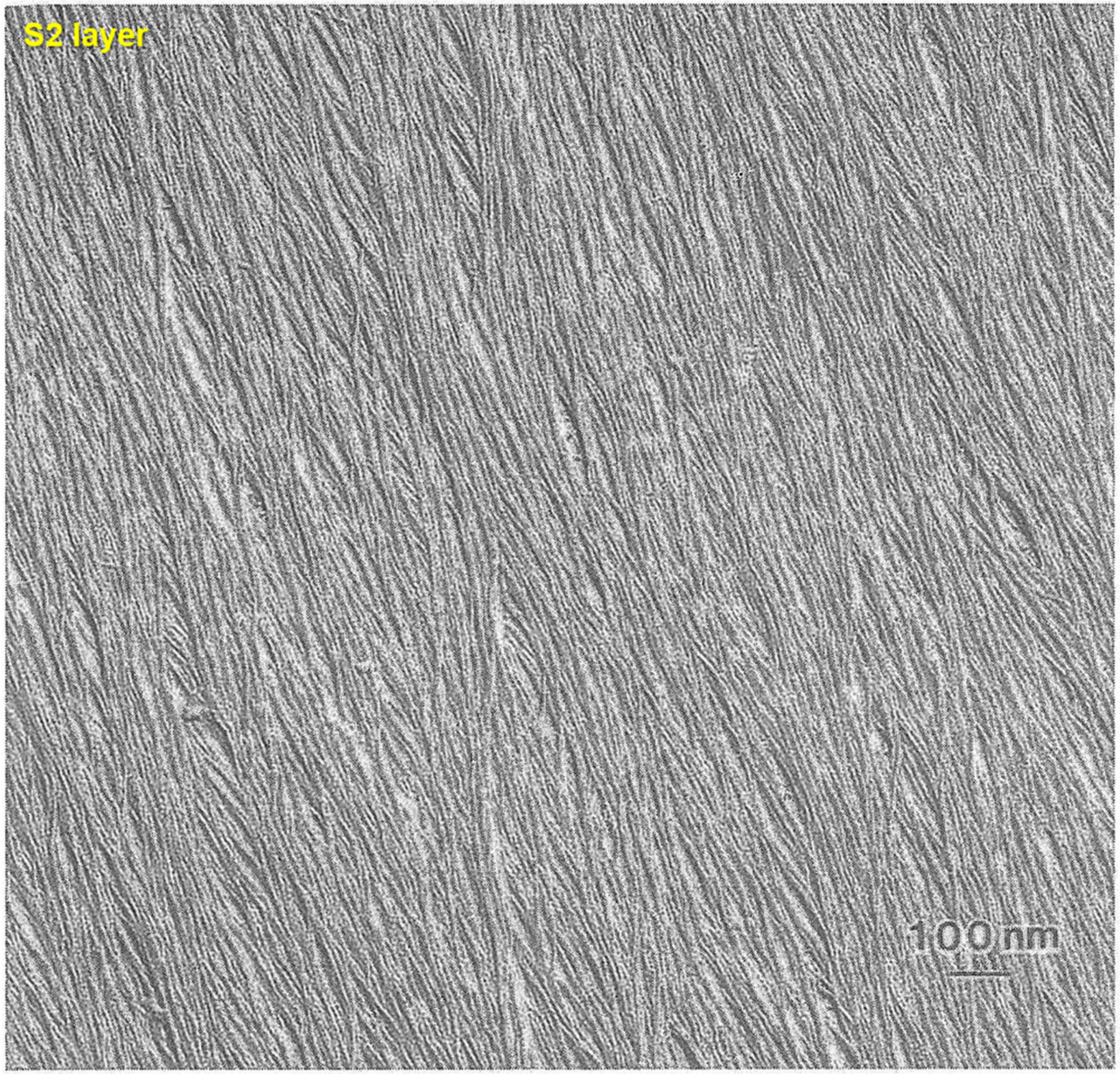
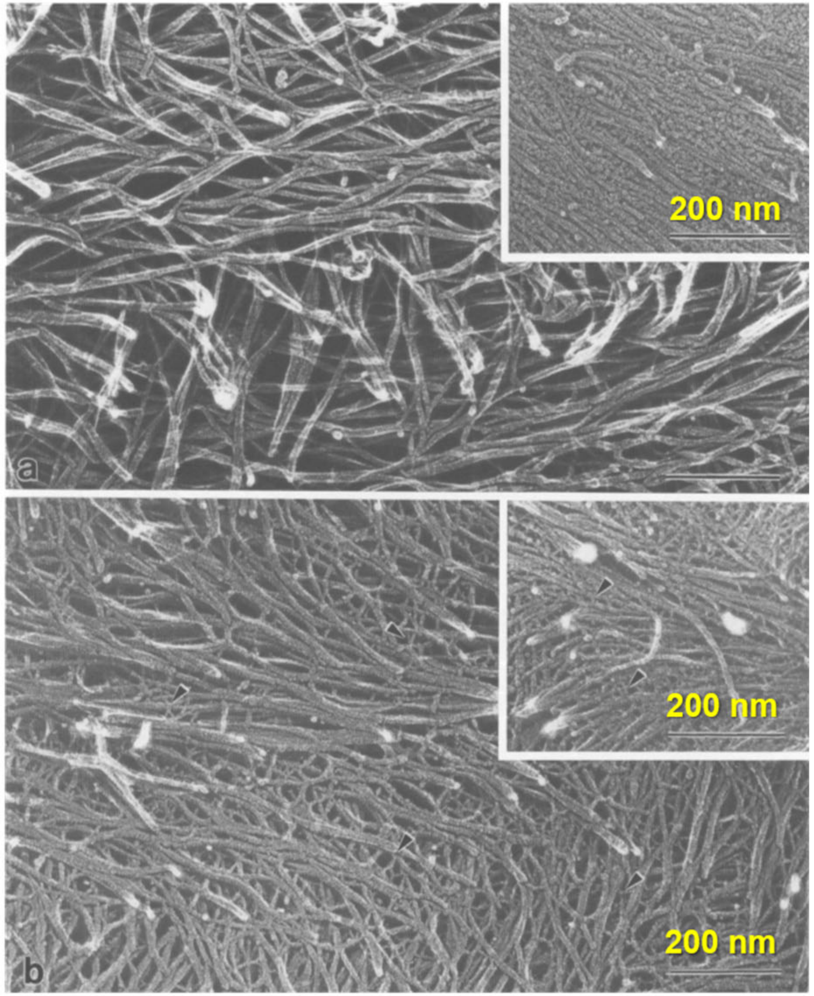
The University of Tokyo, Japan

Outline

- **Structures of wood cellulose microfibrils, contributing to the high mechanical strength and long lifetime of plant bodies**
- Mechanically fibrillated wood cellulose materials
- Individualization of wood fibers to nano-nanomaterials by chemical pretreatment: TEMPO-catalyzed oxidation
- Application of TEMPO-oxidation to fundamental structural analysis of plant cellulose microfibrils
- Unique characteristics of TEMPO-CNFs
- Side reactions of conventional TEMPO/NaBr/NaClO oxidation at pH 10
- New TEMPO-catalyzed oxidation with suppressed side reactions
- Present situation of nanocellulose productions/applications
- Conclusions and future challenges

Wood cellulose microfibrils: the second smallest elements in wood cell wall contributing to high mechanical strength, thermal stability, long lifetime against gravity/wind/rain/biodegradation





Fujino et al., Plant Cell Physiology (2000)

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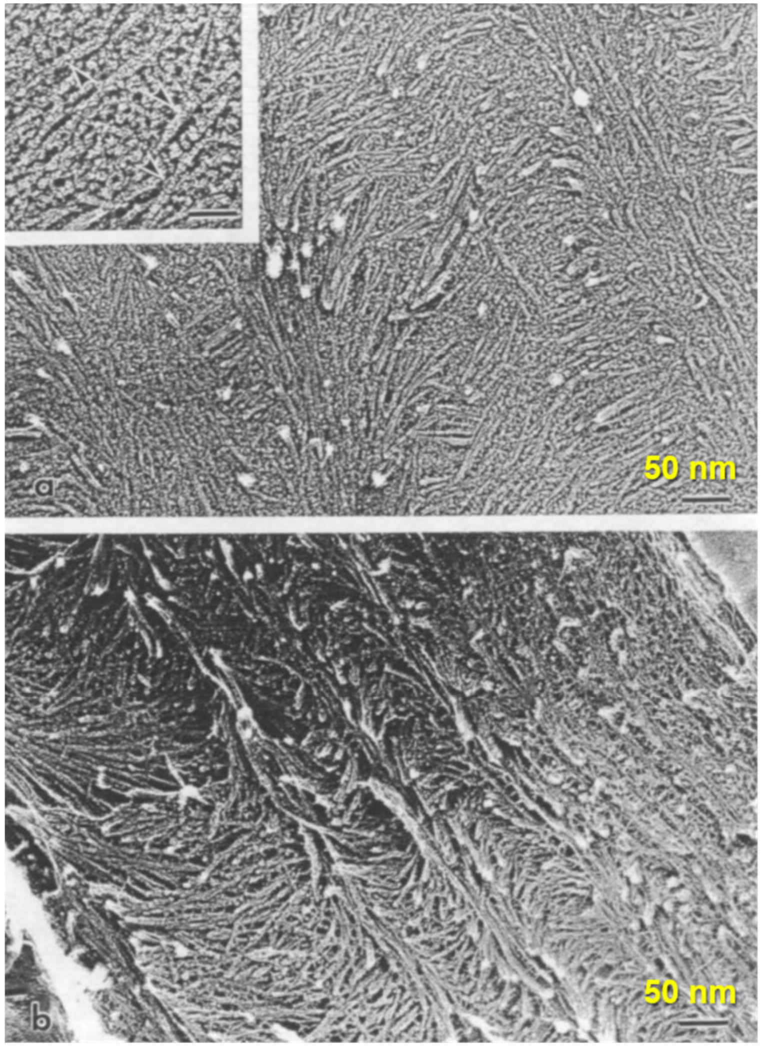
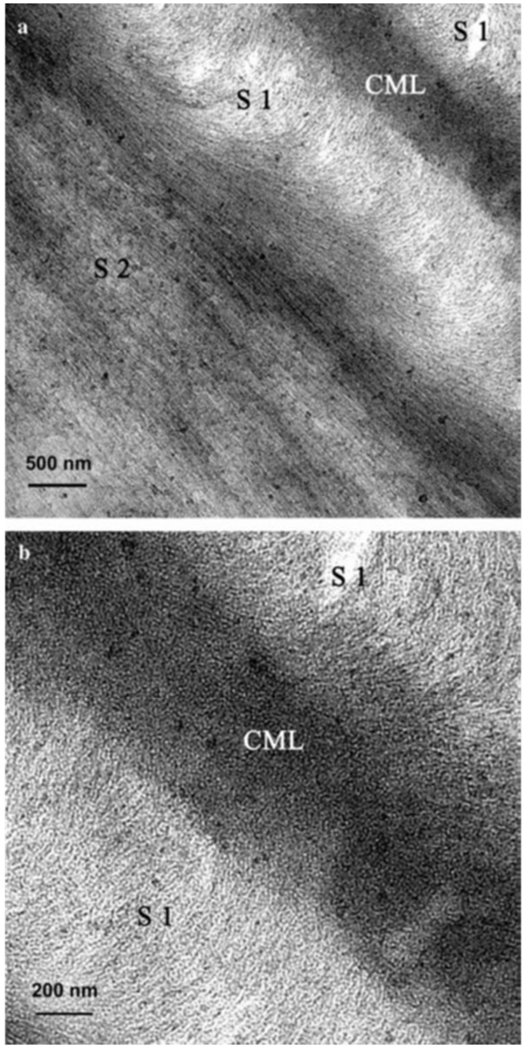
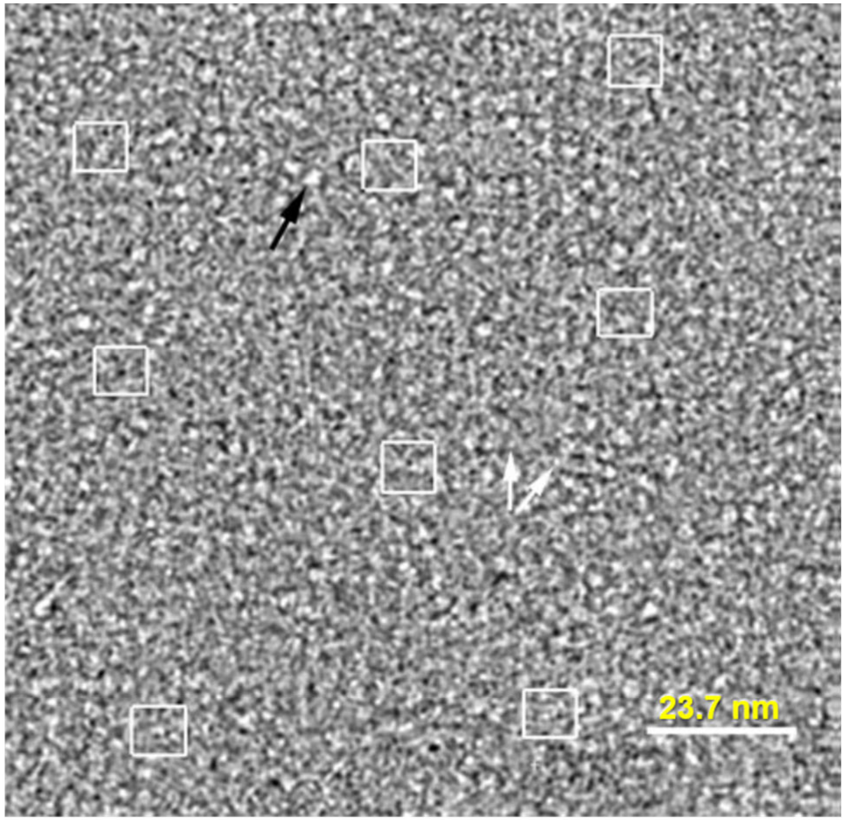


Fujino and Itoh, Plant Cell Physiology (1998)



Fromm et al., Journal of Structural Biology (2003)



Xy et al., Journal of Materials Science (2011)

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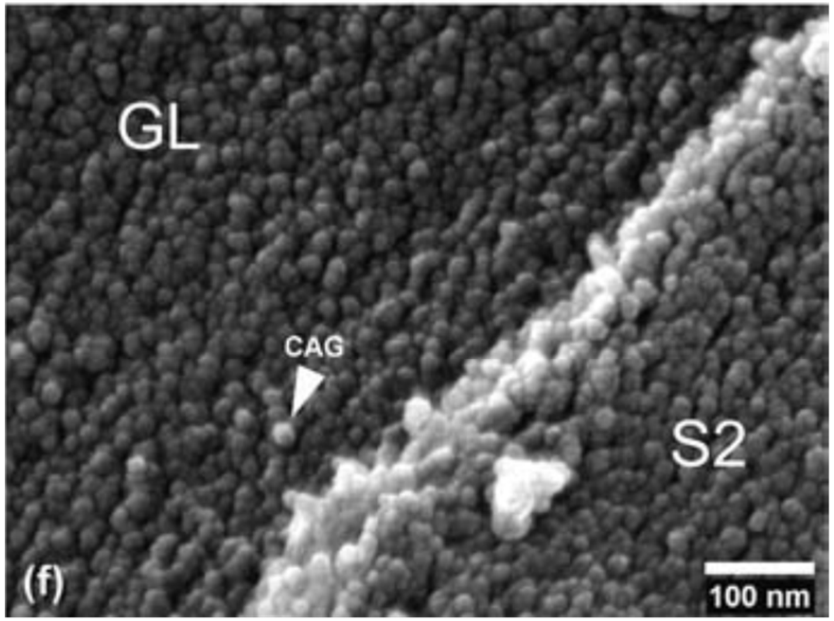
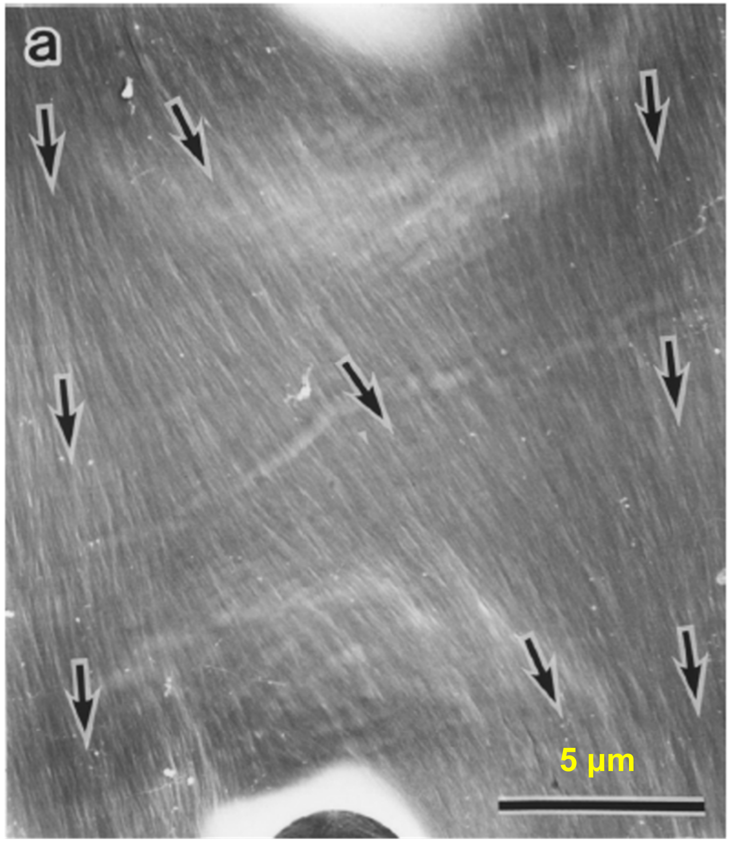
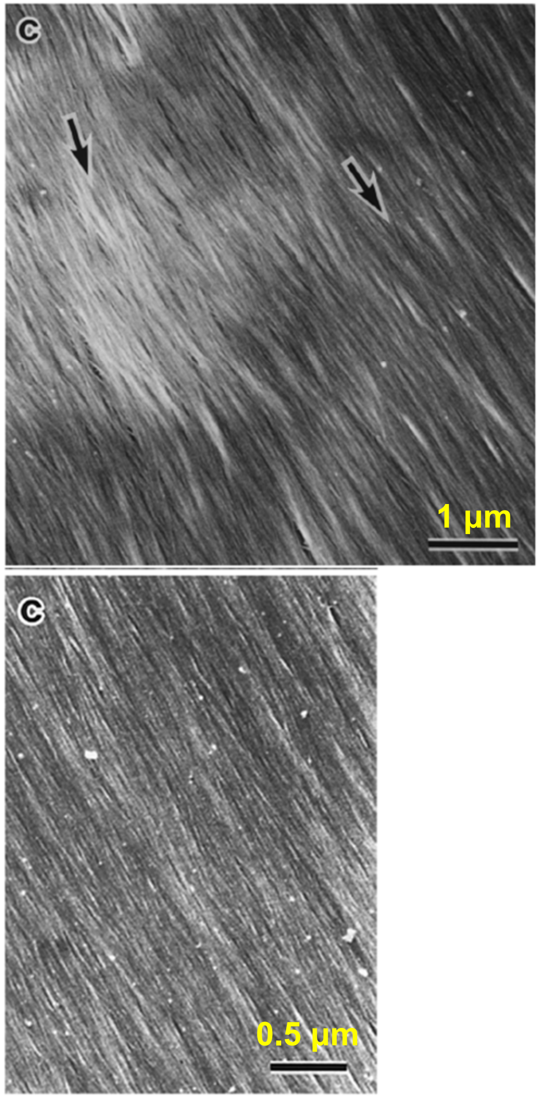


CAG: cellulose aggregates

Fagus et al., Wood Science and Technology (2009)



Abe and Funada, IAWA Journal (2005)



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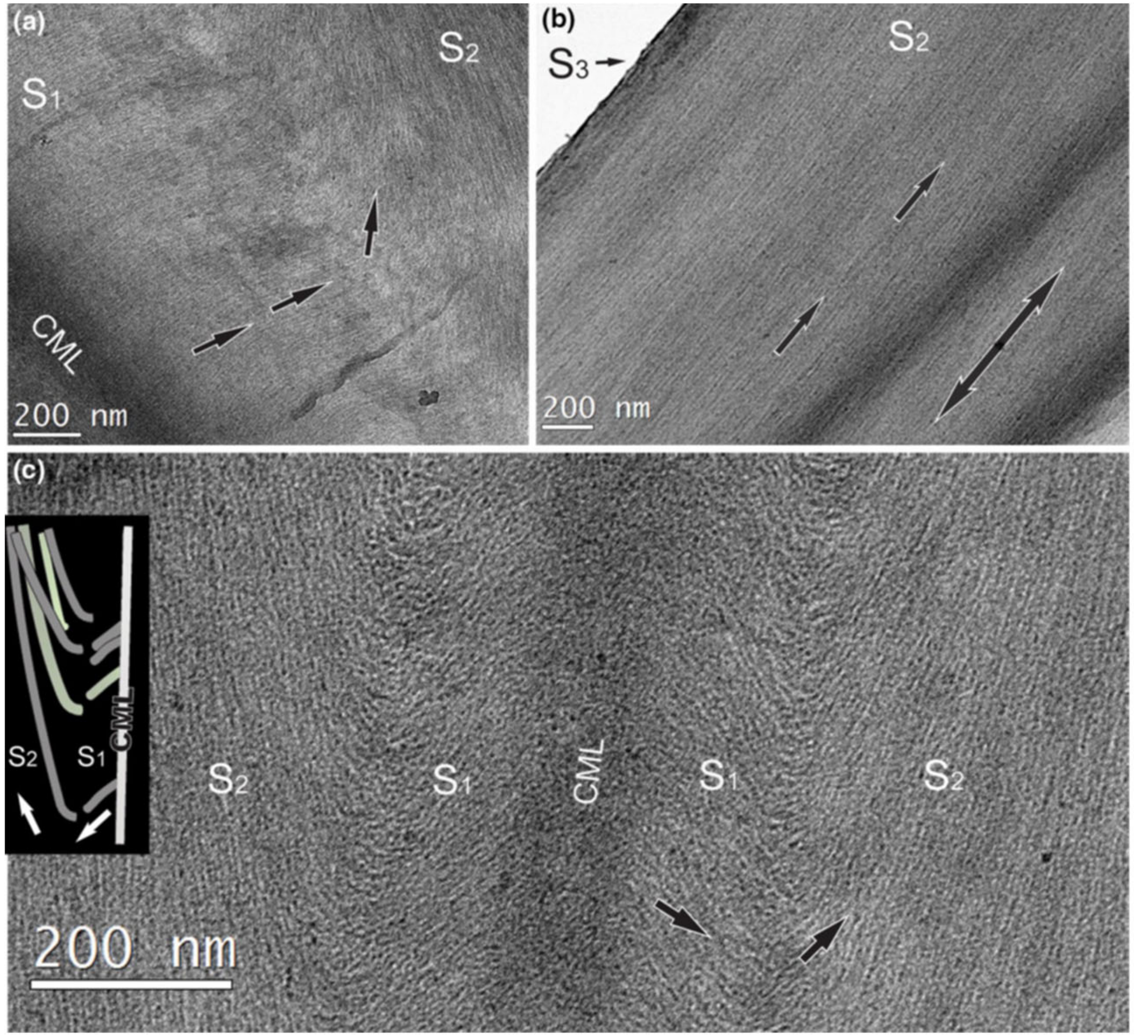

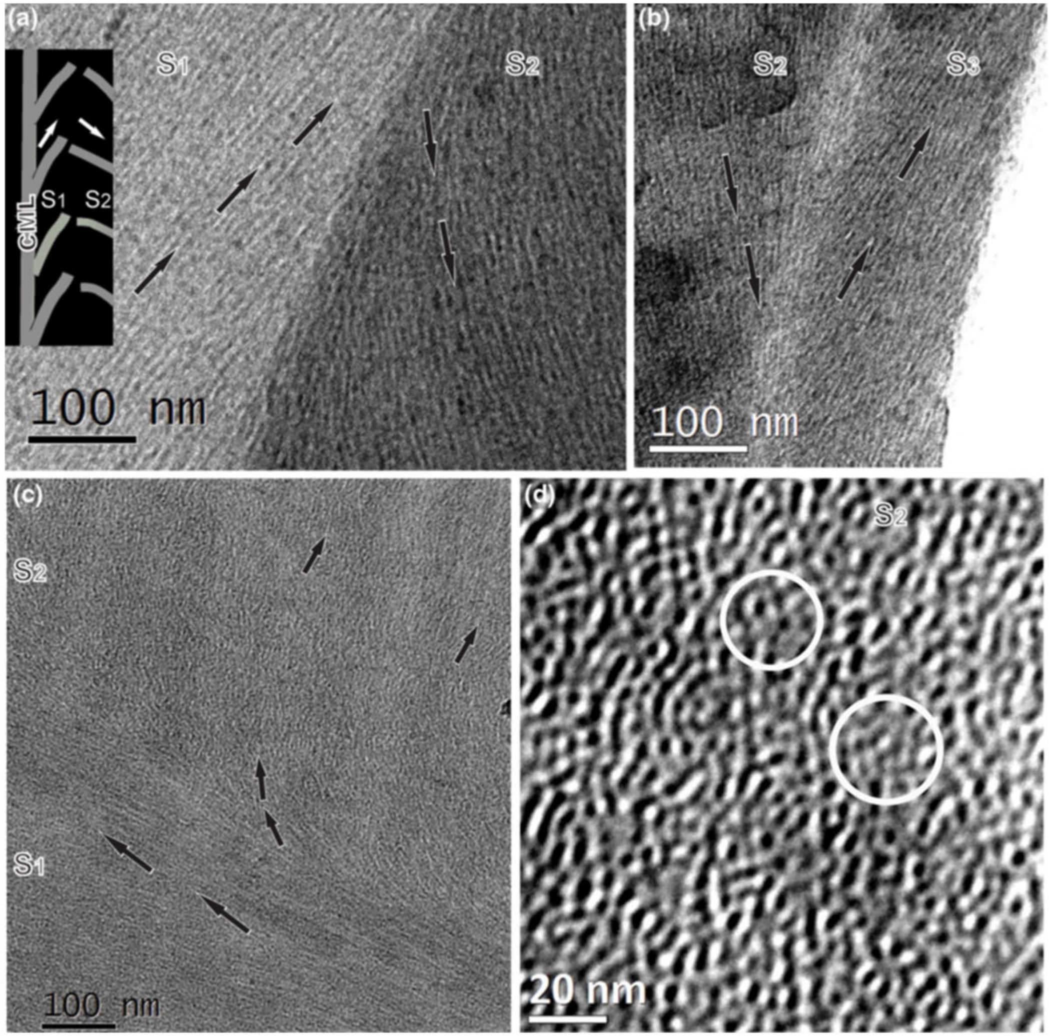

Reza et al., Planta (2014)

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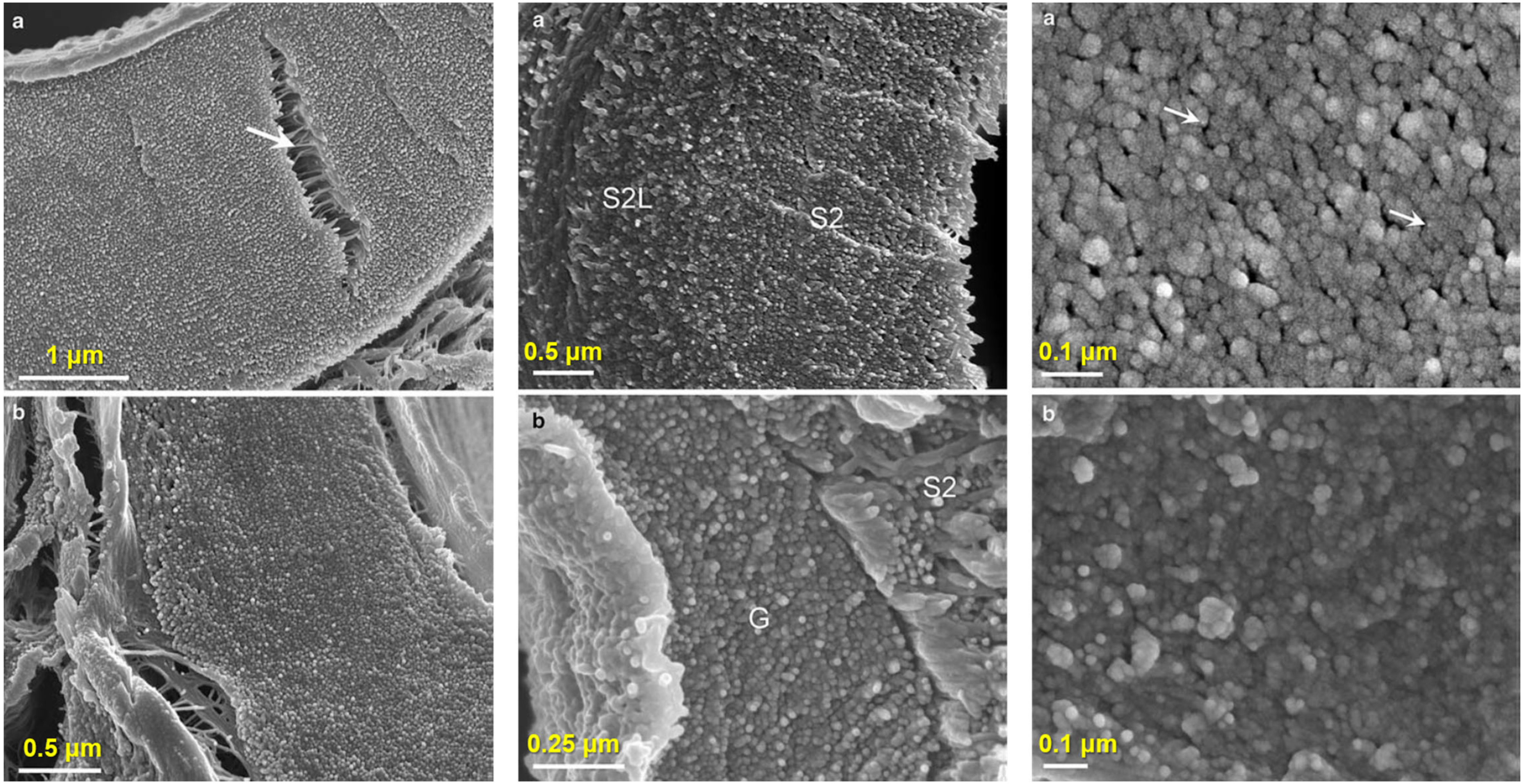
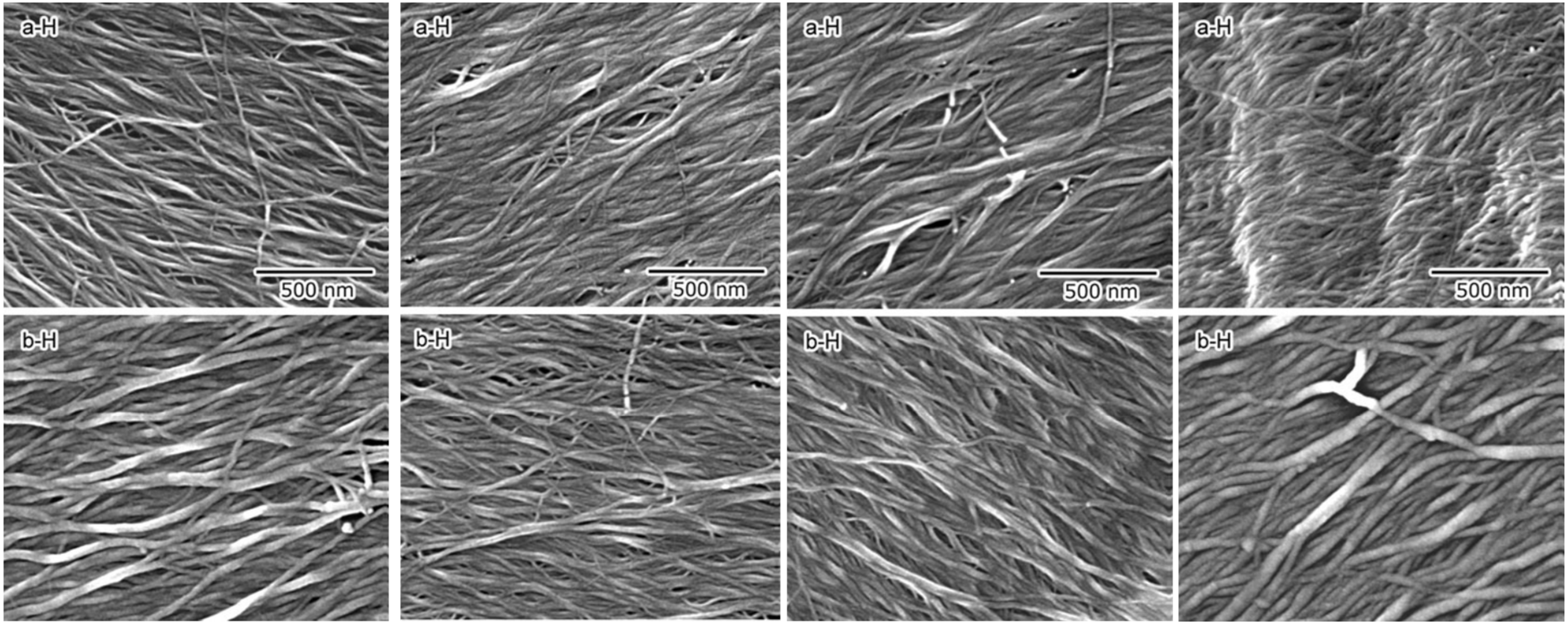


Donaldson, Wood Science and Technology (2007)

Wood cellulose microfibrils: the second smallest elements in chemical pulps, contributing to high mechanical strength, thermal stability, and stability in use as paper and board

SEM images of softwood bleached kraft pulp fiber surfaces, depending on different drying procedures

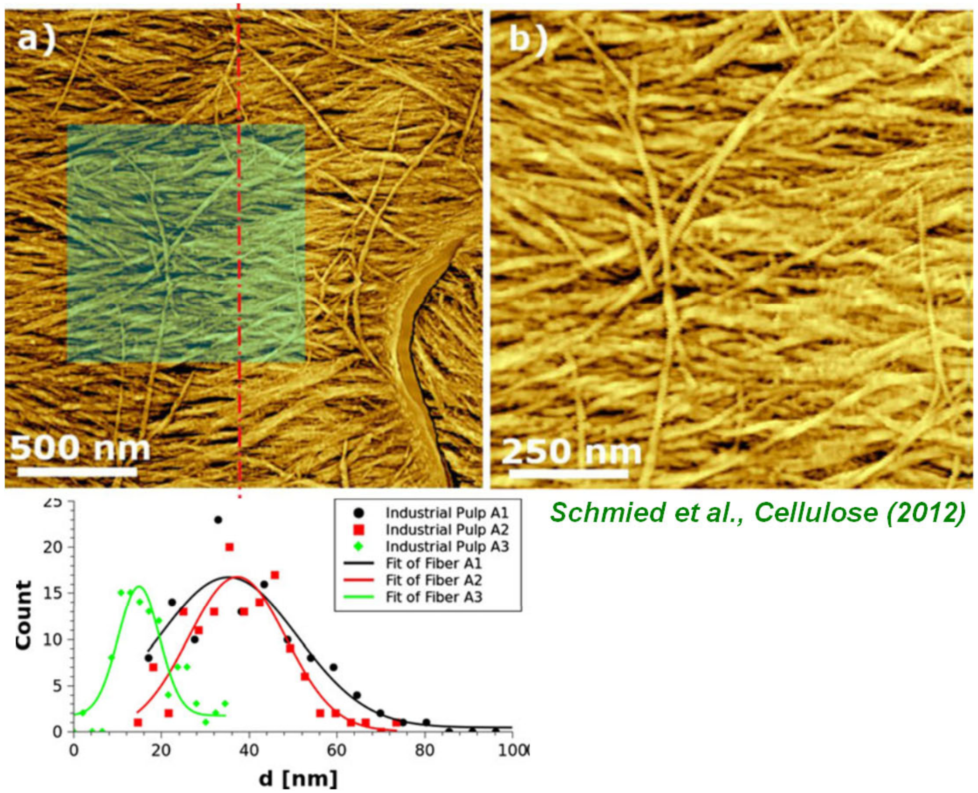


Super critical point (SCP) drying | **Rapid-freezing and freeze-drying** | **Solvent-exchange** | **SCP drying, and thick coating**

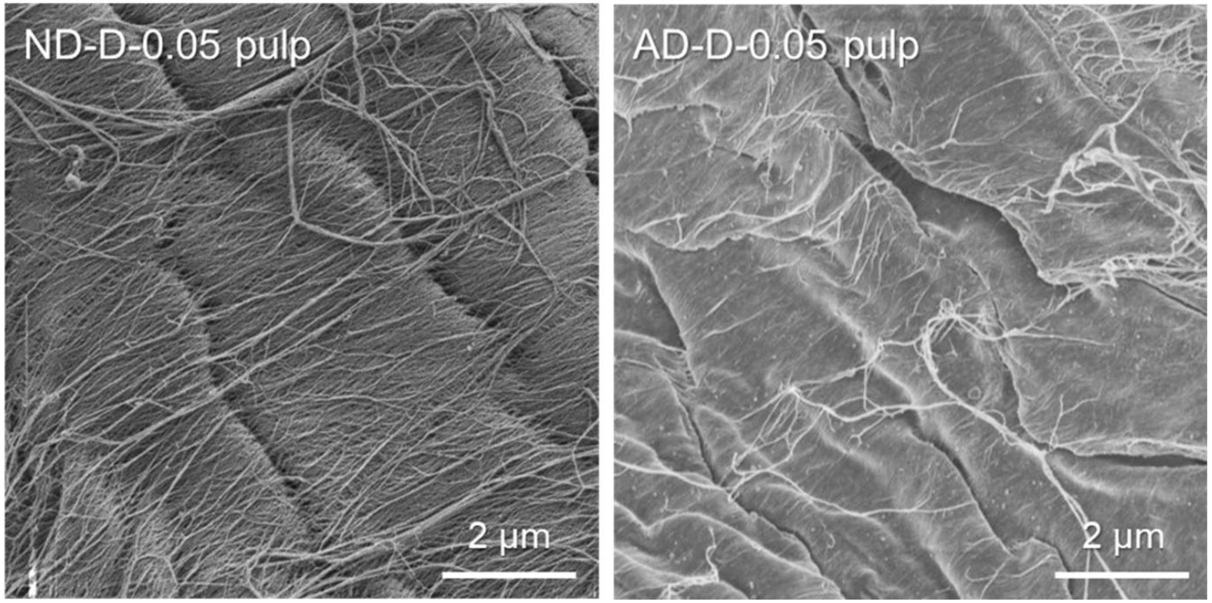
- 50% of wood components are removed by kraft pulping, resulting in formation of 50% voids or pore structures between wood cellulose microfibrils >10 nm in width, observed by SEM after critical point or solvent-exchange drying.

Okamoto and Meshitsuka, Cellulose (2010)

Wood cellulose microfibrils: the second smallest elements in chemical pulps, contributing to high mechanical strength, thermal stability, and stability in use as paper and board



Schmied et al., Cellulose (2012)



Kimura et al., Nordic Pulp & Paper Research Journal (2023)

- Depending on drying methods, most wood cellulose microfibrils can be observed as individual fibrils >5 nm in width, by SEM or TEM.
- After kraft pulping, 50% voids or pore structures are formed, surrounding wood cellulose microfibrils
- However, after air or thermal drying, these fibrils are merged and tightly bound to each other by interfibrillar hydrogen bond formation, to form smooth fiber surfaces, observed by SEM, TEM or AFM, contributing to high mechanical strengths of fiber/paper/board.

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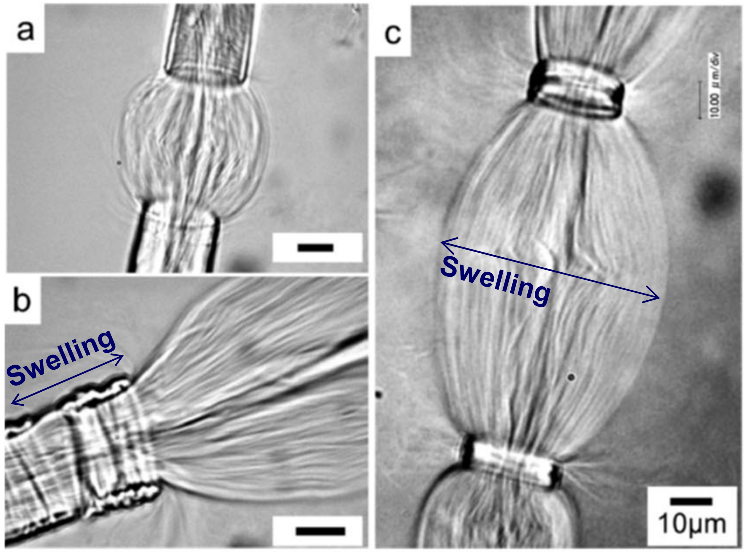
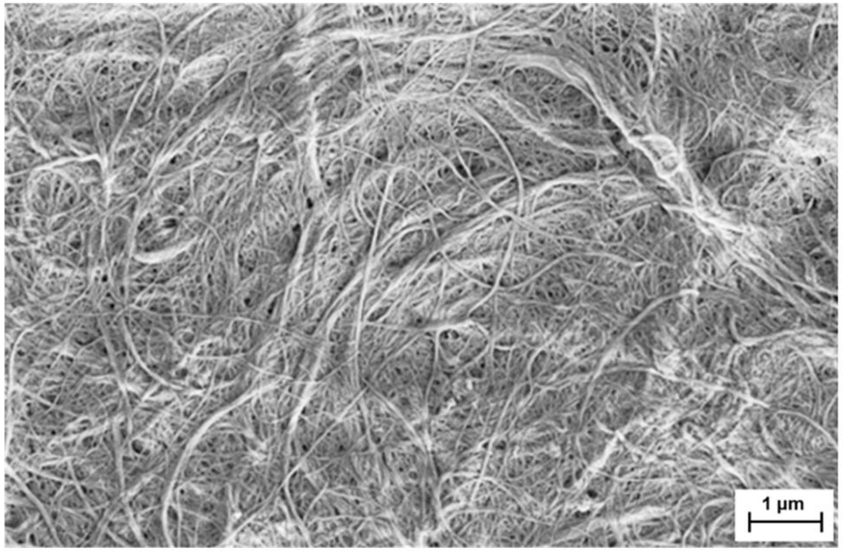
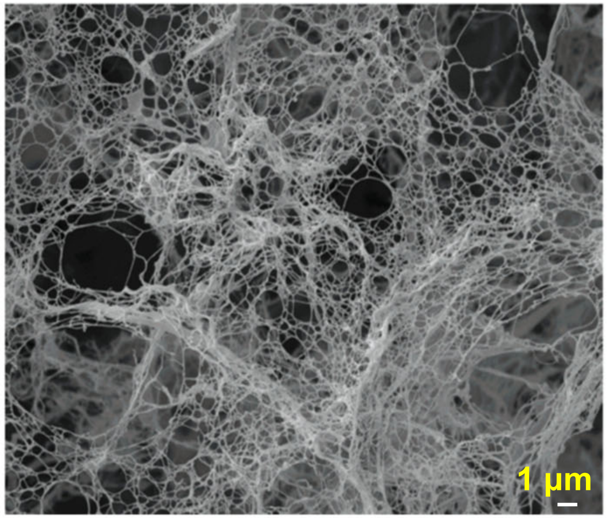
Mechanical fibrillation of wood cellulose fibers in water to MFC via ballon swelling

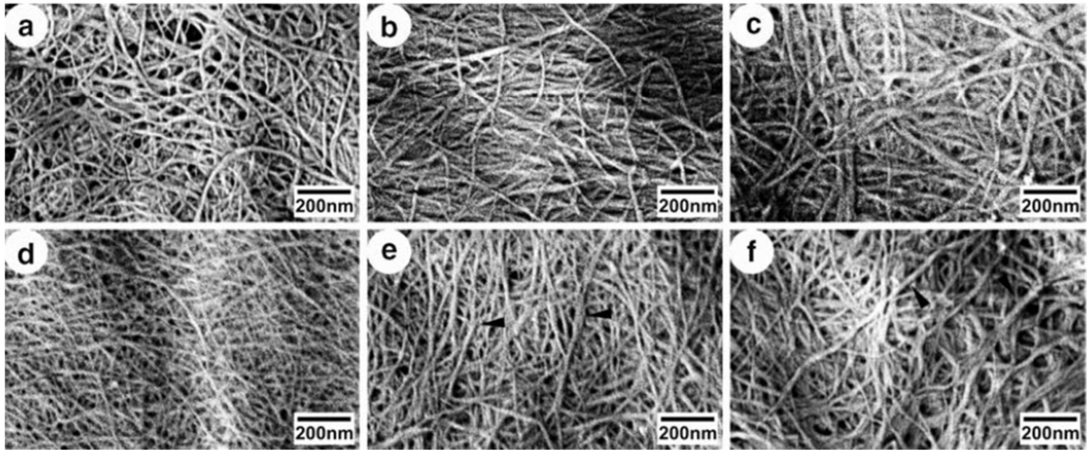




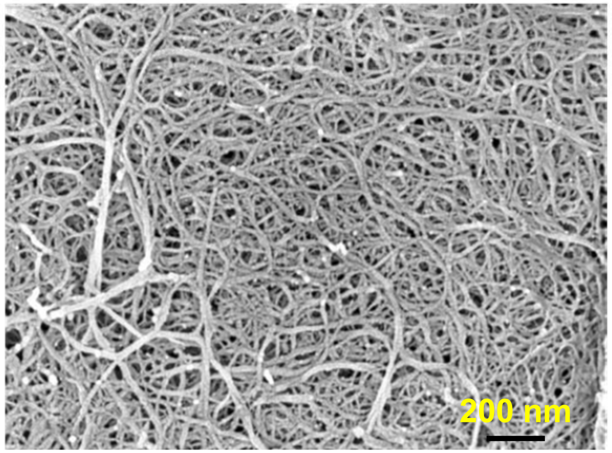
Uetani and Yano, Biomacromolecules (2011)



Tingaut et al., Advances in Nanocomposite Technology, Chapter 14 (2011)

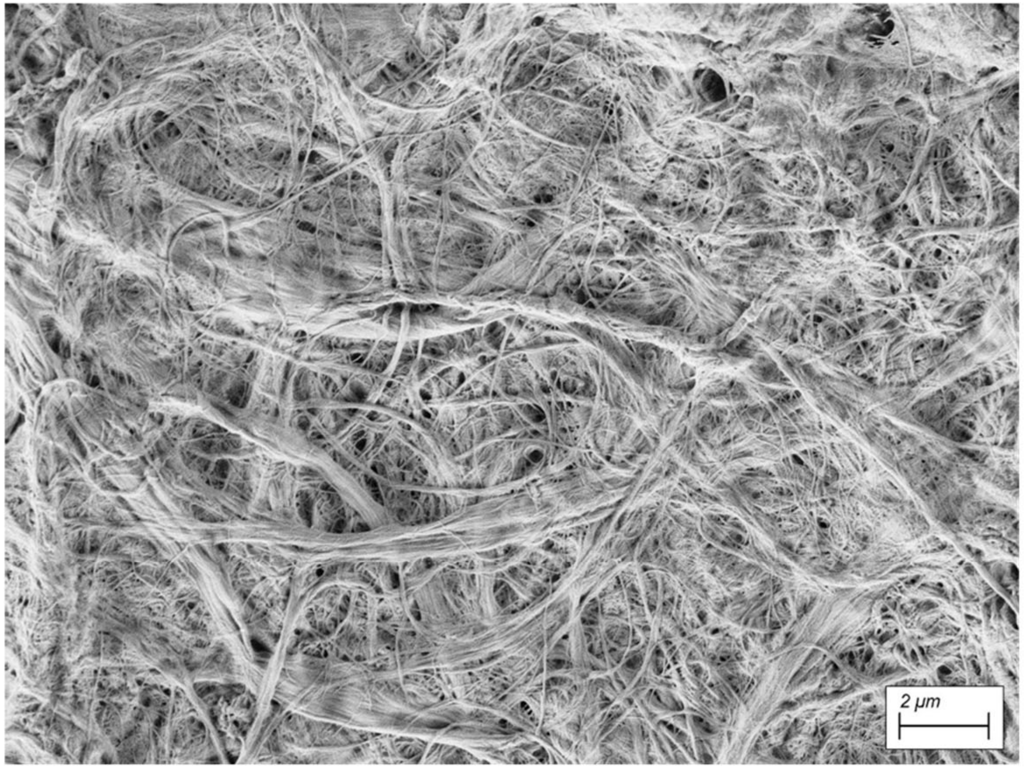


Abe and Yano, Cellulose (2009)

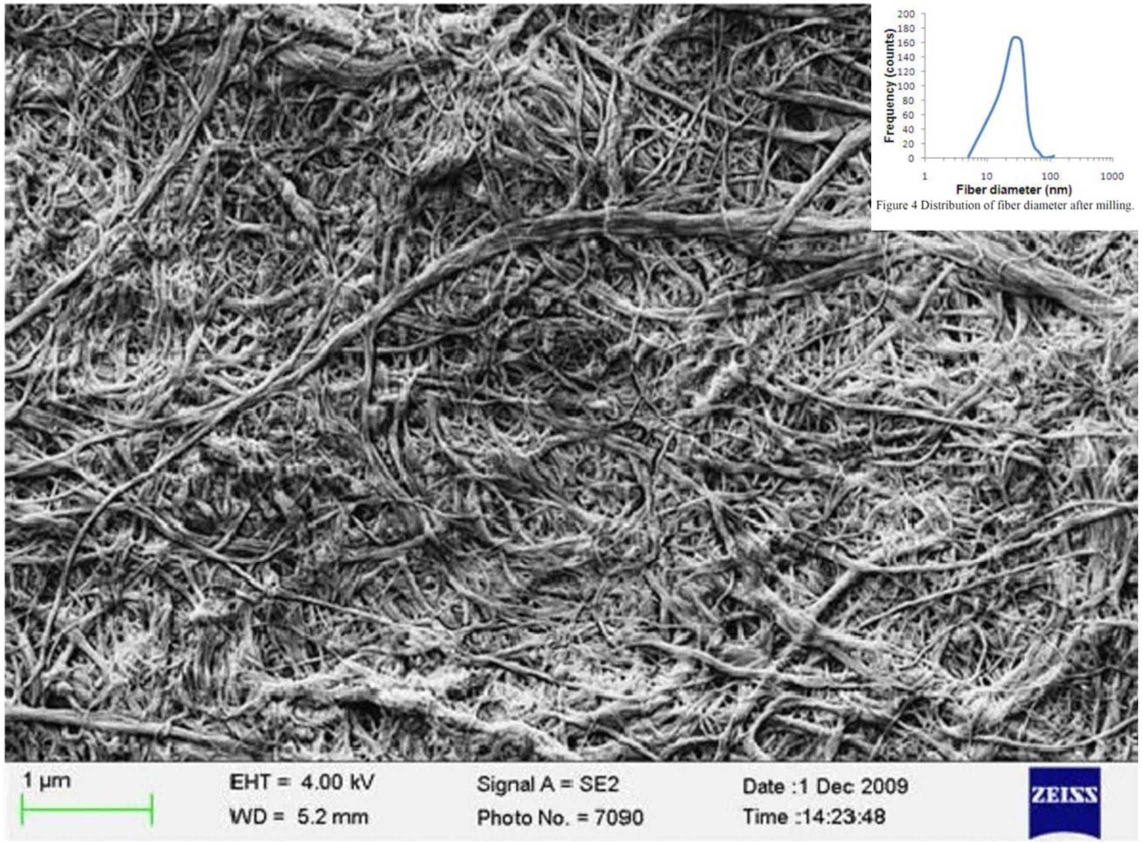


Iwamoto et al., Applied Physics A (2007)

Mechanical fibrillation of wood cellulose fibers in water to form MFC



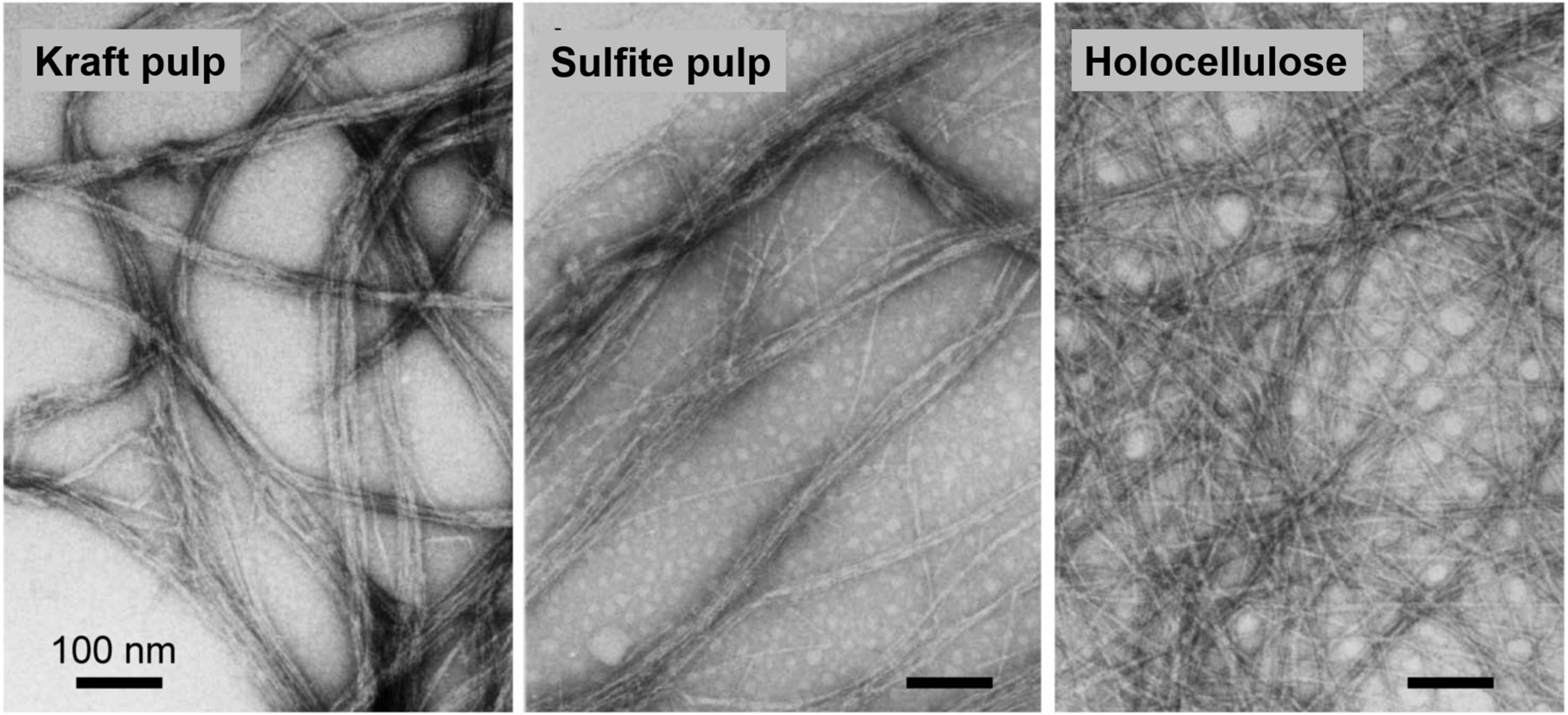
MFC, from web site of Fiberlean (2026)



Zhang et al., Materials Science Forum (2010)

- **Mechanical fibrillation of wood cellulose fibers in water even under harsh conditions cannot be converted to individual cellulose microfibrils but only micro-fibrillated cellulose levels.**

Mechanical fibrillation of wood cellulose fibers in water to form fibril aggregates



- **Mechanical fibrillation of wood cellulose fiber or holocellulose in water even under harsh conditions cannot be converted to individual cellulose microfibrils.**

Hult et al., Cellulose (2003)

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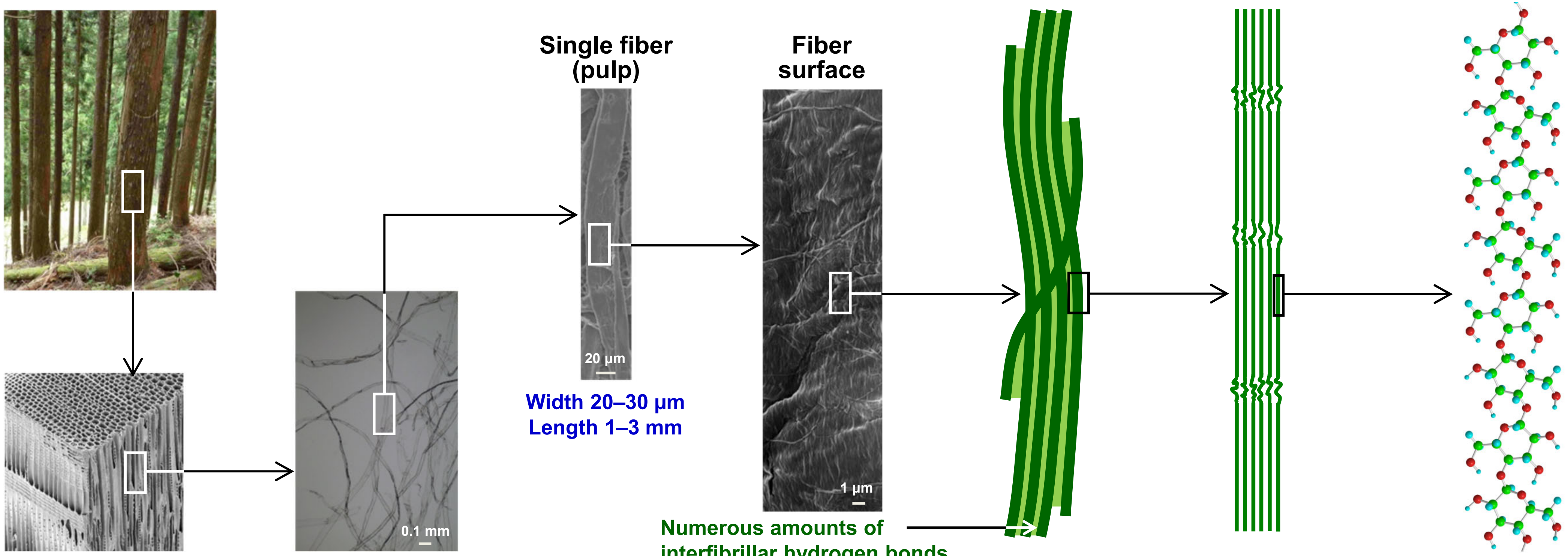
Hierarchical structures of cellulose molecules in plant cell walls



Tree

Wood tissue

Single fiber

Single fiber (pulp)

Width 20–30 μm
Length 1–3 mm

Fiber surface

Numerous amounts of interfibrillar hydrogen bonds

Bundle of microfibrils

Width > 15 nm

Cellulose microfibril

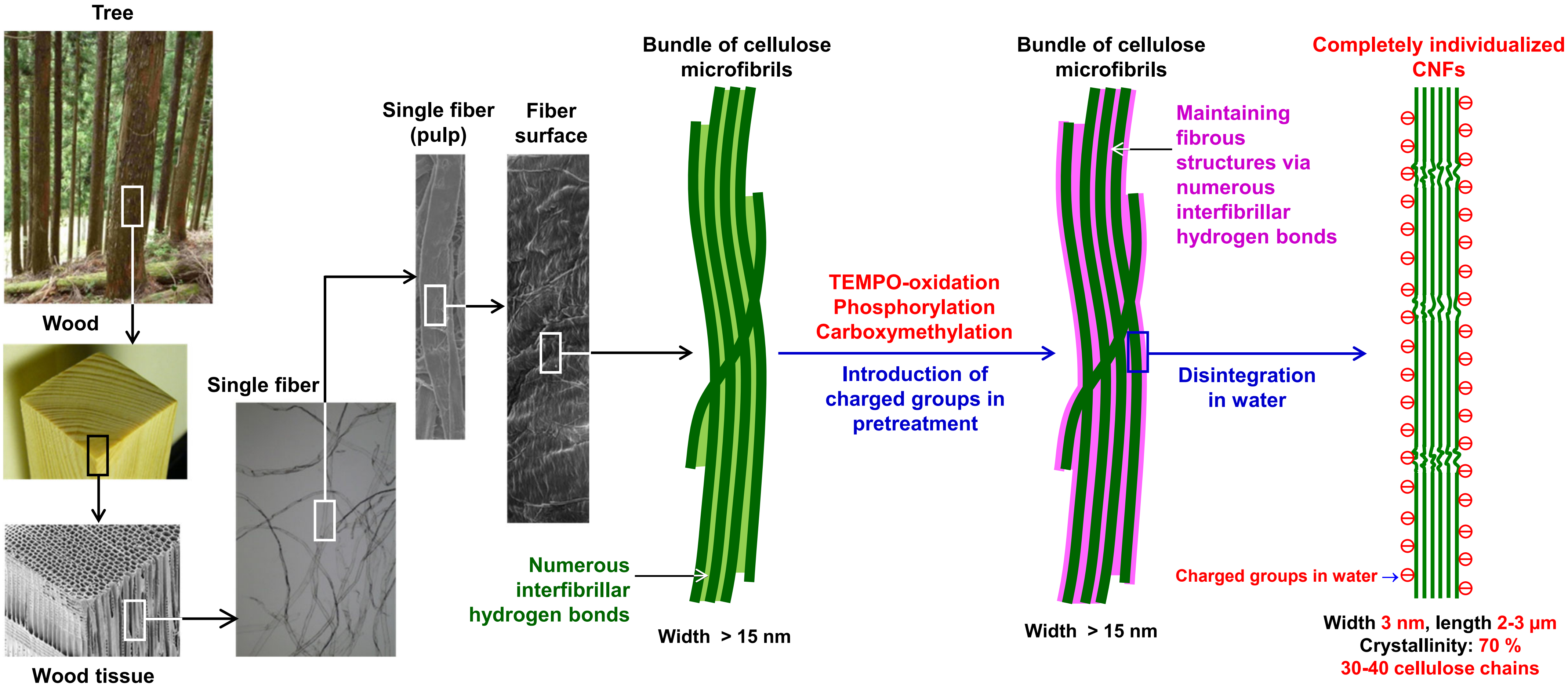
Width 3 nm
Length 2–3 μm
Crystallinity 40 %
30–40 cellulose chains

Cellulose molecule

Width 0.4 nm
Length 500 nm

Isogai et al., Progress in Polymer Science (2018)

Chemistry-assisted nano-fibrillation of wood cellulose fibers



Tree

Wood

Wood tissue

Single fiber

Single fiber (pulp)

Fiber surface

Bundle of cellulose microfibrils

Numerous interfibrillar hydrogen bonds

Width > 15 nm

TEMPO-oxidation
Phosphorylation
Carboxymethylation

Introduction of charged groups in pretreatment

Bundle of cellulose microfibrils

Maintaining fibrous structures via numerous interfibrillar hydrogen bonds

Width > 15 nm

Disintegration in water

Completely individualized CNFs

Charged groups in water →

Width 3 nm, length 2-3 μm
Crystallinity: 70 %
30-40 cellulose chains

- Osmotic effect and electrostatic repulsion efficiently work between surface-charged cellulose microfibrils in water.

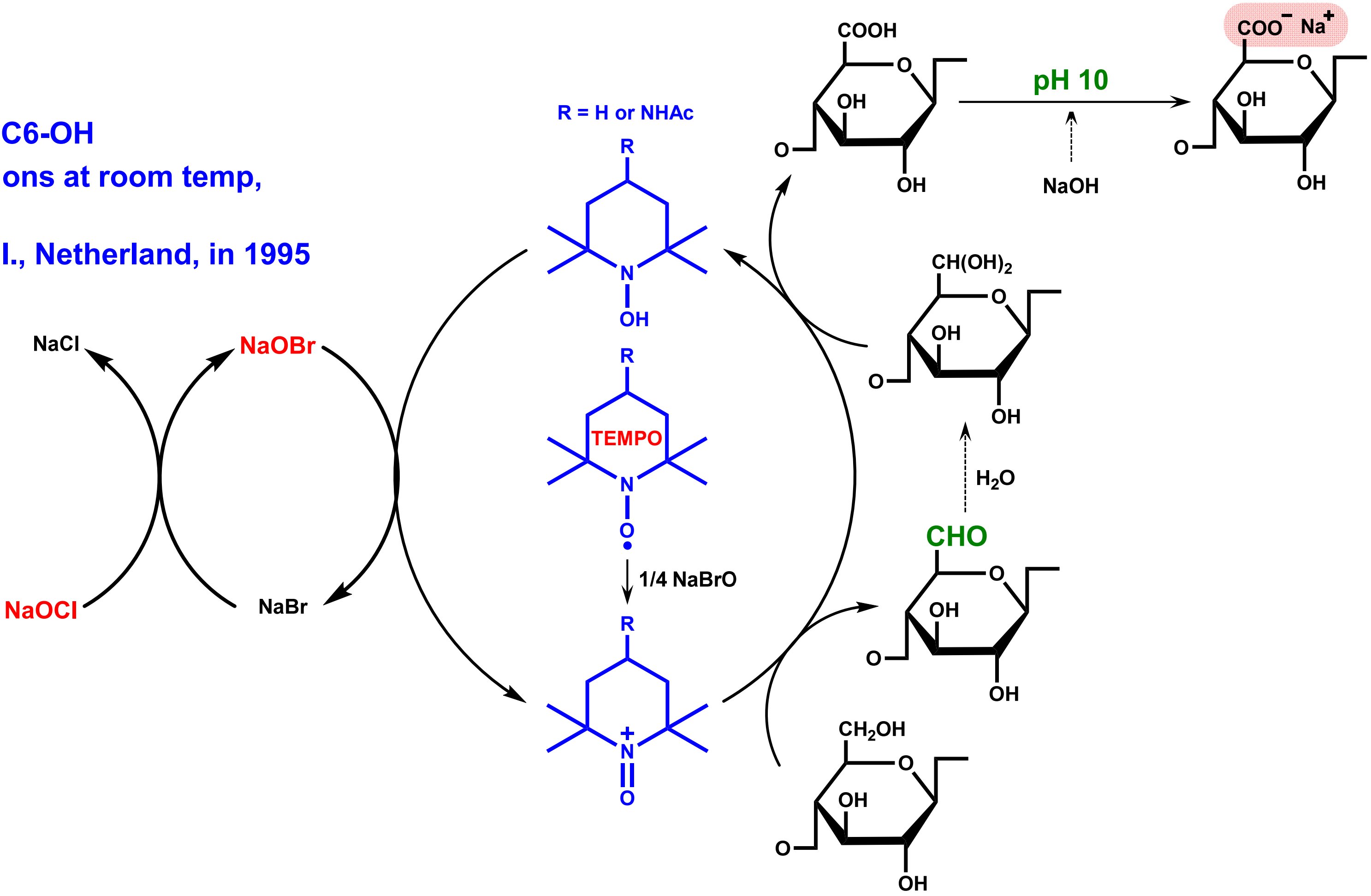
Isogai et al., Progress in Polymer Science (2018)

Conventional TEMPO/NaBr/NaClO-oxidation of cellulose in water at pH 10,

starting from 1996 in our laboratory

Advantageous points :

- Aqueous media at pH 5-10
- Mostly position-selective reaction at C6-OH
- Proceeds in water under mild conditions at room temp, atmospheric pressure, < 2 h
- Originally developed by de Nooy et al., Netherland, in 1995



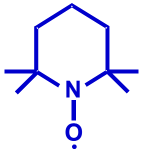
- TEMPO-catalyzed oxidation proceeds similarly to enzymatic reactions but does more rapidly.

Isogai et al., Progress in Polymer Science (2018)

TEMPO/NaBr/NaClO oxidation of wood cellulose fibers, such as bleached kraft pulp

Wood cellulose fibers (1 g)

Water (100 mL)
TEMPO (0.0125 g)
NaBr (0.125 g)



Cellulose fiber/water dispersion at R.T.

NaClO

0.4 M NaOH to maintain pH 10

Stirring for ~90 min

Filtration by washing with water

Washing effluent

TEMPO
NaCl
NaBr

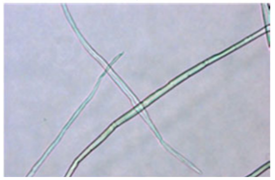
Recycling

Desalting

Fibrous TEMPO-oxidized cellulose

Carboxy content: 0.01 mmol/g

Carboxylate content: 1.7 mmol/g



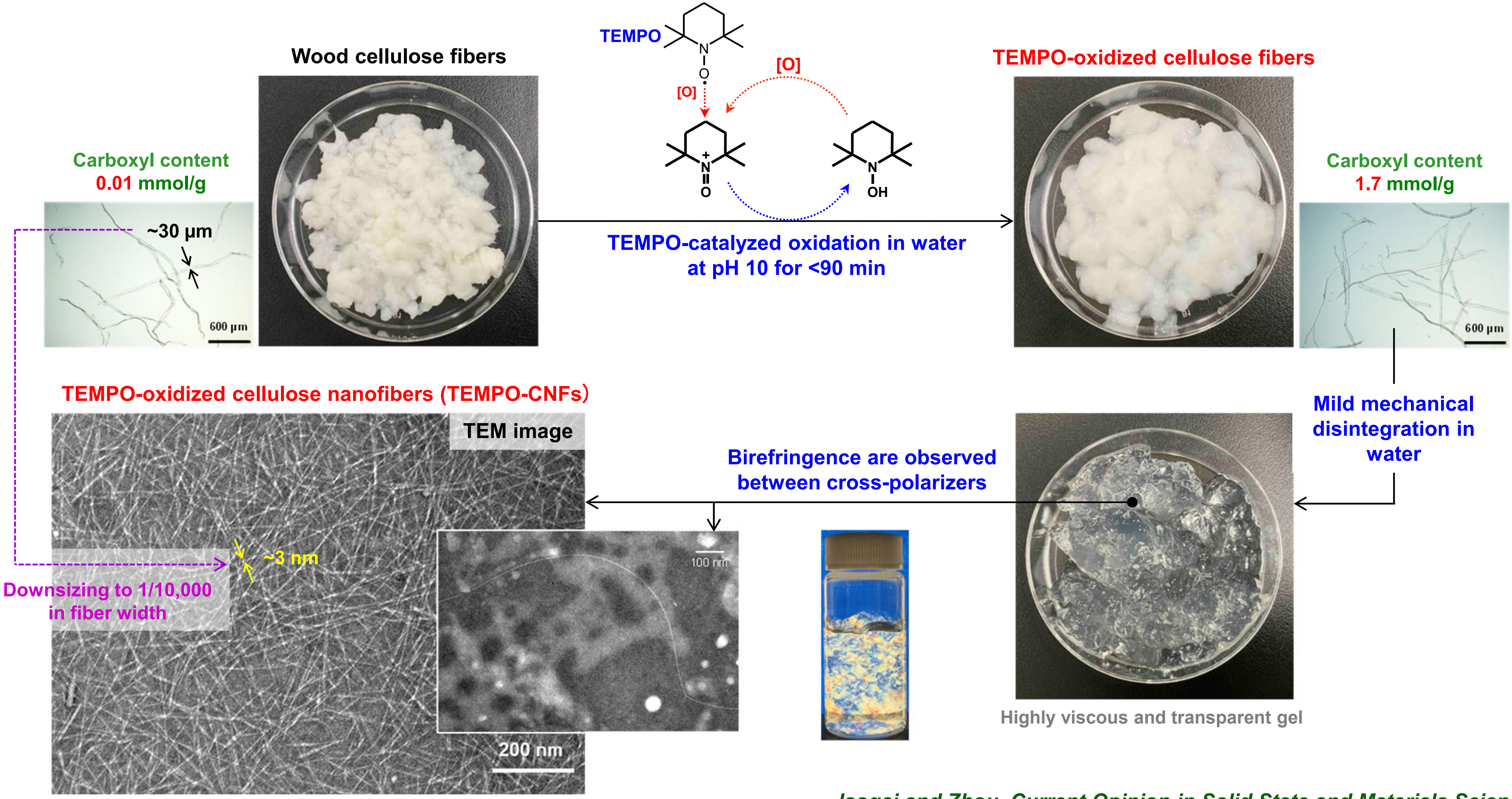
Fibrous morphologies are unchanged before and after oxidation.

- **Carboxylate content of oxidized fibers increases from 0.01 to 1.7 mmol/g (170 folds !).**

Shinoda et al., Biomacromolecules (2012)

Conversion of TEMPO-oxidized wood cellulose fibers to TEMPO-cellulose nanofibrils

TEMPO-CNFs



Wood cellulose fibers

TEMPO

[O]

[O]

TEMPO-catalyzed oxidation in water at pH 10 for <90 min

TEMPO-oxidized cellulose fibers

Carboxyl content 0.01 mmol/g

~30 µm

600 µm

Carboxyl content 1.7 mmol/g

600 µm

Mild mechanical disintegration in water

Highly viscous and transparent gel

Birefringence are observed between cross-polarizers

TEMPO-oxidized cellulose nanofibers (TEMPO-CNFs)

TEM image

~3 nm

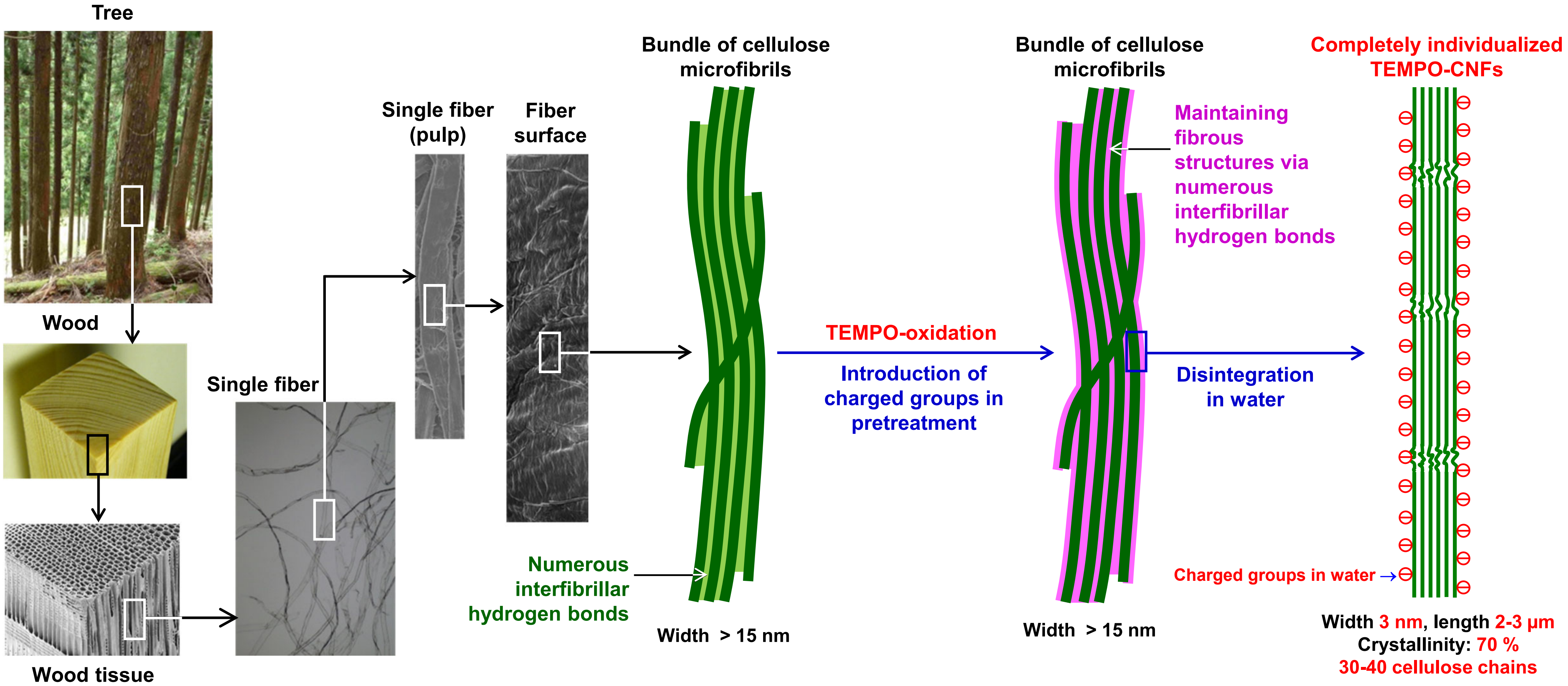
100 nm

200 nm

Downsizing to 1/10,000 in fiber width

Isogai and Zhou, Current Opinion in Solid State and Materials Science (2019)

Chemistry-assisted nano-fibrillation of wood cellulose fibers



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Wood tissue

Single fiber

Single fiber (pulp)

Fiber surface

Bundle of cellulose microfibrils

Numerous interfibrillar hydrogen bonds

Width > 15 nm

TEMPO-oxidation

Introduction of charged groups in pretreatment

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Disintegration in water

Completely individualized TEMPO-CNFs

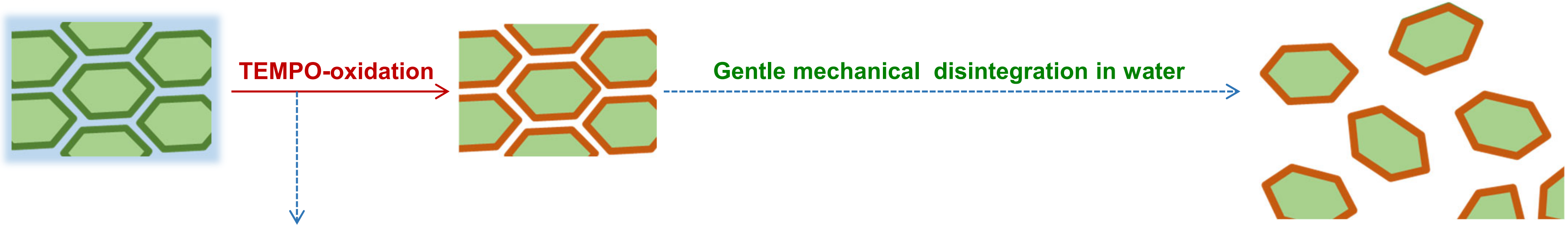
Charged groups in water →⊖

Width 3 nm, length 2-3 μm
Crystallinity: 70 %
30-40 cellulose chains

- Osmotic effect and electrostatic repulsion efficiently work between surface-charged cellulose microfibrils in water.

Isogai et al., Progress in Polymer Science (2018)

Mechanism to convert individual TEMPO-CNFs from wood cellulose fibers



Each cellulose microfibril is
surrounded with sponge-like non-crystalline
hemicelluloses in wood cellulose fiber

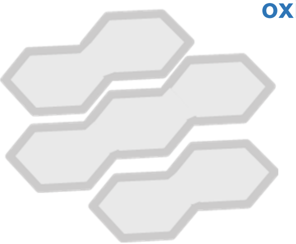
TEMPO-oxidized wood cellulose
microfibrils in cellulose fiber

Individually nano-dispersed TEMPO-CNFs

TEMPO-oxidation

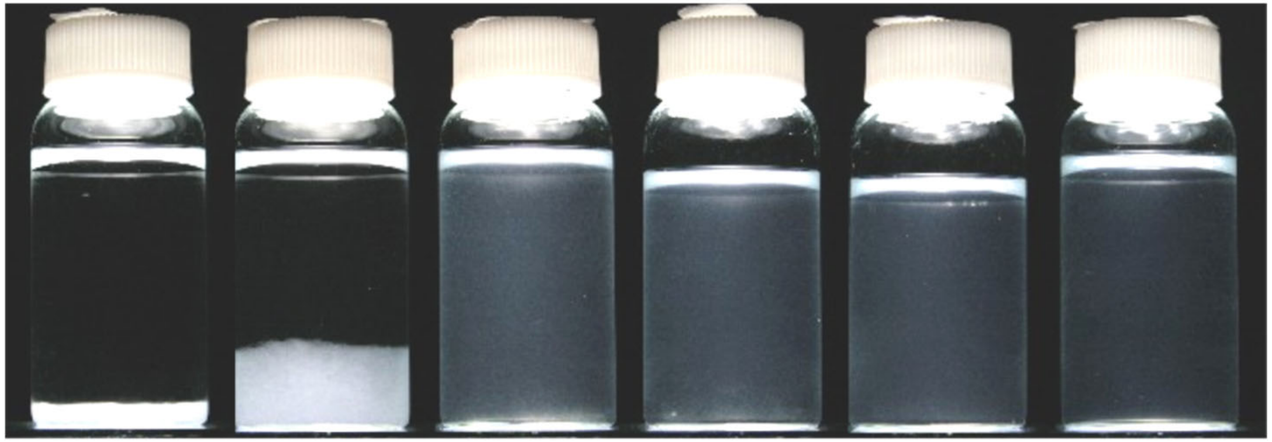
Gentle mechanical disintegration in water

Most hemicelluloses
are degraded into
water-soluble fractions
and removed from the
water-insoluble
oxidized fibers



No such aggregated structures of
cellulose microfibrils in wood cellulose fiber

Stirring time **(1500 rpm)**

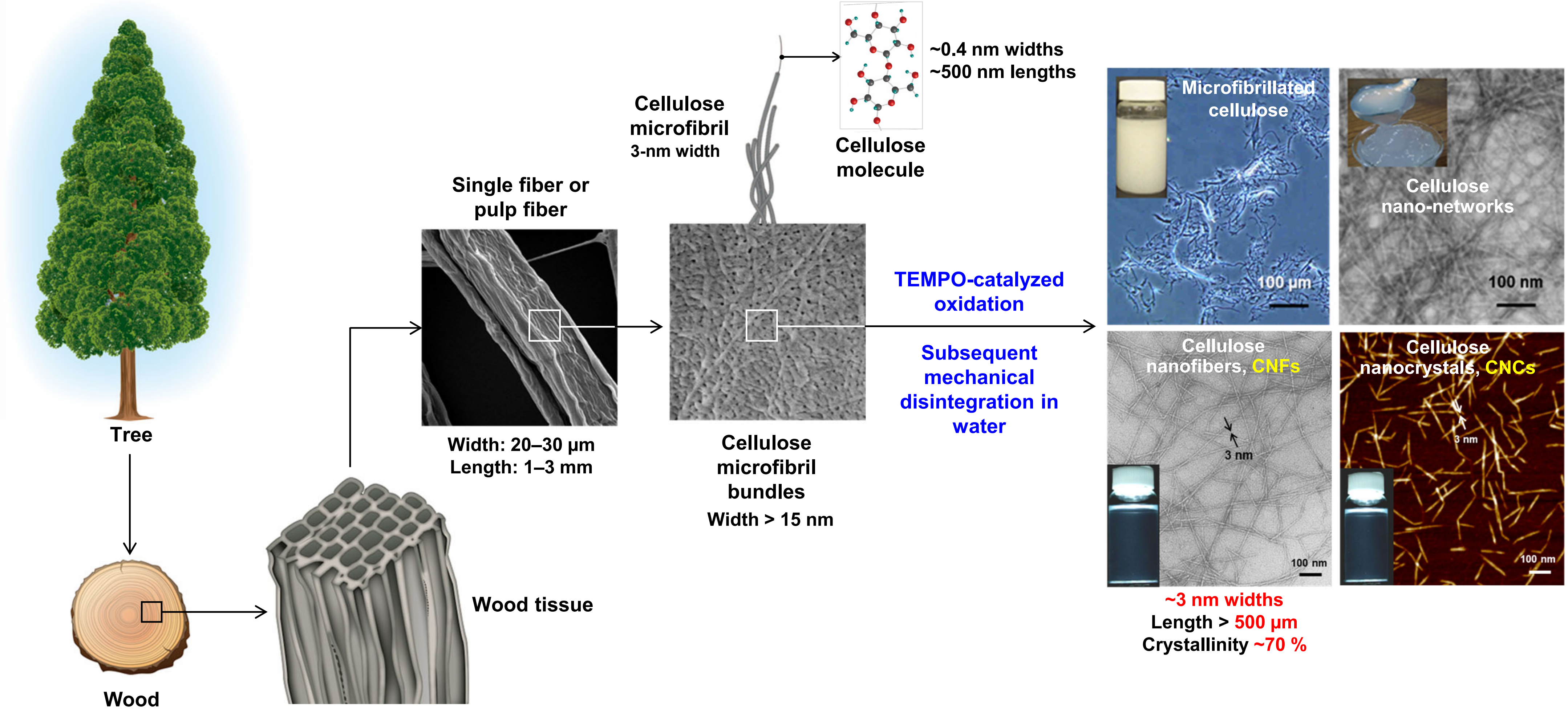


Cellulose in supernatant fraction

0 % → 97%

- **TEMPO-CNFs can be prepared from TEMPO-oxidized cellulose fibers by gentle magnetic stirring in water, showing that each wood cellulose microfibril is surrounded with sponge-like hemicelluloses, into which TEMPO$^+$ molecules can smoothly penetrate.**

From wood cellulose fibers to TEMPO-CNFs: new cellulose nanomaterials



Tree

Wood

Wood tissue

Single fiber or pulp fiber

Width: 20–30 µm
Length: 1–3 mm

Cellulose microfibril bundles

Width > 15 nm

Cellulose microfibril
3-nm width

Cellulose molecule

~0.4 nm widths
~500 nm lengths

TEMPO-catalyzed oxidation

Subsequent mechanical disintegration in water

Microfibrillated cellulose

Cellulose nano-networks

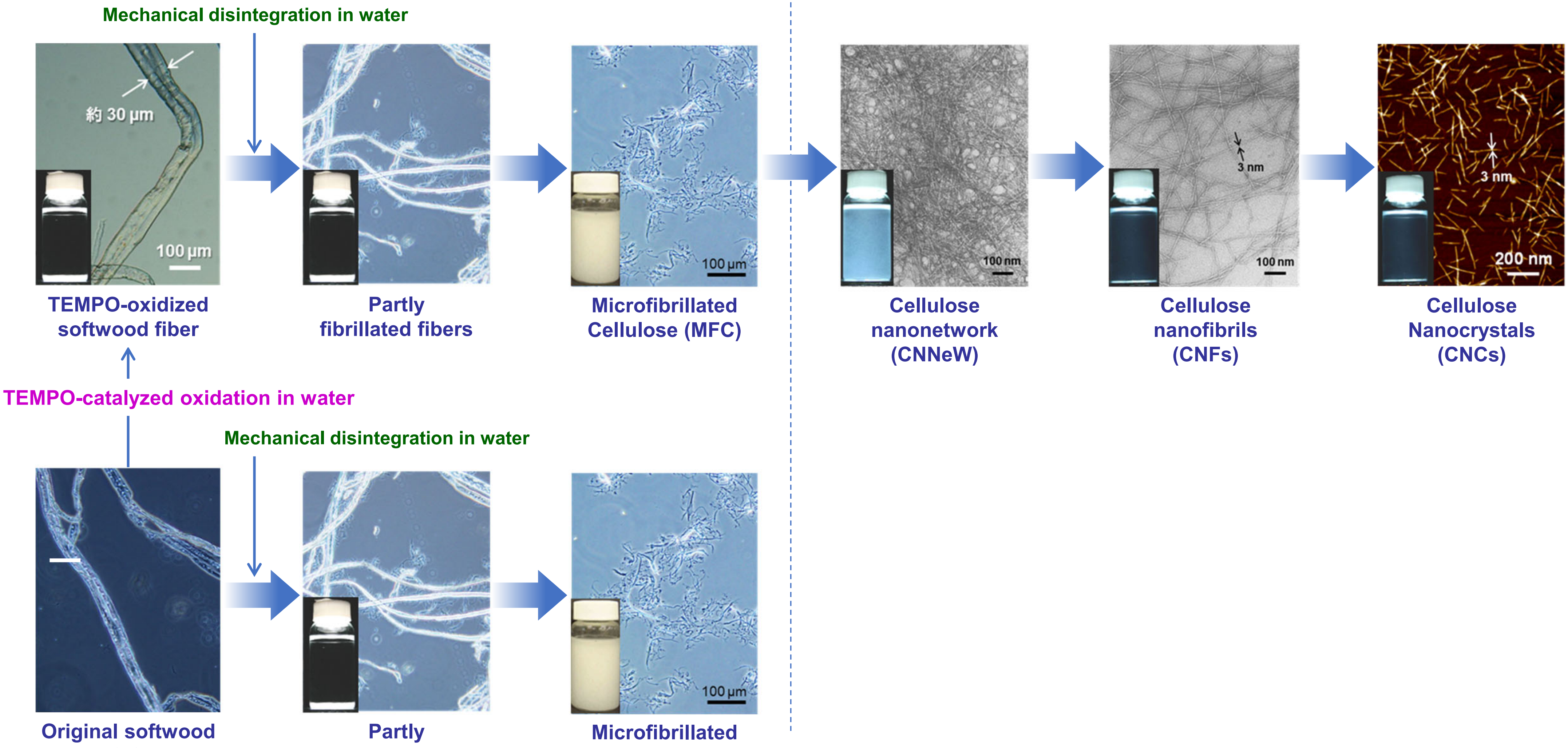
Cellulose nanofibers, CNFs

Cellulose nanocrystals, CNCs

~3 nm widths
Length > 500 µm
Crystallinity ~70 %

- However, TEMPO-CNFs have been developed as new material seeds by curiosity-driven research, not by target-oriented R&D.
- Therefore, it is difficult to find killer applications of TEMPO-CNFs.

Diverse carboxy group-rich fibers/MFC/CNFs/CNCs can be prepared from TEMPO-oxidized wood cellulose fibers by controlling degree of fibrillation in water



Mechanical disintegration in water

TEMPO-oxidized softwood fiber

Partly fibrillated fibers

Microfibrillated Cellulose (MFC)

Cellulose nanonetwork (CNNeW)

Cellulose nanofibrils (CNFs)

Cellulose Nanocrystals (CNCs)

TEMPO-catalyzed oxidation in water

Mechanical disintegration in water

Original softwood kraft fiber

Partly fibrillated fibers

Microfibrillated Cellulose (MFC)

Isogai et al., Progress in Polymer Science (2018)

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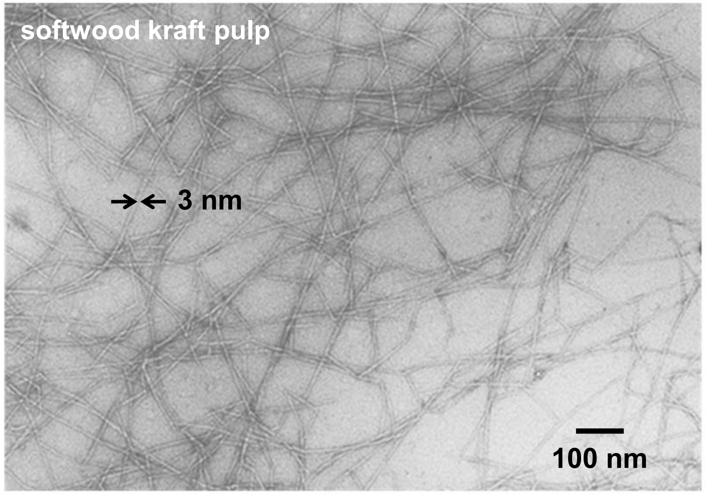
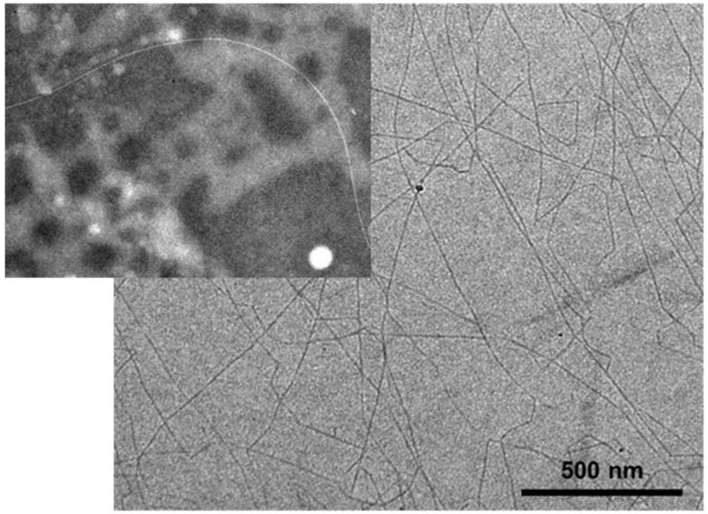
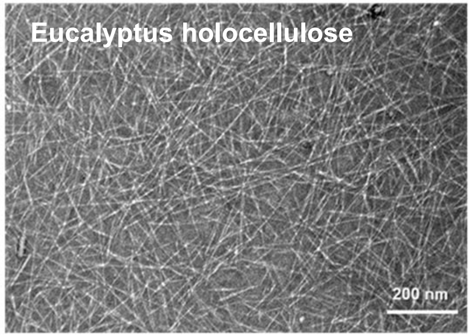
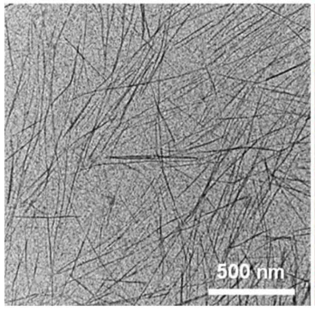
TEMPO-catalyzed oxidation can be used to plant cellulose fibers for complete individualization to single microfibrils observable by TEM and AFM



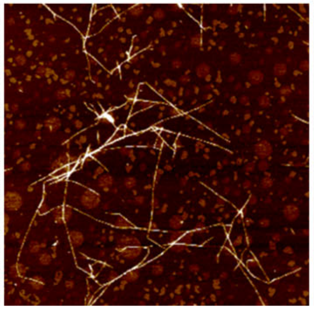




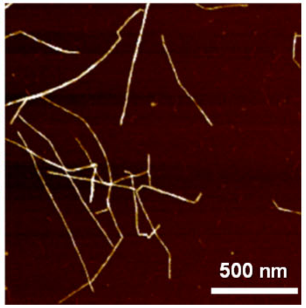
Chara TO-CNFs

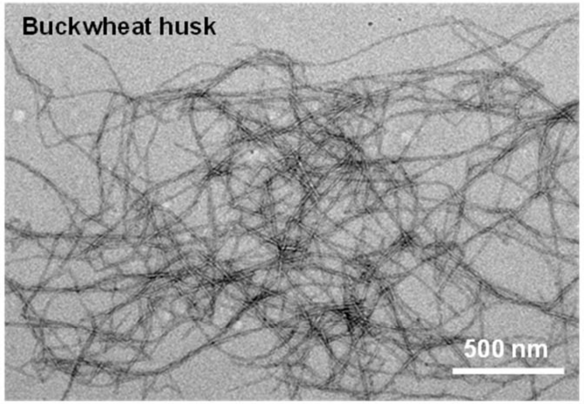


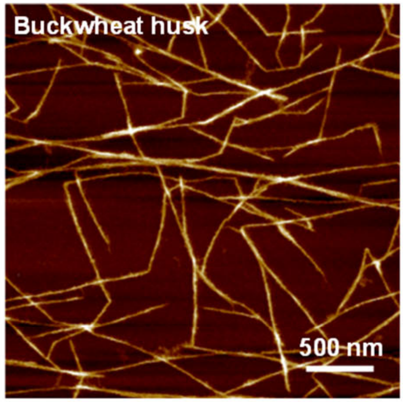
Haircap moss TO-CNFs

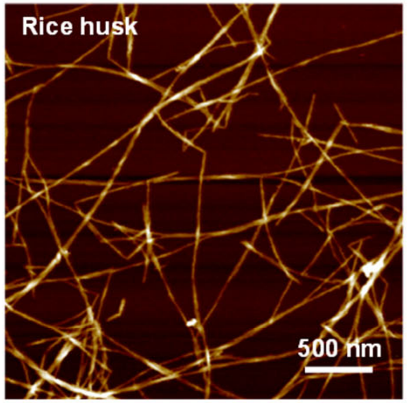


Adiantum TO-CNFs





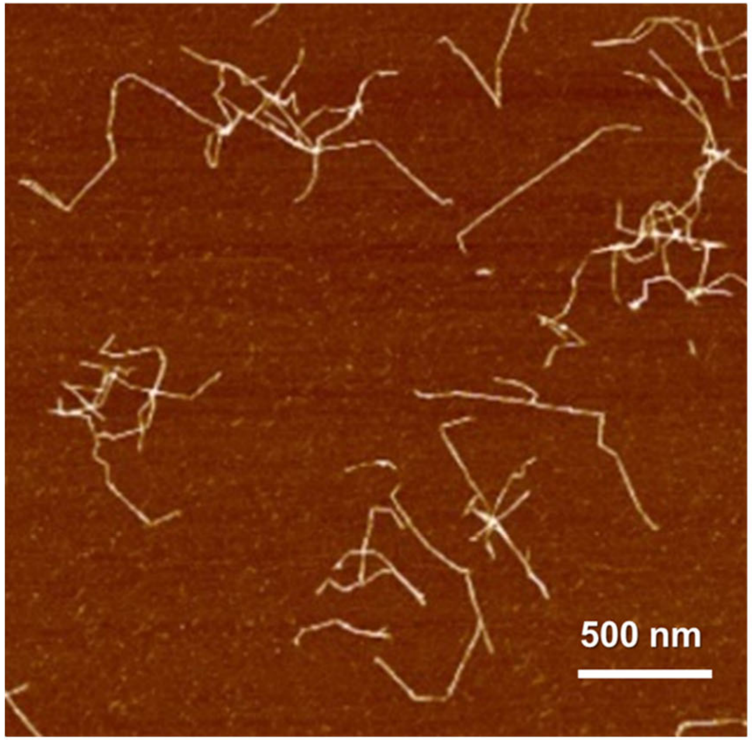




- **All terrestrial plant fibers consist of crystalline cellulose microfibrils with homogeneous ~3-nm widths.**

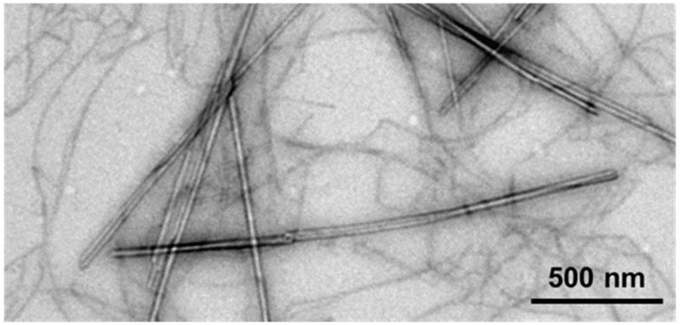
AFM images of TEMPO-CNFs from wood, buckwheat husk, and tunicate

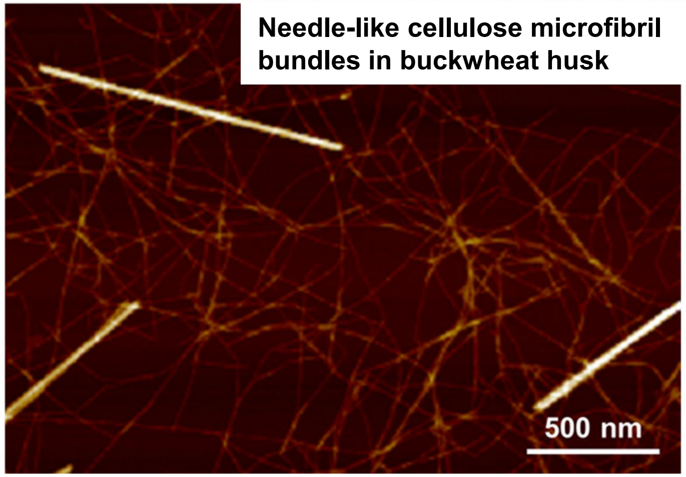
TEMPO-oxidized wood CNFs



Nakamura et al. Cellulose (2019)

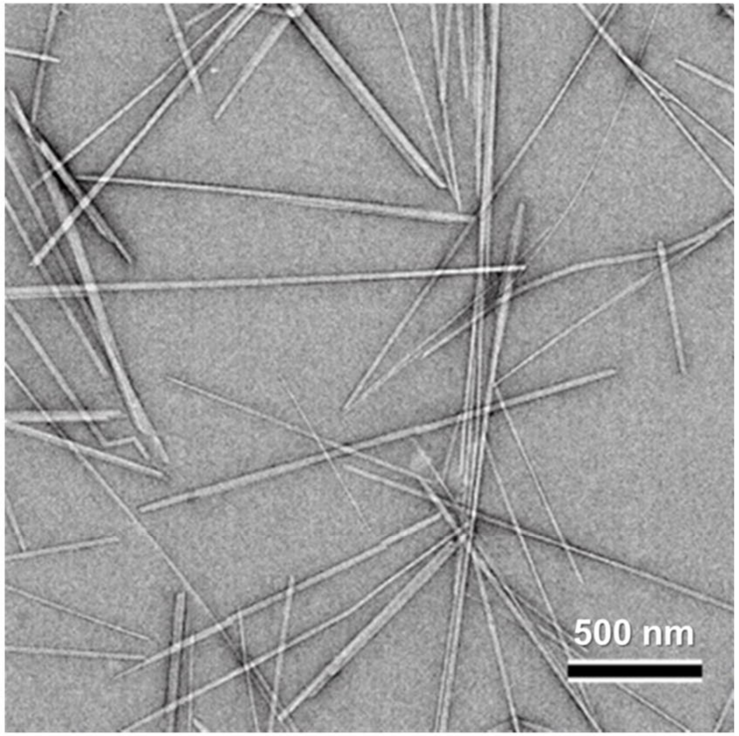
TEMPO-oxidized buckwheat husk, after partial fibrillation in water





Needle-like cellulose microfibril bundles in buckwheat husk

Tunicate CNCs



Ogawa and Putaux, Cellulose (2019)

- TEMPO-oxidized wood CNFs behave like flexible, non-crystalline, and random-coil polymers, whereas tunicate CNCs appear as needle-like morphologies with almost perfect crystallites.
- TEMPO-CNF bundles before nano-fibrillation in water have needle-like morphologies (probably) with high crystallinities.

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- Mechanically fibrillated wood cellulose materials
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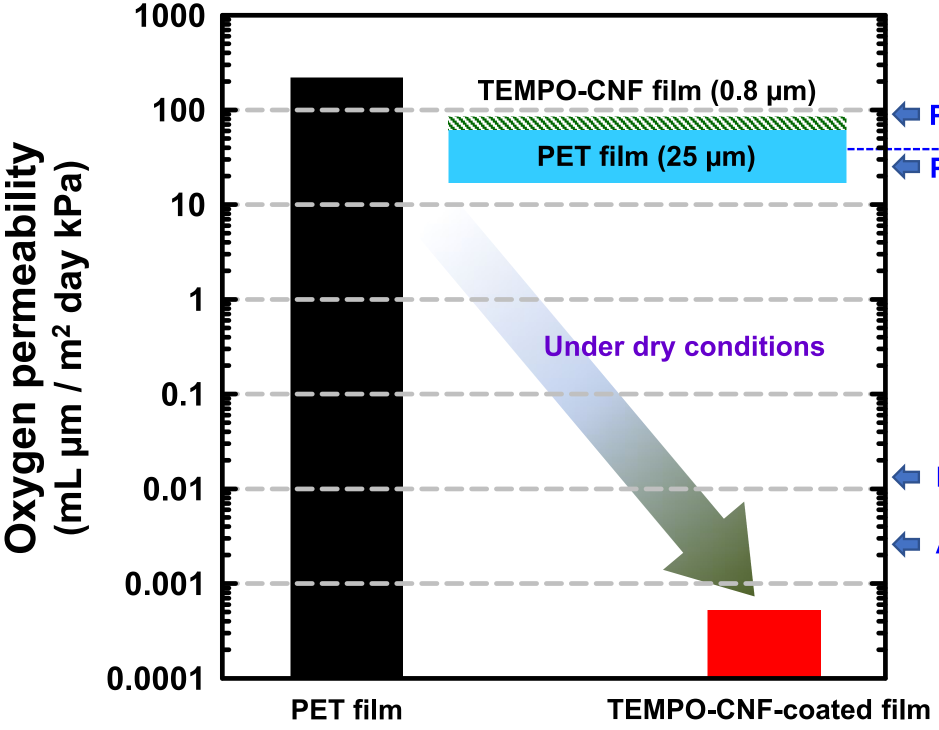
- Application of TEMPO-oxidation to fundamental structural analysis of plant cellulose microfibrils
- **Unique characteristics of TEMPO-CNFs**
- Side reactions of conventional TEMPO/NaBr/NaClO oxidation at pH 10
- New TEMPO-catalyzed oxidation with suppressed side reactions
- Present situation of nanocellulose productions/applications
- Conclusions and future challenges

Oxygen-barrier properties were extremely improved
by coating thin TEMPO-CNF layer on PET film

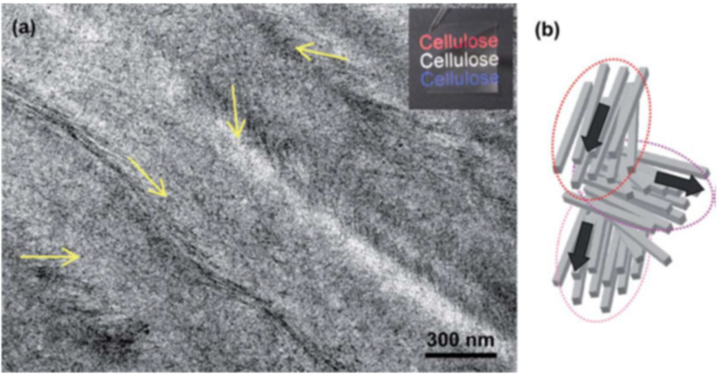


PE film

PET film

EVOH film for food/medicine package film

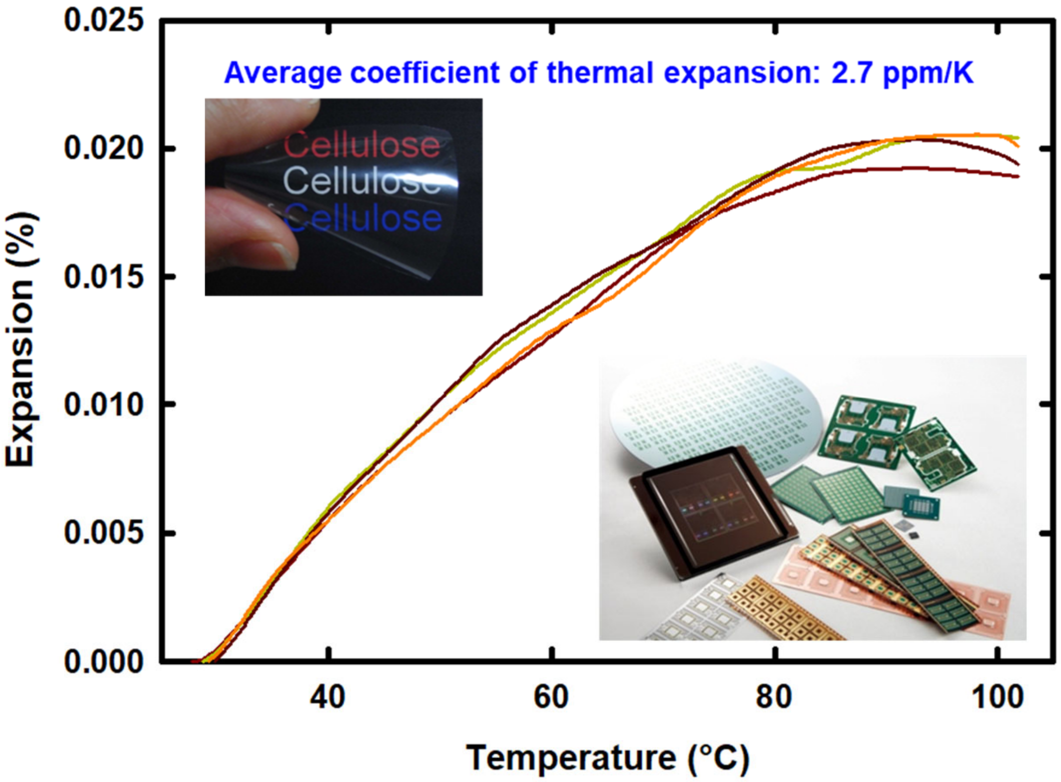
Aluminum vapor deposited EVOH film



- Oxygen permeability decreases to 1/500000 by coating thin film of TEMPO-CNFs on PET film.
- Positron-annihilation-lifetime spectroscopy shows that TEMPO-CNF film contains extremely small pores, d=0.47nm, without connections.

Fukuzumi et al., Biomacromolecules (2009)

Quite low coefficient of thermal expansion of transparent TEMPO-CNF films



- Low coefficient of thermal expansion or thermal dimensional stability is required for electronic boards, flexible display, etc.
- Another unique characteristic: clear shear-thinning properties of TEMPO-CNF/water dispersions

Fukuzumi et al., Biomacromolecules (2009)

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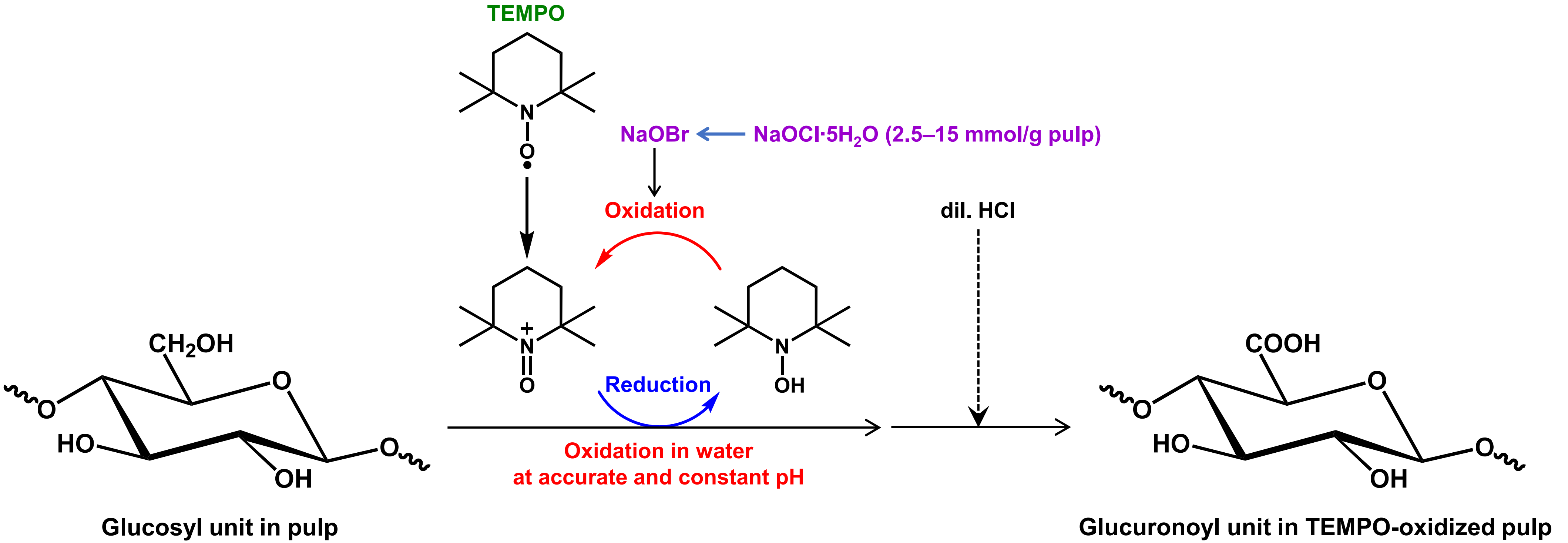
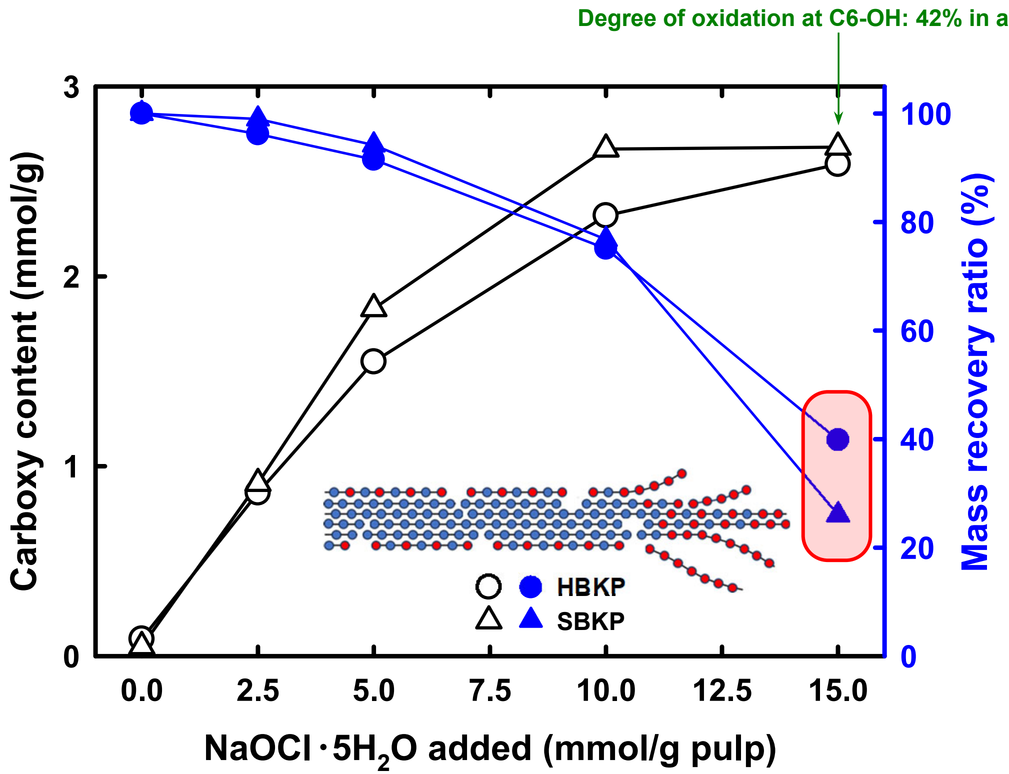
TEMPO/NaBr/solid NaClO•5H_2O oxidation system at pH 10

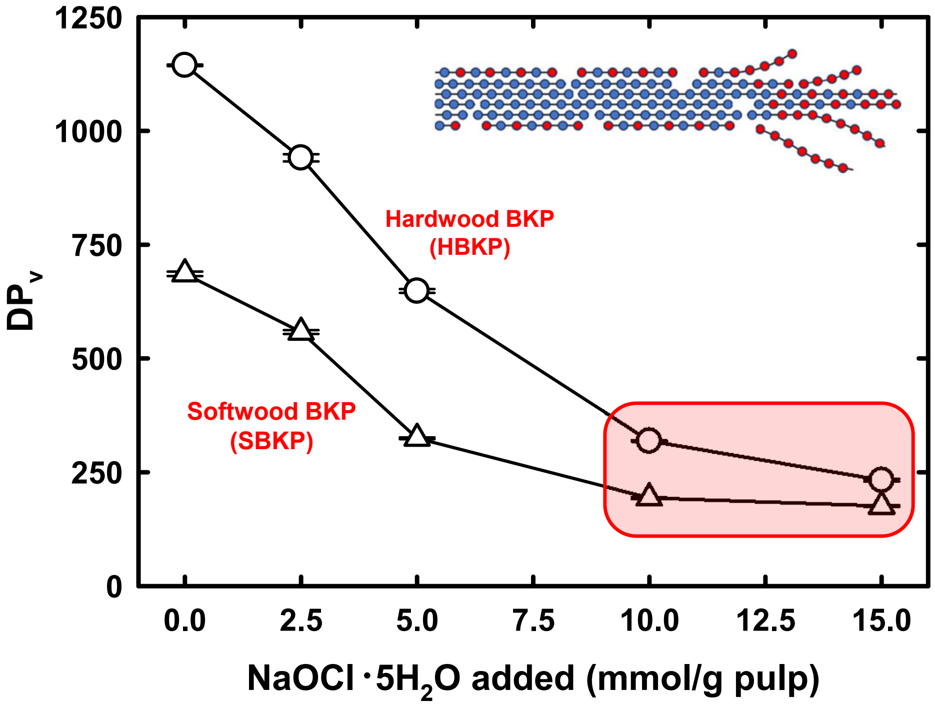


- The conventional NaClO solution is unstable and always contains some NaOH (+ Cl_2 → NaClO).
- Detailed oxidation kinetics and side reactions on oxidized cellulose molecules, without considering the effect of an excess NaOH present in aqueous NaClO solution, can be investigated, when solid NaClO•5H_2O is used in oxidation of wood cellulose fibers, in place of NaClO solution.

Hou G. et al., ACS Sustainable Chemistry & Engineering (2023), Carbohydrate Polymers (2024)

Changes in carboxy content, mass recovery ratio, and DP_v of water-insoluble fractions prepared from wood cellulose fibers by TEMPO/NaBr/NaClO system at pH 10


Degree of oxidation at C6-OH: 42% in average !

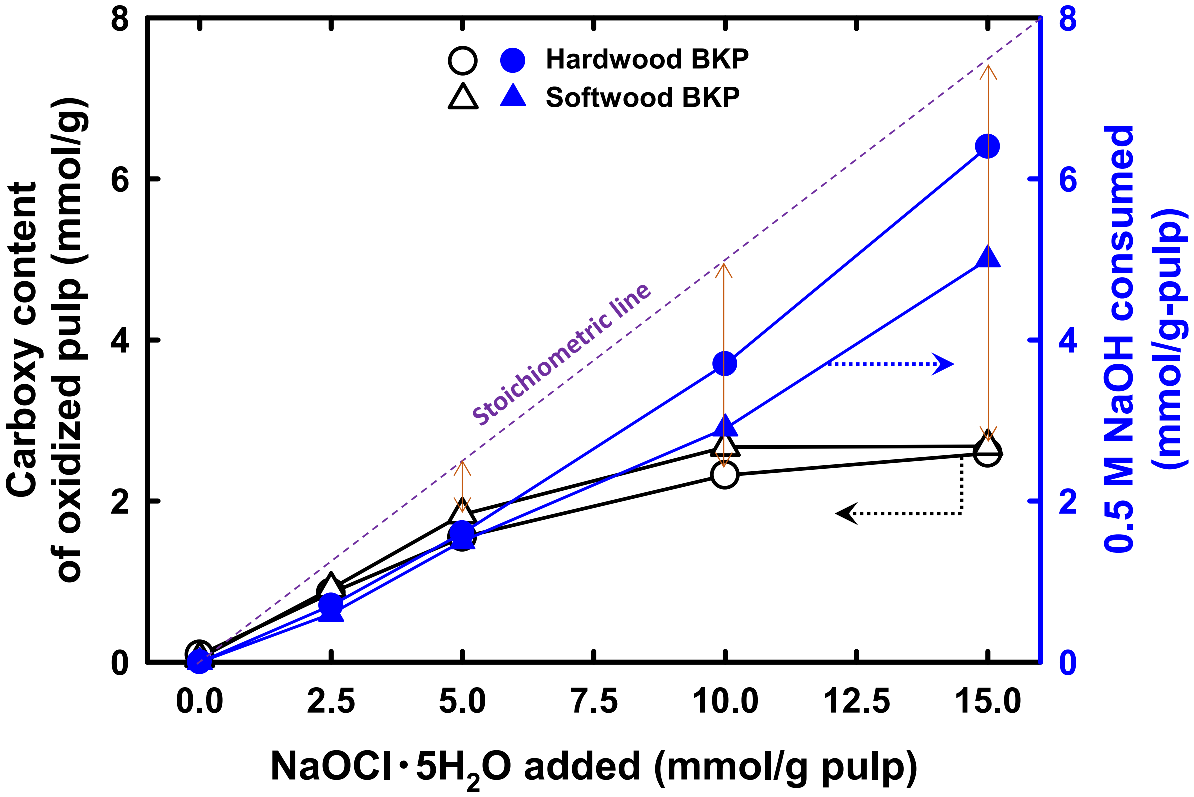


- **Side reactions, such as depolymerization of not only surface but also inside cellulose chains, formation of polyglucuronate homopolymer tails, carboxylation of inside crystallites, etc. cause remarkable decreases in mass recovery ratio and DP_v of water-insoluble TEMPO-oxidized products, accompanied by remarkable increases in carboxy content.**

Hou G. et al., ACS Sustainable Chemistry & Engineering (2023)

Side reactions during oxidation of wood cellulose fibers by TEMPO/NaBr/NaClO system at pH 10

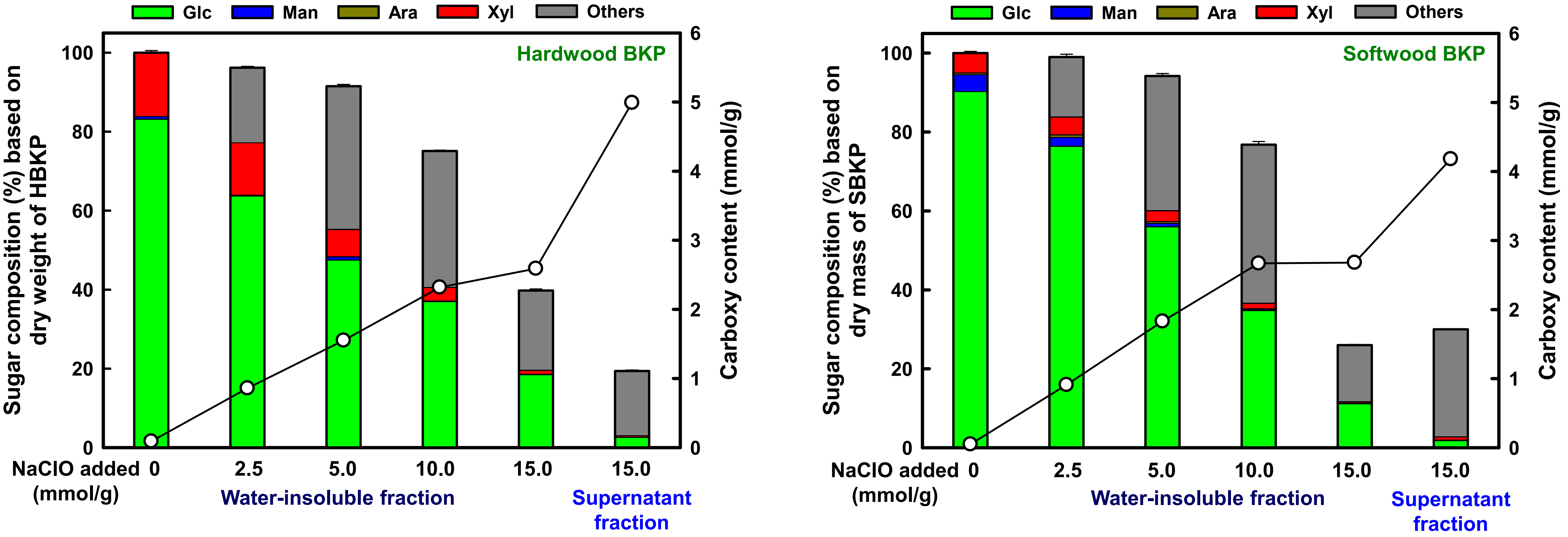
Cellulose-CH_2OH + 2NaClO + NaOH ⟶ Cellulose-COONa + 2NaCl + $2H_2O$



- When the amount of NaClO added increases to >10 mmol/g, the NaClO and NaOH are clearly consumed largely by side reactions such as depolymerization and formation of polyglucuronate chains.

Hou G. et al., ACS Sustainable Chemistry & Engineering (2023)

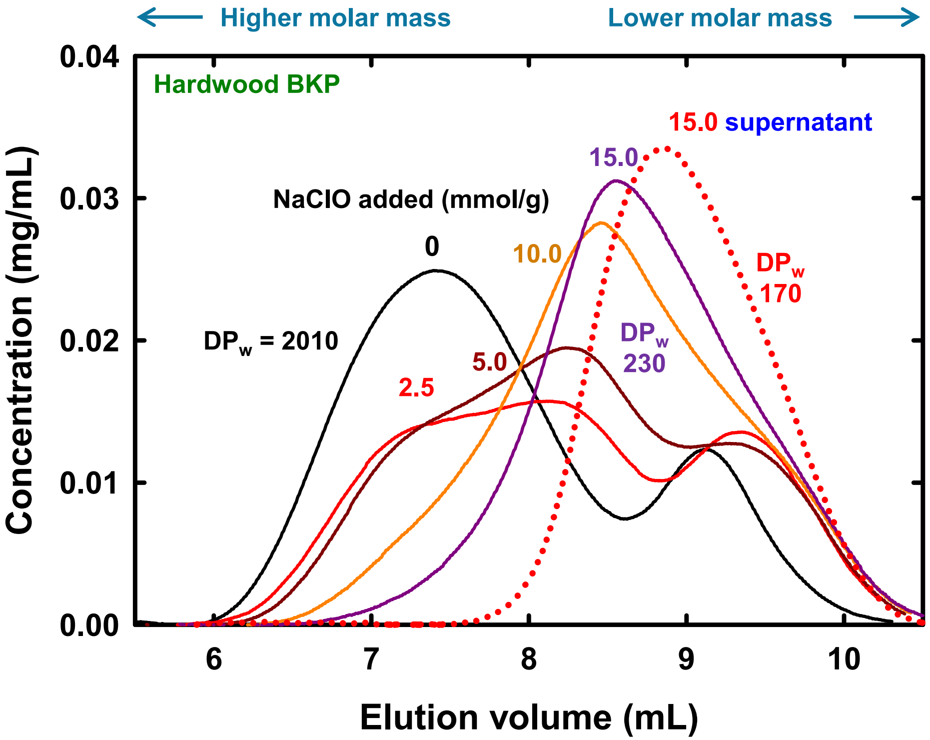
Neutral sugar compositions and carboxy content of oxidized wood cellulose fibers Prepared by TEMPO/NaBr/NaClO at pH 10

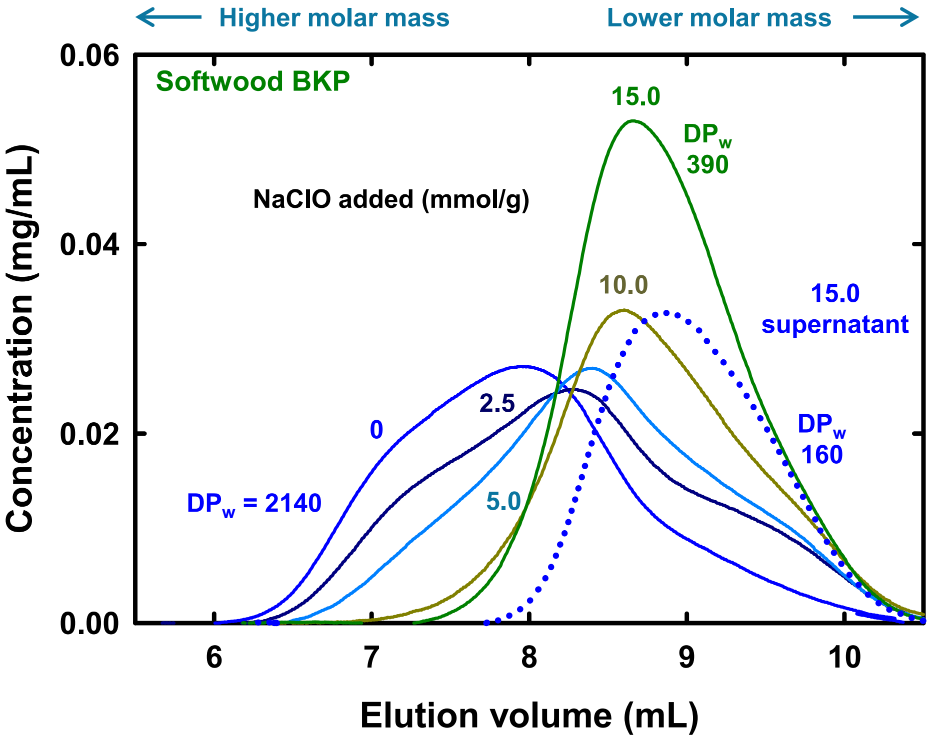


- Mass recovery ratio decreases to 30-40% by TEMPO-catalyzed oxidation with NaClO of 15 mmol/g.
- Hemicellulose molecules in wood cellulose fibers are removed as water-soluble oxidized/degraded products with increasing amount of NaClO added in oxidation.
- Formation of TEMPO-oxidized cellulose molecules causes the “others” faction in neutral sugar composition analysis.

Hou G. et al., ACS Sustainable Chemistry & Engineering (2023), Carbohydrate Polymers (2024)

Depolymerization behavior of oxidized products prepared from wood cellulose fibers by TEMPO/NaBr/NaClO at pH 10

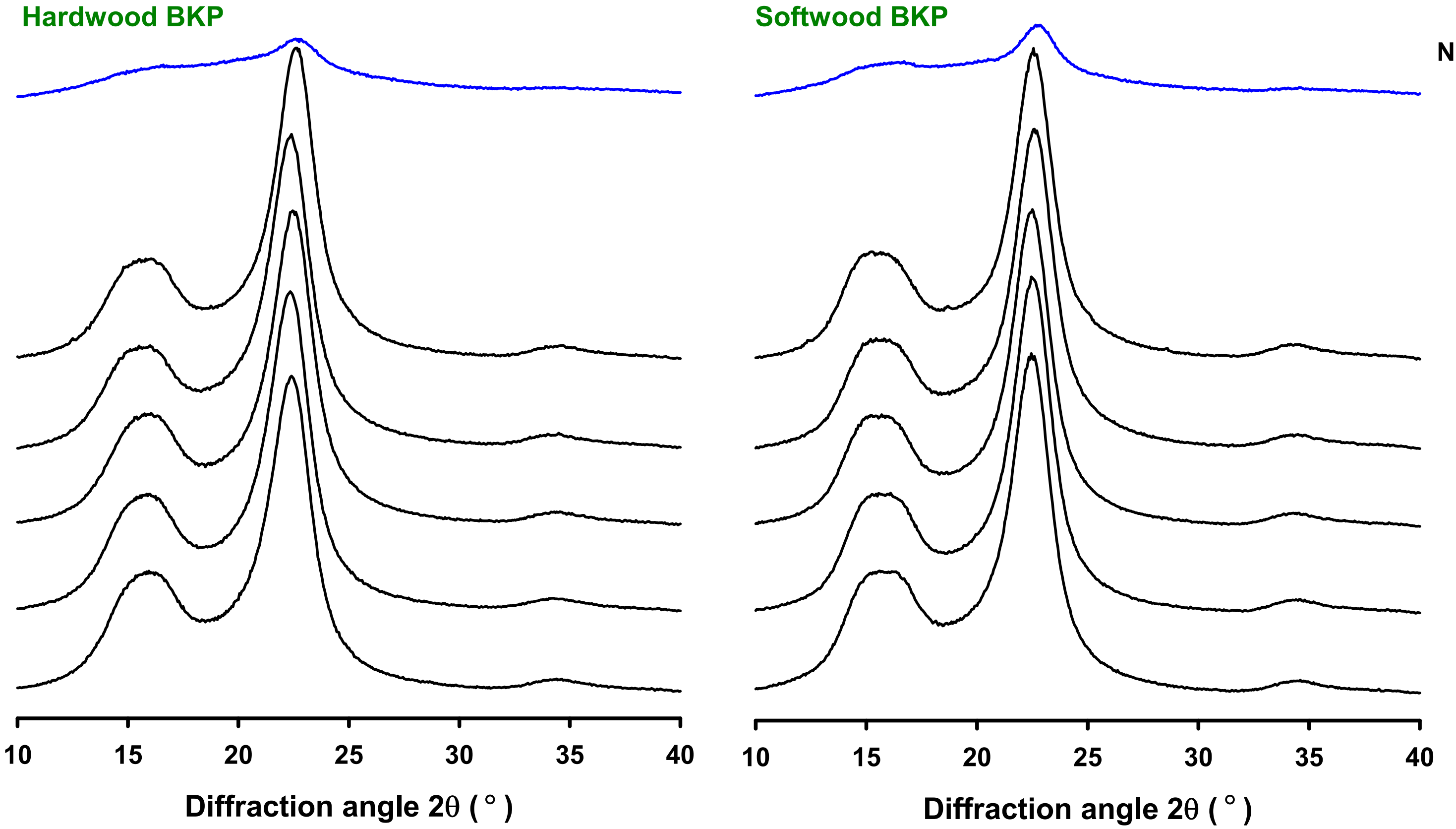




- **SEC/MALLS/RI analysis shows that clear depolymerization occurs on cellulose, oxidized cellulose, and hemicellulose molecules during TEMPO/NaBr/NaClO oxidation at pH 10, as the amount of NaClO added is increased.**
- **The molar mass of water-insoluble fraction and supernatant oxidized fraction, prepared with NaClO of 15 mmol/g, have similar molar masses between hardwood and softwood kraft pulps.**

Hou G. et al., Cellulose (2025)

XRD patterns of water-insoluble products and water-phase fractions prepared from wood cellulose fibers by TEMPO/NaBr/NaClO at pH 10

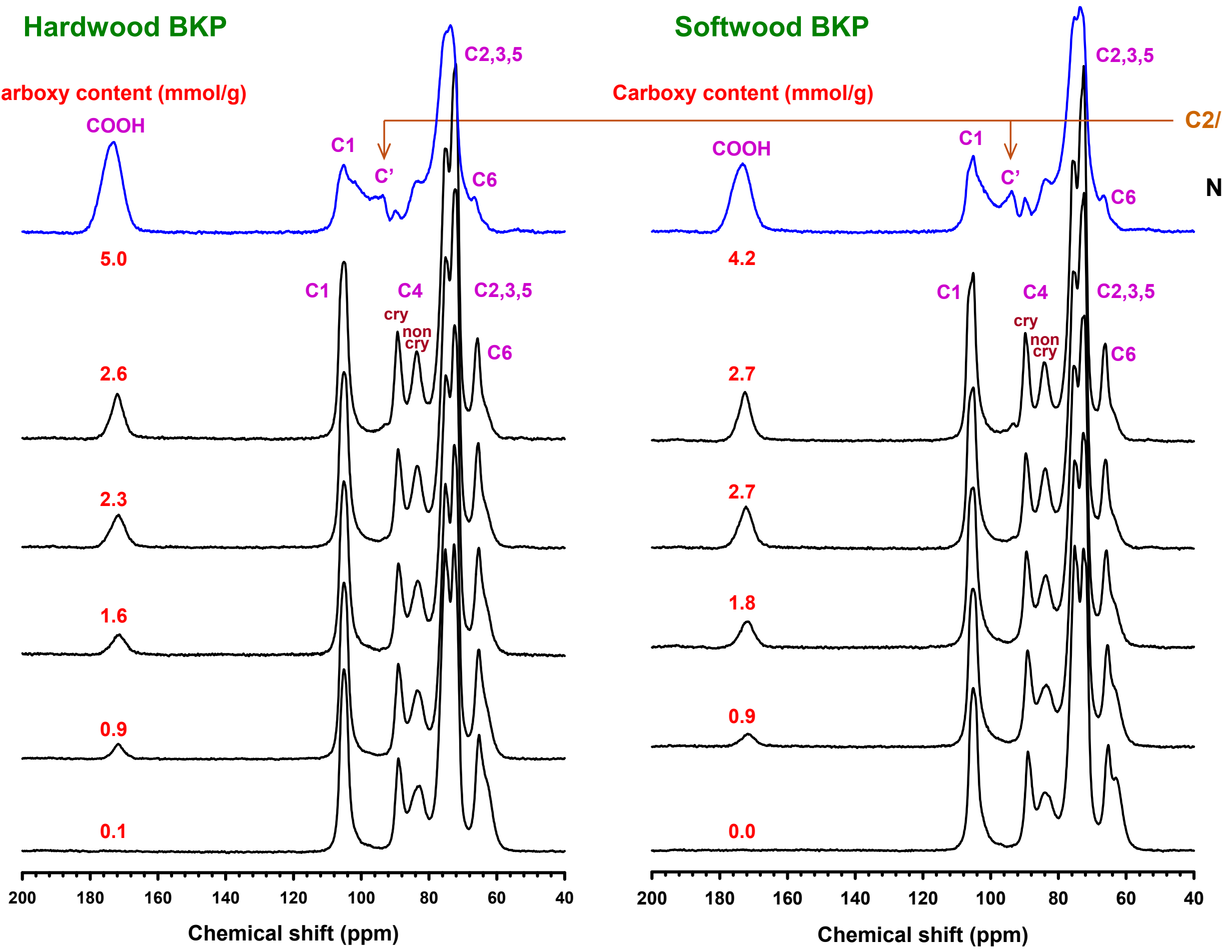


NaOCl added	Mass recovery (%) HBKP	Mass recovery (%) SBKP
15 mmol/g Supernatant fraction	30	19
Water-insoluble fraction		
15 mmol/g	40	26
10 mmol/g	75	77
5 mmol/g	92	94
2.5 mmol/g	96	99
0 mmol/g	100	100

- **Crystallinities of cellulose I are unchanged for water-insoluble fractions, regardless of the amount of NaClO added in oxidation, or low mass-recovery ratio of the fractions.**

Hou G. et al., ACS Sustainable Chemistry & Engineering (2023), Carbohydrate Polymers (2024)

Solid-state ^{13}C-NMR spectra of water-insoluble products and water-phase fractions prepared from wood cellulose fibers by TEMPO/NaBr/NaClO at pH 10

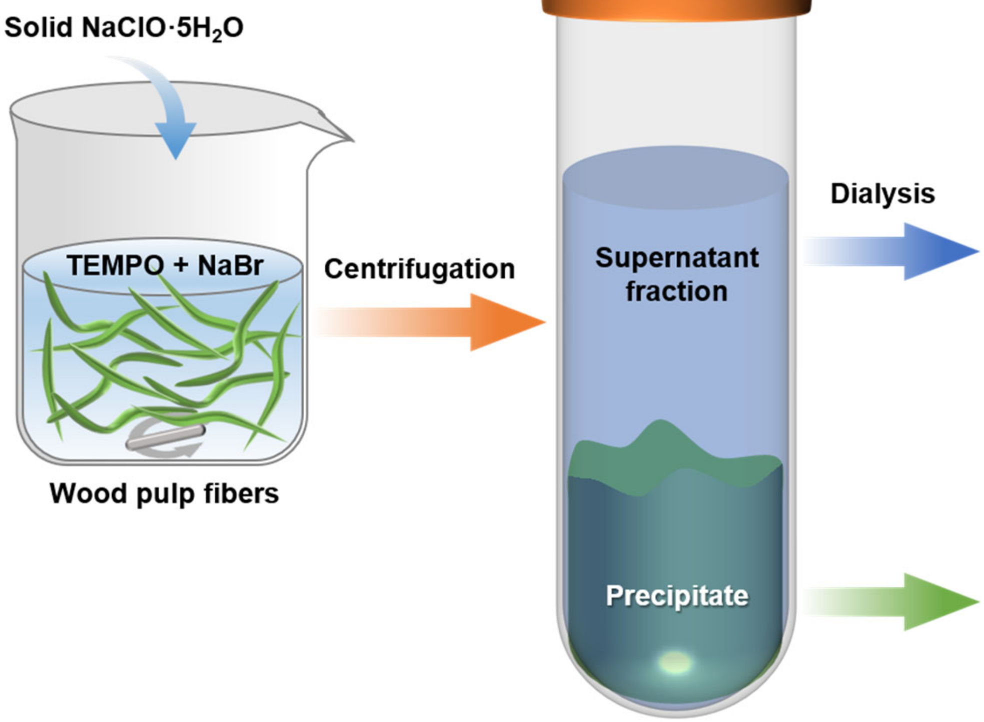


NaClO added	Mass recovery (%) HBKP	 SBKP
15 mmol/g **Water-phase fraction**	30	19
Water-insoluble fraction 15 mmol/g	40	26
10 mmol/g	75	77
5 mmol/g	92	94
2.5 mmol/g	96	99
0 mmol/g	100	100

- **The water-insoluble fractions show representative NMR spectra of TEMPO-oxidized cellulose with high crystallinity of cellulose I.**
- **The supernatant fractions show anomalous C' signal owing to C2/C3-ketone hydrates and/or their inter-molecular hemiacetal structures.**

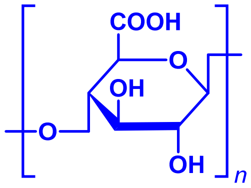
Hou G. et al., ACS Sustainable Chemistry & Engineering (2023), Carbohydrate Polymers (2024)

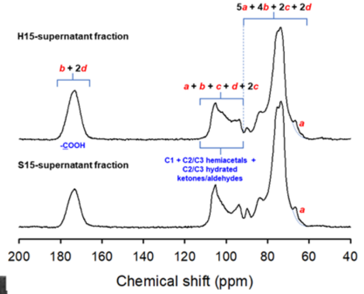
Supernatant fractions of TEMPO/NaBr/NaClO-oxidized wood cellulose fibers prepared with NaClO of 15 mmol/g at pH 10

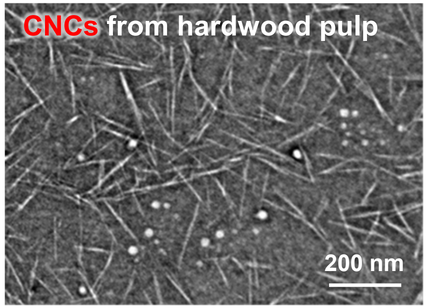


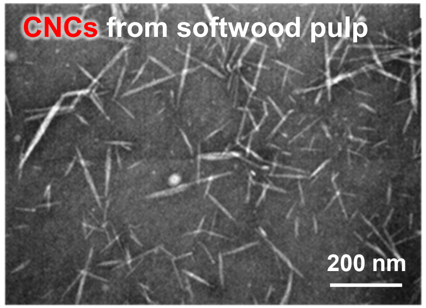
Degree of C6-oxidation: 64–76%

Mixture of
water-soluble C6-carboxy cellulose and
Others: cellulose nanocrystals (CNCs)

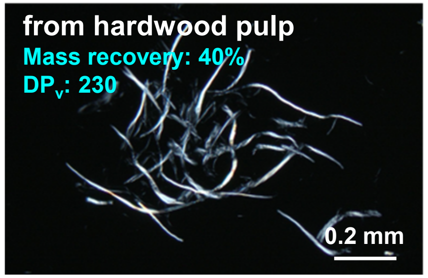


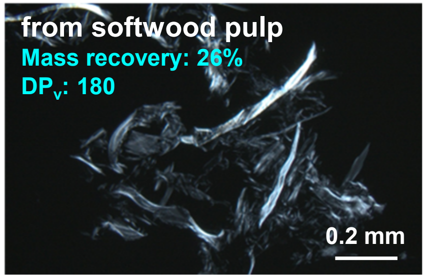



CNCs from hardwood pulp


CNCs from softwood pulp

Oxidized cellulose fibers

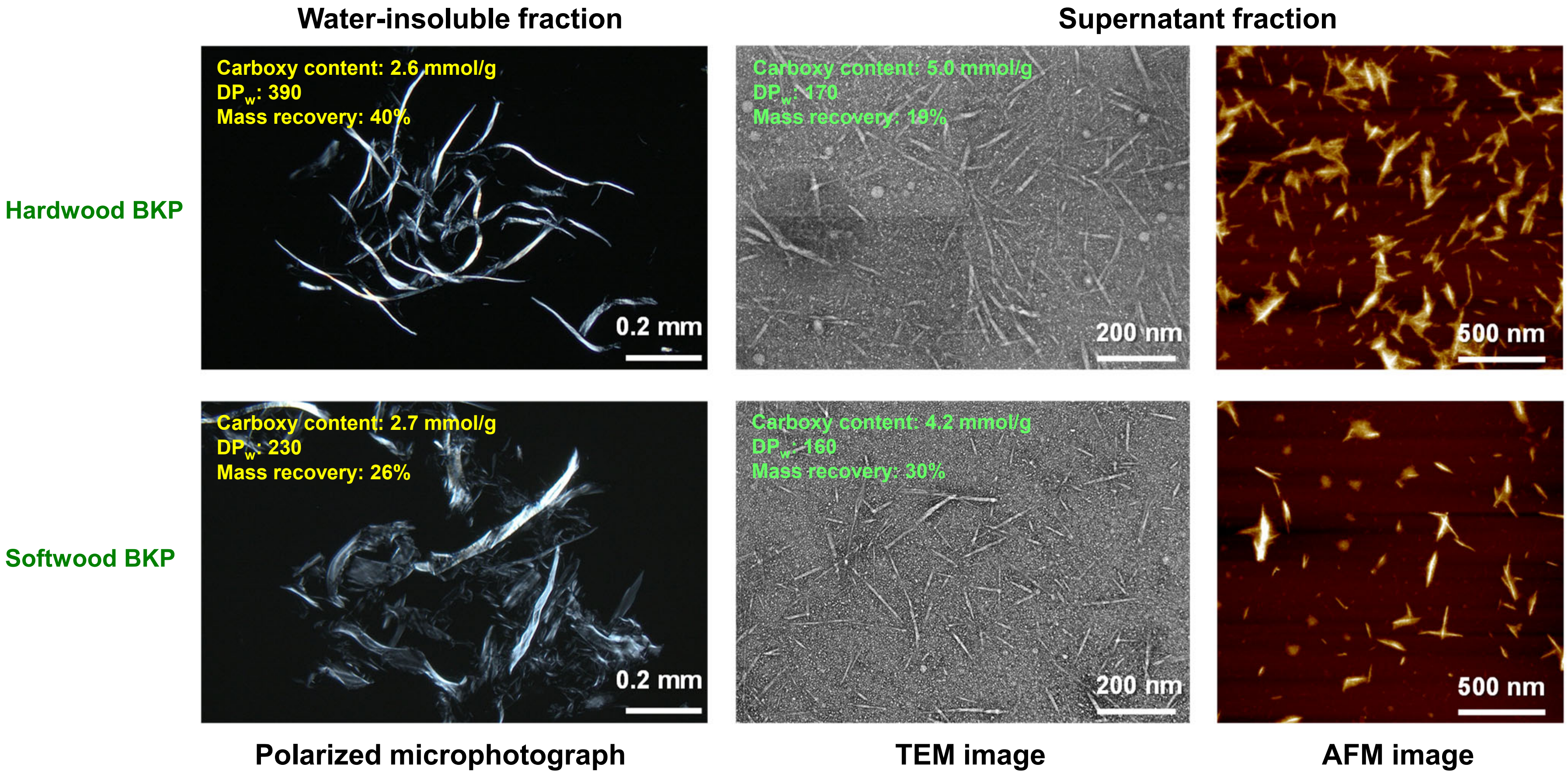

from hardwood pulp
Mass recovery: 40%
DP_v: 230


from softwood pulp
Mass recovery: 26%
DP_v: 180

- **Supernatant fractions mainly consist of water-soluble sodium polyglucuronates formed from wood cellulose fibers by TEMPO/NaBr/NaClO oxidation with NaClO of 15 mmol/g in water at pH 10.**

Hou G. et al., Carbohydrate Polymers (2024)

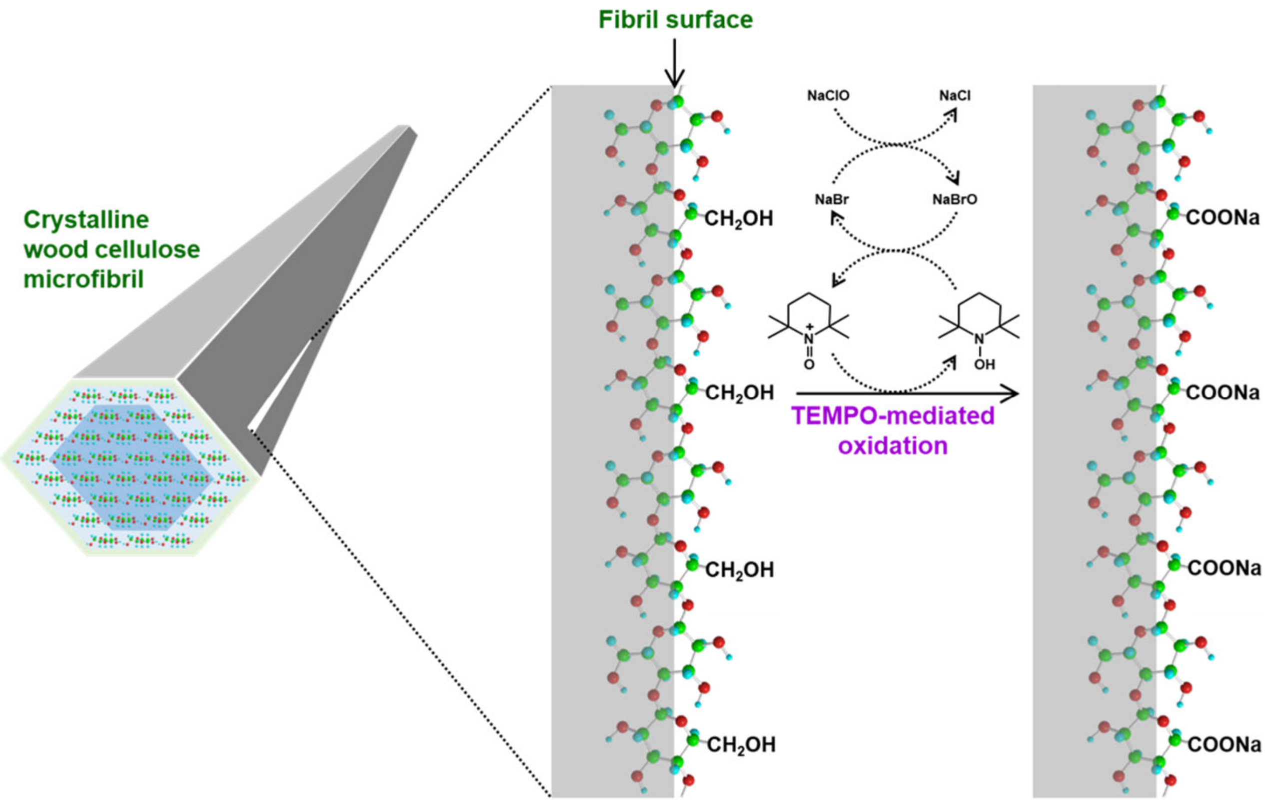
TEMPO/NaBr/NaClO-oxidized products prepared from wood cellulose fibers with NaClO of 15 mmol/g-pulp in water at pH 10

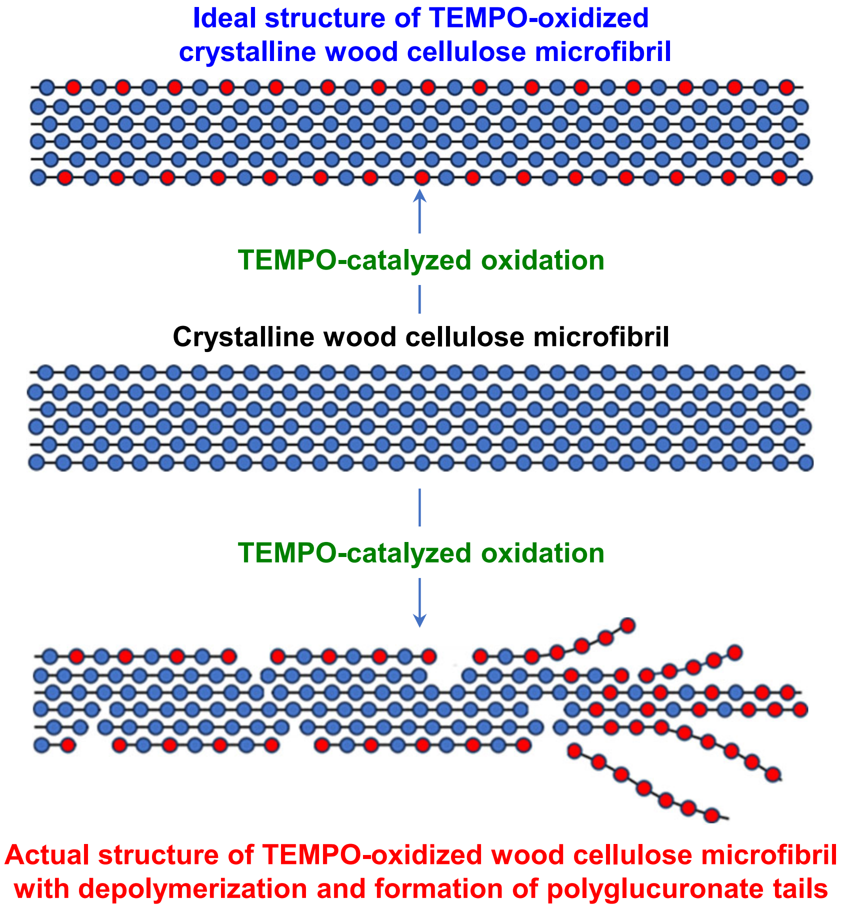


- **The supernatant fractions obtained by TEMPO/NaBr/NaClO oxidation of wood cellulose fibers with NaClO of 15 mmol/g-pulp in water at pH 10, consist of CNC but in low quantity.**

Hou G. et al., ACS Sustainable Chemistry & Engineering (2023), Carbohydrate Polymers (2024)

Ideal position-selective oxidation of C6-OH groups on crystalline cellulose microfibril surfaces by TEMPO-catalyzed oxidation





Ideal structure of TEMPO-oxidized crystalline wood cellulose microfibril

TEMPO-catalyzed oxidation

Crystalline wood cellulose microfibril

TEMPO-catalyzed oxidation

Actual structure of TEMPO-oxidized wood cellulose microfibril with depolymerization and formation of polyglucuronate tails

- **Despite ideal position-selective oxidation of C6-OH groups on crystalline cellulose microfibril surfaces, remarkable depolymerization and subsequent formation of sodium polyglucuronate tails are unavoidable during TEMPO/NaBr/NaClO oxidation of wood cellulose fibers.**

Isogai et al., Progress in Polymer Science (2018)

Outline

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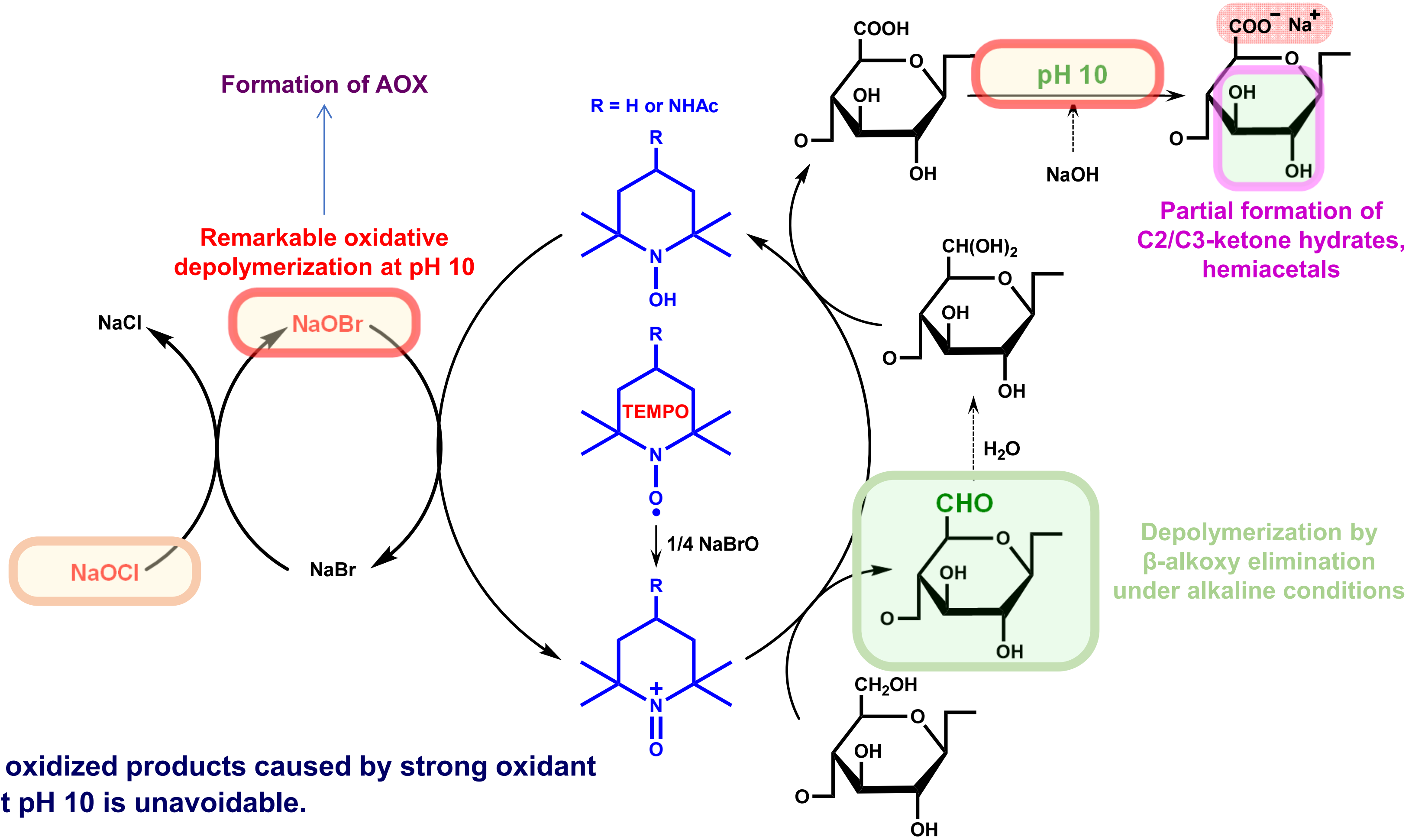
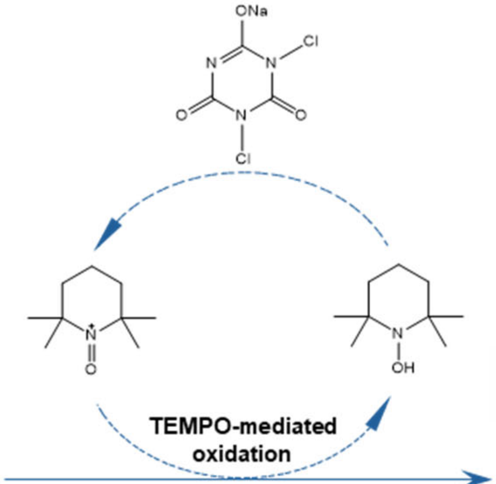
Side reactions of cellulose in TEMPO-catalyzed oxidation in water at pH 10



- Significant depolymerization of oxidized products caused by strong oxidant **NaBrO** formed *in situ* in water at pH 10 is unavoidable.
- Partial oxidation of C2/C3-OH groups, forming C2/C3-ketone hydrates or hemiacetals: low position-selectivity at C6-OH in some case.
- AOX (adsorbable organic halogens like dioxins) was detected in washing effluents of TEMPO-oxidized cellulose, probably because of **NaBrO** (Olli Dahl, Aalto University, Finland, 2026)

New TEMPO/NaDCC oxidation of wood cellulose fibers in water at pH 9

Sodium dichloroisocyanurate (NaDCC)
without NaBr



TEMPO-mediated oxidation

NaDCC granules have been used as a disinfectant of swimming pool, drinking water, food, food packages, and beneficial than NaClO solution in terms of stability, safety, handling, cost, storage, etc.

Wood cellulose fibers → in water at pH 9 and room temp. → **Water-insoluble Oxidized cellulose fibers**

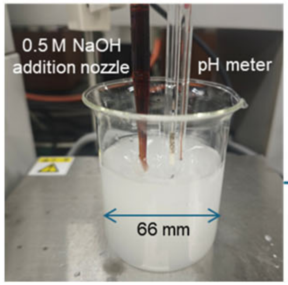
Water-insoluble Oxidized cellulose fibers → Mechanical fibrillation in water → **Cellulose nanofibrils**

Cellulose nanofibrils →
- TEM image
- Particle size distribution

→ **Structural models of original and oxidized crystalline wood cellulose microfibrils**

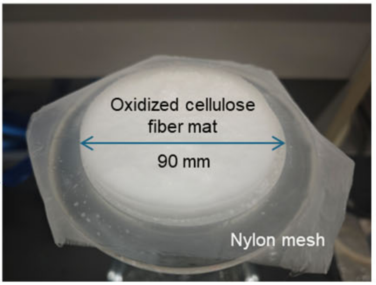
Water-insoluble Oxidized cellulose fibers → With post reduction with $NaBH_4$ →
- Mass recovery ratio
- Carboxy content
- Sugar composition
- Molar mass/molar mass distribution
- Solid-state ^{13}C-NMR
- X-ray diffraction
- Fiber morphology observation
- Fiber length/width distributions

Continuous addition of 0.5 M NaOH → Monitoring of kinetics



Nylon mesh on glass filter

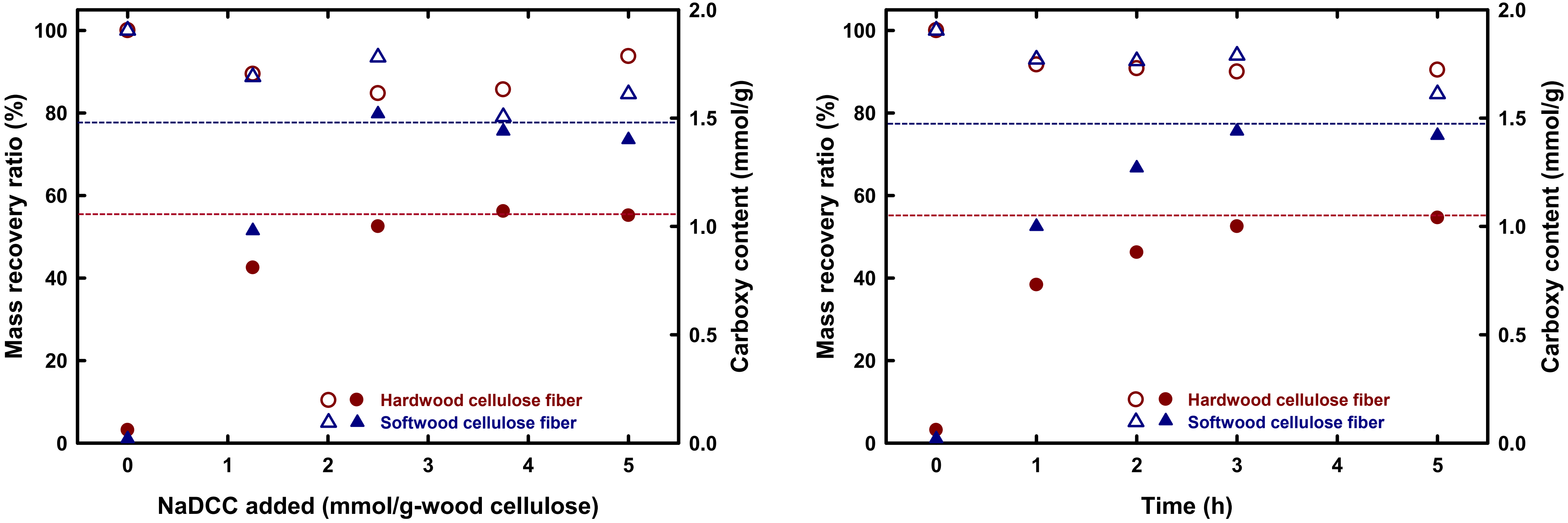
Filtration system



Hou R. et al., Carbohydrate Polymers (2026)

TEMPO/NaDCC oxidation of wood cellulose fibers in water at pH 9

$$\text{R-CH}_2\text{OH} + \text{C}_3\text{N}_3\text{O}_2\text{Cl}_2(\text{ONa})\ (\text{NaDCC}) + 5\ \text{NaOH} \longrightarrow \text{R-COONa} + \text{C}_3\text{N}_3(\text{ONa})_3 + 2\text{NaCl} + 4\text{H}_2\text{O}$$

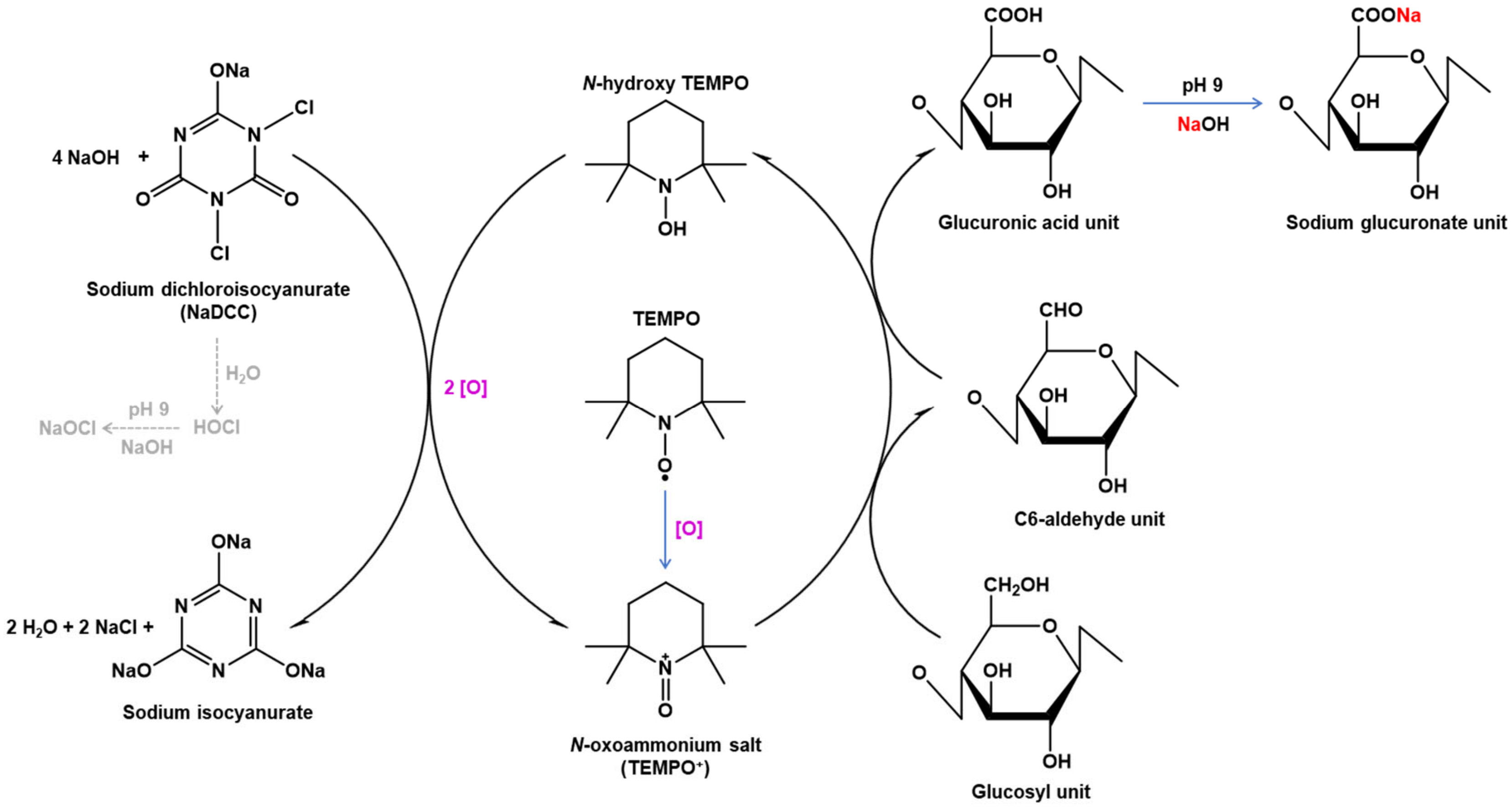


- Mass recovery ratios are mostly >90%.
- The maximum carboxy contents for hardwood and softwood cellulose fibers are 1.1 and 1.5 mmol/g, respectively, even by excess amounts of NaDCC added or extended oxidation time; only cellulose microfibril surfaces are oxidized without inside microfibril.
- The different upper limit carboxy contents are caused by hemicelluloses between the oxidized wood cellulose fibers.

Hou R. et al., Carbohydrate Polymers (2026)

TEMPO/NaDCC oxidation of wood cellulose fibers in water at pH 9

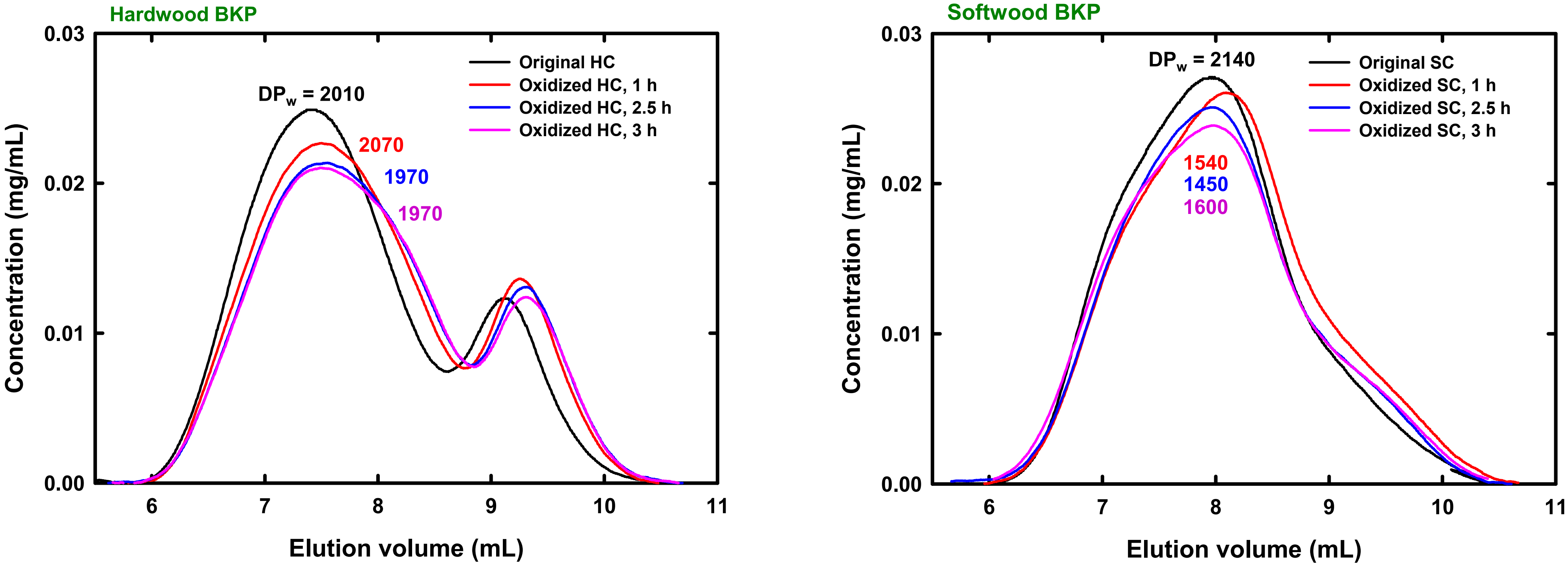
$R\text{-}CH_2OH + C_3N_3O_2Cl_2(ONa)\ (NaDCC) + 5\ NaOH \longrightarrow R\text{-}COONa + C_3N_3(ONa)_3 + 2NaCl + 4H_2O$



- NaDCC directly oxidizes TEMPO-OH to TEMPO$^+$ without passing through NaClO from NaDCC.

Isogai et al., Carbohydrate Polymers (2026)

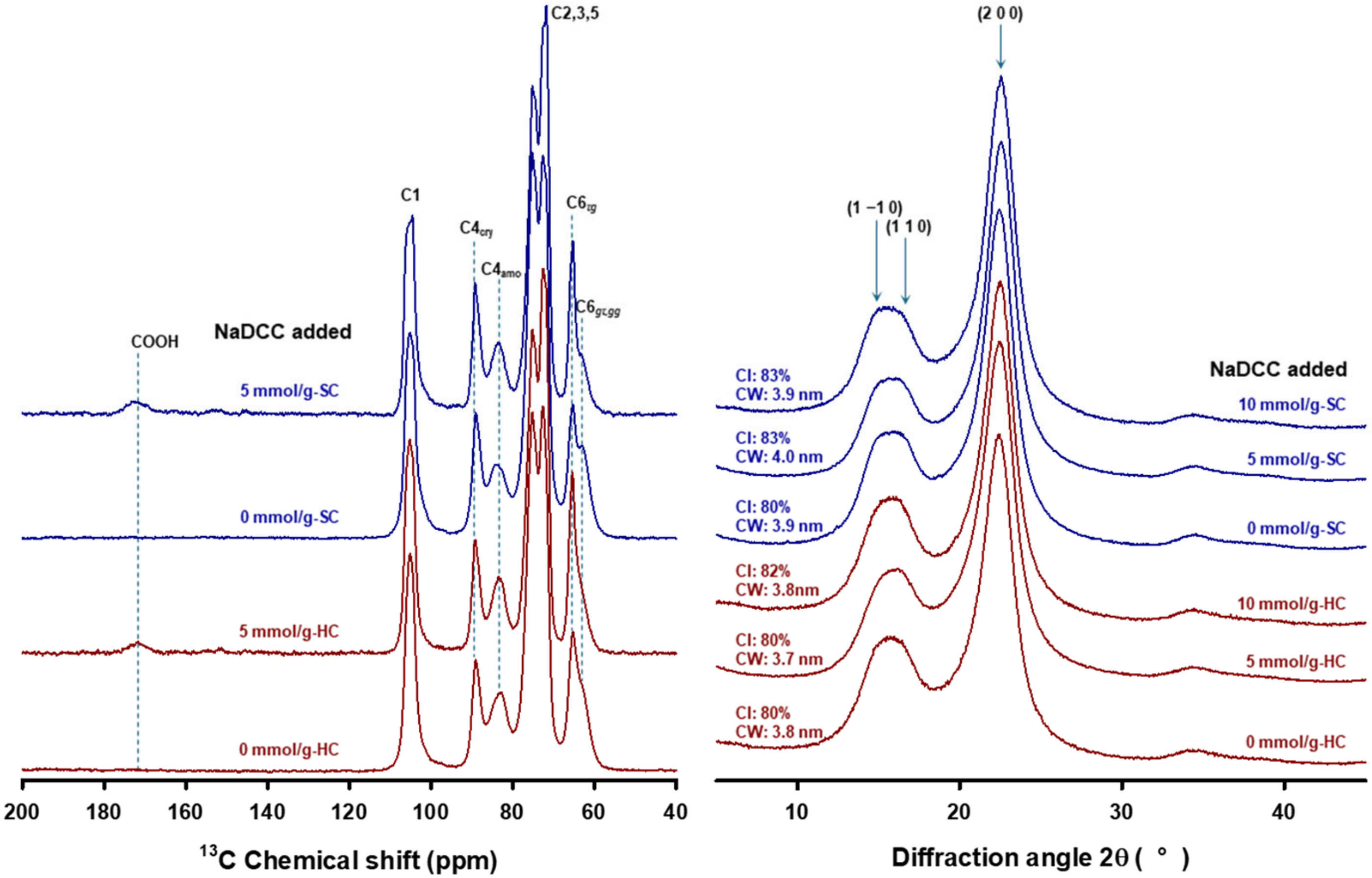
Molar masses and molar mass distributions of TEMPO/NaDCC-oxidized wood cellulose fibers determined by SEC/MALLS/RI



- **Depolymerization of cellulose molecules is mostly suppressed by the TEMPO/NaDCC oxidation in water at pH 9, compared with the conventional TEMPO/NaBr/NaClO system in water at pH 10.**

Hou R. et al., Carbohydrate Polymers (2026)

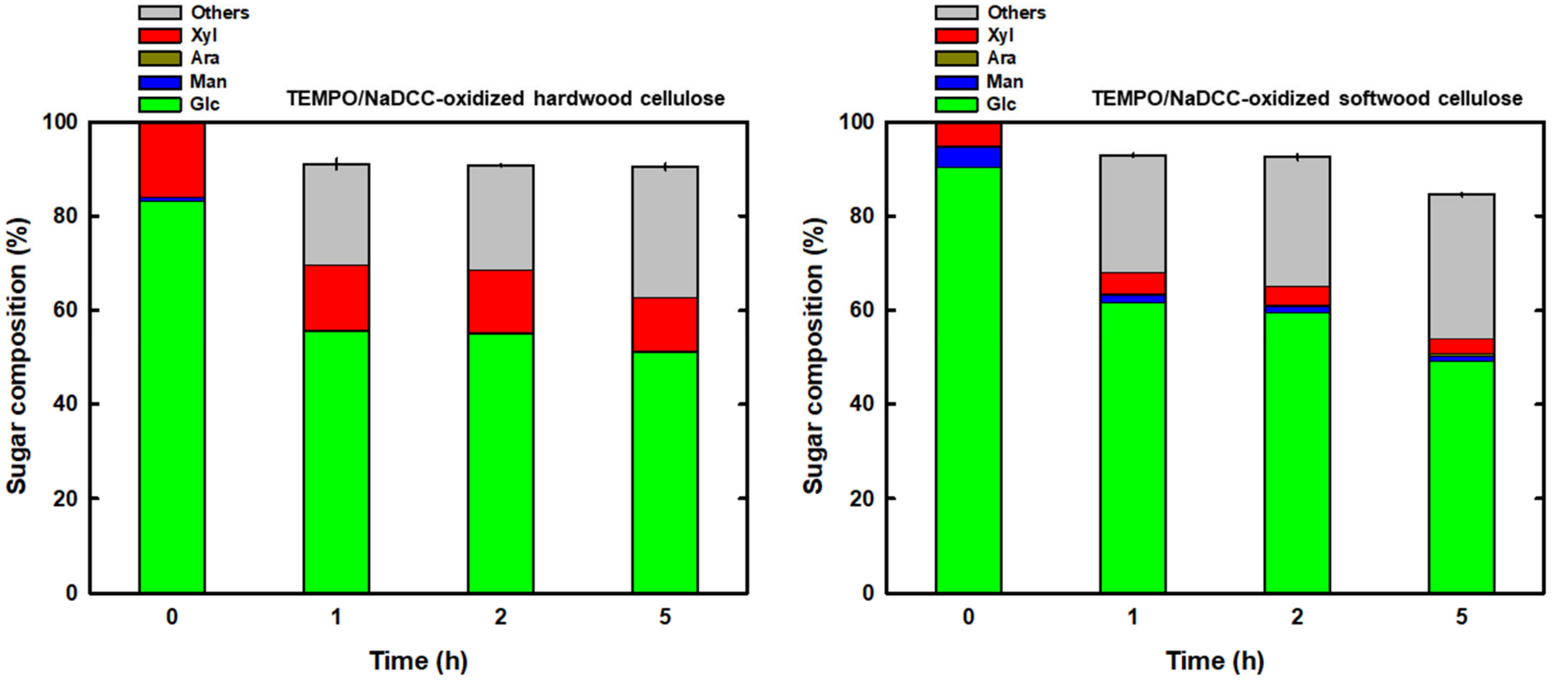
Solid-state ^{13}C-NMR patterns and XRD patterns of TEMPO/NaDCC-oxidized wood cellulose fibers



- **Crystal structure, crystallinity, and crystal size are almost unchanged before and after TEMPO/NaDCC oxidation, showing that sodium C6-carboxylate groups are position-selectively formed on crystalline cellulose microfibril surfaces in wood cellulose fibers by oxidation.**

Hou R. et al., Carbohydrate Polymers (2026)

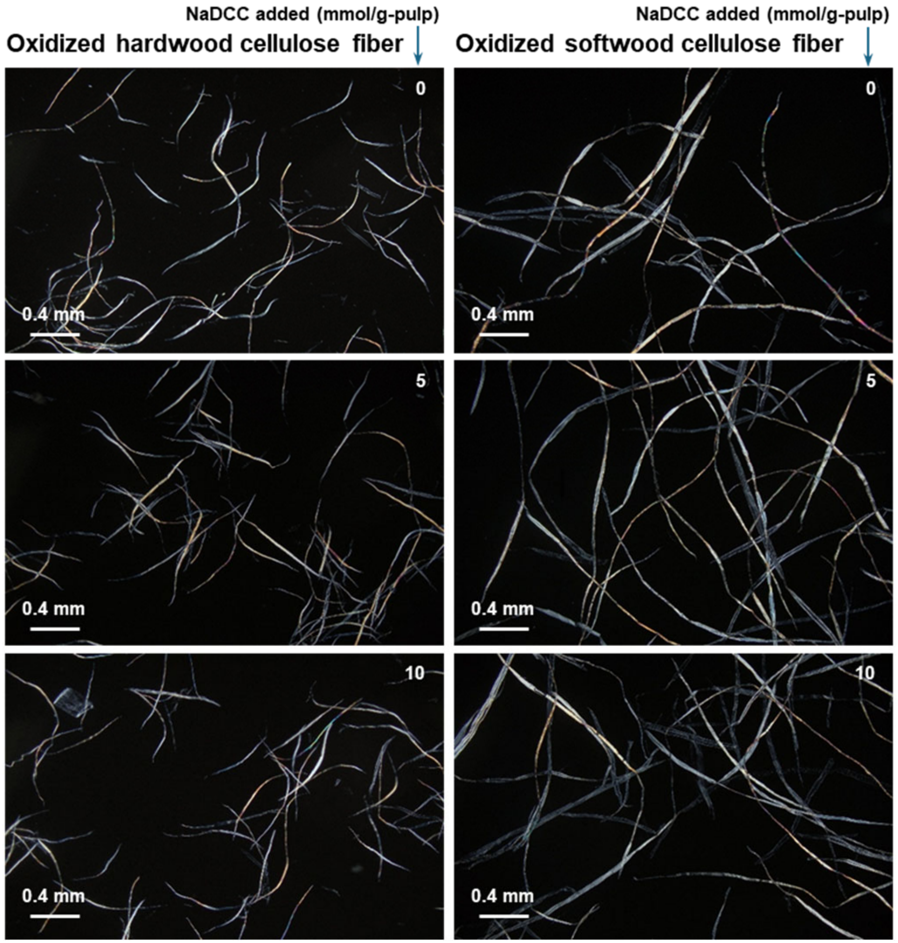
Sugar compositions of water-insoluble TEMPO/NaDCC-oxidized wood cellulose fibers

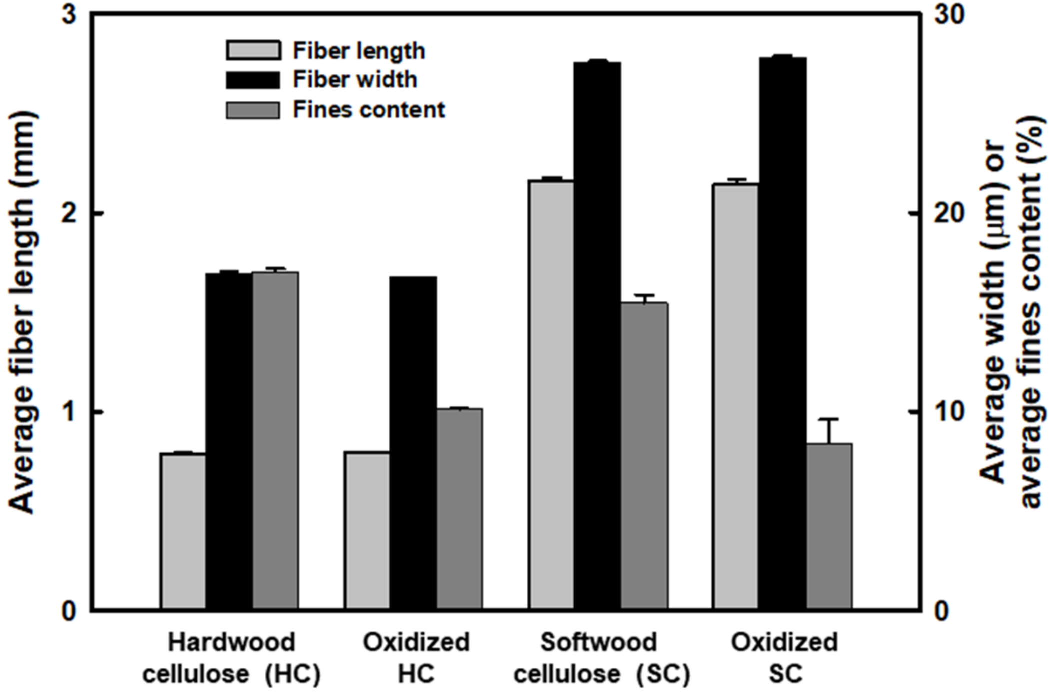


- **Xylan molecules (because of no C6-OH groups) are resistant to TEMPO/NaDCC oxidation and mostly remain in the water-insoluble oxidized products, whereas glucomannan molecules with C6-OH groups are degraded and removed from the water-insoluble oxidized products.**

Hou R. et al., Carbohydrate Polymers (2026)

Morphologies of TEMPO/NaDCC-oxidized wood cellulose fibers



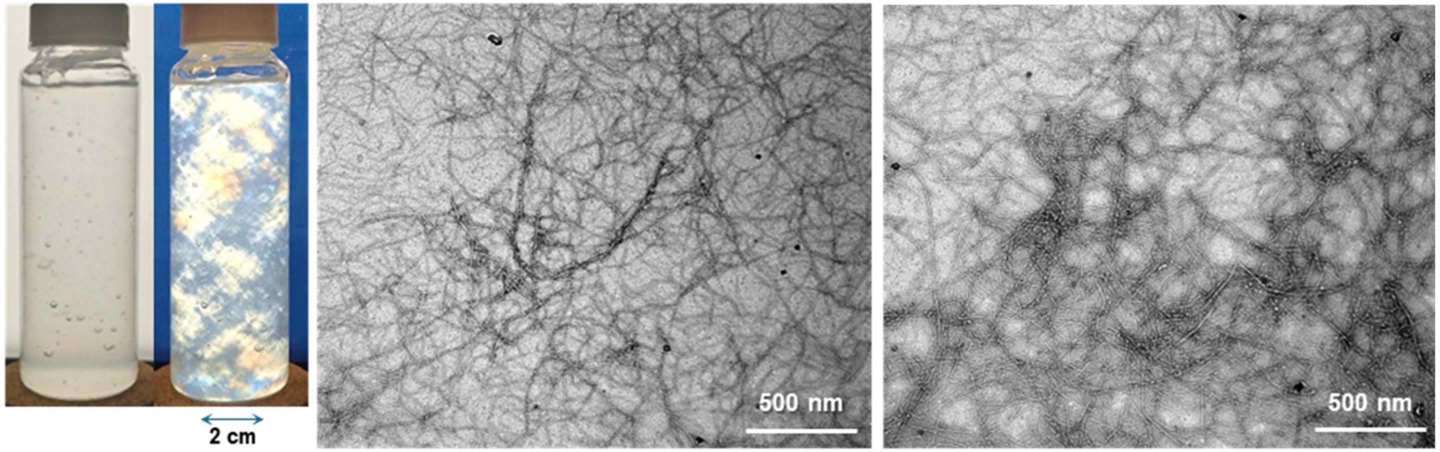


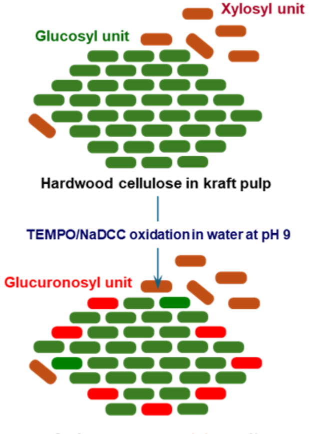
- The lengths and widths of wood cellulose fibers are unchanged before and after oxidation
- The oxidized wood cellulose fibers can be used for functional sheet materials with abundant carboxylate groups using the conventional papermaking or coating facilities.

Hou R. et al., Carbohydrate Polymers (2026)

CNFs prepared from TEMPO/NaDCC-oxidized wood cellulose fibers by high-pressure homogenization in water

TEMPO/NaDCC-oxidized hardwood cellulose (HC) nanofibrils, average width: ~10 nm



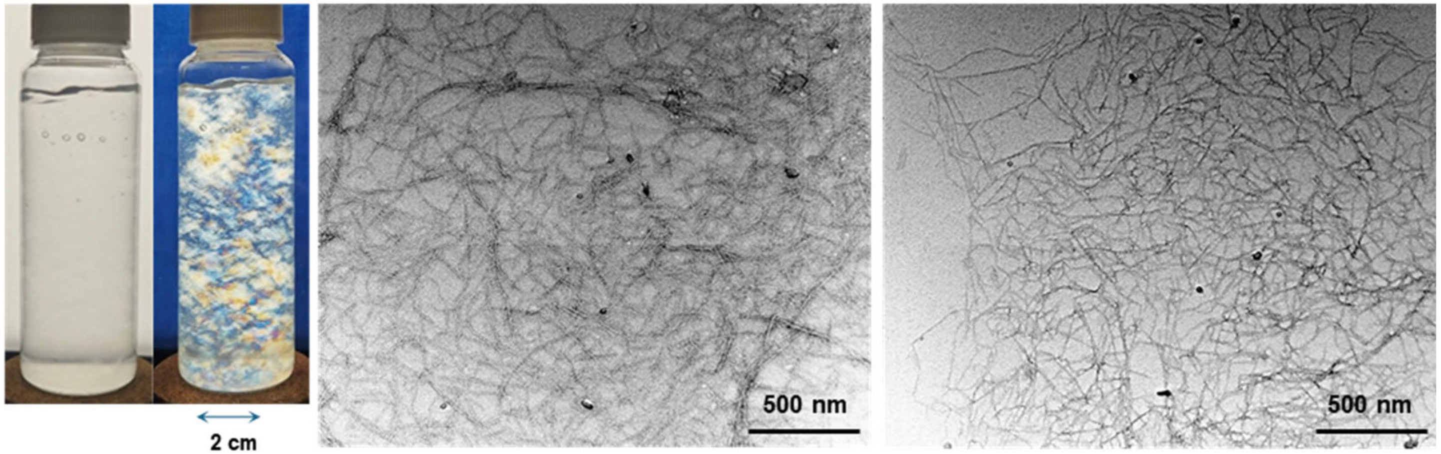


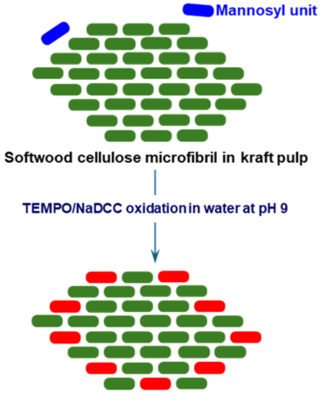
Hardwood cellulose in kraft pulp

TEMPO/NaDCC oxidation in water at pH 9

Carboxy content: ~1.1 mmol/g
$= 1000 \times 7 / (162 \times 29 + 176 \times 7 + 132 \times 6)$

TEMPO/NaDCC-oxidized softwood cellulose (SC) nanofibrils, average width: ~6 nm





Softwood cellulose microfibril in kraft pulp

TEMPO/NaDCC oxidation in water at pH 9

Carboxy content: ~1.5 mmol/g
$= 1000 \times 9 / (162 \times 27 + 176 \times 9)$

- **TEMPO/NaDCC-oxidized wood cellulose nanofibrils with homogeneous widths and lengths >1 μm are prepared by high-pressure homogenization in water, resulting in homogeneous fibril cross-sections.**

Hou R. et al., Carbohydrate Polymers (2026)

Outline

- Structures of wood cellulose microfibrils, contributing to the high mechanical strength and long lifetime of plant bodies
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- Unique characteristics of TEMPO-CNFs
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- **Present situation of nanocellulose productions/applications**
- Conclusions and future challenges

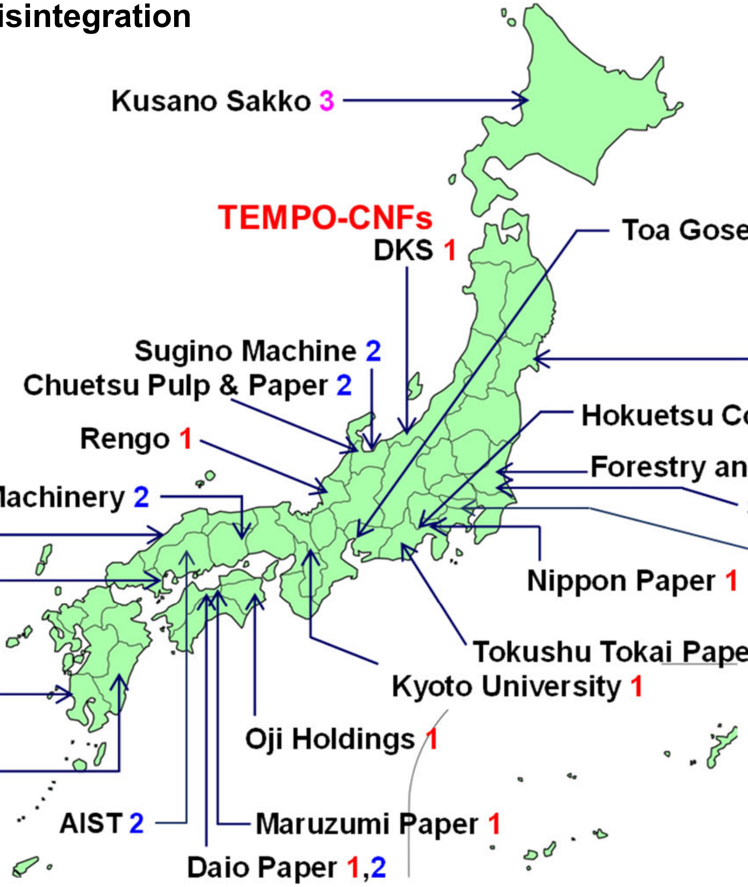
Diverse position-selective surface chemical modifications of crystalline cellulose microfibrils in wood cellulose fibers as pretreatment for CNF production

Raw material	Pretreatment	Chemicals	Production company	Charged groups of CNF surface	Safety
Wood cellulose fibers	None	–	Daio Paper, Mitsubishi Paper, Tokushu Tokai Paper, etc.	Residual hemicellulose-COO^{-}	☺
	C6-oxidation	TEMPO/NaBr/NaClO in water at RT, pH 10	Nippon Paper, Co. DKS, ITT Rayonier, FPL, etc.	C6-carboxylate cellulose-COO^{-}	😐
	Phosphorylation	$H_2(NH_4)PO_4$/melted urea at >150°C	Oji Holdings, Co.	Phosphorylate ester cellulose-OP(=O)O_2^{-}	😐
	Phosphite esterification	$H(NH_4)PO_3$/melted urea at >120°C	Daio Paper, Co.	Phosphite ester cellulose-OP(=O)O^{-}	😐
	Carbamylation	Melted urea at >150°C	Daio Paper, Co., AIST	Carbamated cellulose-OC(=O)NH_2	😐
	Carboxymethyl etherification	$ClCH_2COONa$/NaOH/water at high Temp.	Nippon Paper, Co.	Carboxymethylcellulose-OCH_2COO^{-}	☺
	Endo-type cellulase treatment	Endo-type cellulase/water	Some companies	Residual hemicelluloses-COO^{-}	☺
	Xanthate esterification	CS_2/NaOH/water at RT	Rengo, Co.	Xanthate ester cellulose-OCSS^{-}	😐
	Alkenylsuccinate esterification	ASA/KCO_3/NMP at high Temp.	Seiko PMC, Co.	Alkenylsuccinate ester cellulose-$OCOCH_2CRHCOO^{-}$	😐
	Sulfate esterification	Sulfamic acid/urea/water at >120 °C	Maruzumi Paper, Co.	Sulfate ester cellulose-OSO_3^{-}	😐
	C2,3-Dicarboxylation	NaClO • $5H_2O$/water at RT	TOA Chemical, Co.	C2,3-dicarboxylate cellulose-$(COO^{-})_2$	😐

Production facilities of CNFs, Cellulose nanonetworks, and MFC in Japan

1: Chemical pretreatment and subsequent mechanical disintegration
2: Mechanical disintegration in water
3: Bacterial nanocellulose

Mitsubishi Paper 2
Daicel 2
Ehime Paper 2
Osaka Gas, KRI 1
Hattori Store 2
Omura Paint 2
Star Light Ind. 2
Marine Nanofiber 2
Filler Bank 2
Masuko 2



Kusano Sakko 3
TEMPO-CNFs
DKS 1
Toa Gosei 1
Sugino Machine 2
Chuetsu Pulp & Paper 2
Rengo 1
Mori Machinery 2
Nippon Paper 1
Nippon Paper 1
TEMPO-CNFs
Chuetsu Pulp & Paper 2
Asahi Chemicals 2
AIST 2
Daio Paper 1,2
Maruzumi Paper 1
Oji Holdings 1
Kyoto University 1
Tokushu Tokai Paper 2
Nippon Paper 1
Hokuetsu Corp. 1
Forestry and Forest Research Institute 2
Seiko PMC 1
Yokokawa Biofrontier 1

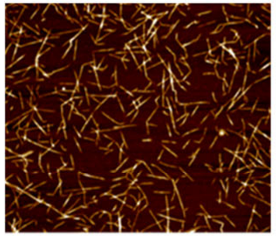
Nippon Paper 1 TEMPO-CNFs
500t / y

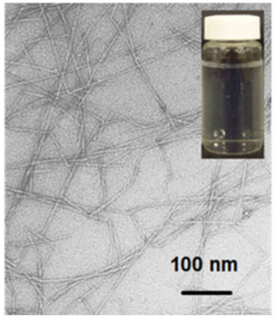
- TEMPO-CNFs have been produced at the industrial level from 2013.

Nanocellulose production capacity lists in the world from TAPPI, Jack Miller's Bio Consultant, 2022

CNC

CelluForce, Canada (300 t/y) C
Anomera, Canada (250 t/y) C
GranBio, USA (130 t/y) C
Sweetwater Energy, USA C
FPL, USA C
Navitas, Slovenia C
Melodea, Israel C
Hangzhou Yeuha Technology, China C
Tainjin Haojia Cellulose, China C





CNF

Sappi Biotech, Global (650 t/y)
University of Main, USA (260 t/y) M
GranBio, USA (130 t/y) C
ITT Rayonier, USA C
Cellulose Lab, Canada C
CelluComp, UK (100 t/y) C
VTT, Finland M,E

Nippon Paper, Japan C
Oji Holdings, Japan C
Chuetsu Pulp & Paper, Japan M
Sugino Machine, Japan M
Seiko PMC, Japan C
Daio Paper, Japan M,C
Tokushu Tokai Paper, Japan
Hokuetsu Corp., Japan C
Yokokawa Biofrontier, Japan C
Toa Gosei, Japan C
Kusano Sakko, Japan B
Rengo, Japan C
Maruzumi Paper, Japan C
DKS, Japan C

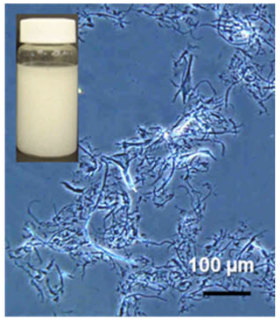
Tianjin Haojia Cellulose, China C

MFC

FiberLearn Technologies, UK (13,000 t/y) M
Sappi Biotech, Netherland (6,220 t/y) M
Borregaard, Norway (1,000 t/y) M
Norske Skog, Norway (365 t/y) M
RISE, Transportable container factory, Sweden (200 t/y) M,E
CTP/FCBA, France M,E
InoFib, France C
UPM, Finland M
Suzano, Brazil M
Empa, Switzerland E
Stora Enso, Finland E
Weidmann Fiber Technology, Switzerland M

Daicel, Japan M

Tianjin Haojia Cellulose, China C,M



Cellulose Filaments

Performance Biofilaments, Canada (7,000 t/y) M
Kruger, Canada (6,000 t/y) M

Tianjin Haojia Cellulose, China M

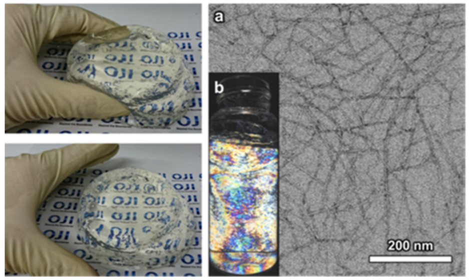
C: Chemically pretreated CNFs
M: Mechanical fibrillated CNFs
E: Enzymatically pretreated CNFs
B: Bacterial CNFs

Three representative Japanese paper companies producing nanocellulose materials

■ **Nippon Paper Industry:** TEMPO-oxidized nanocellulose materials **Cellulose-COONa**

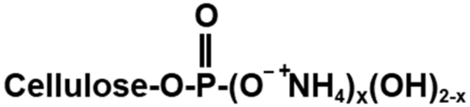
NIPPON PAPER INDUSTRIES CO., LTD.

■ **Oji Holdings:** Phosphorylated CNFs



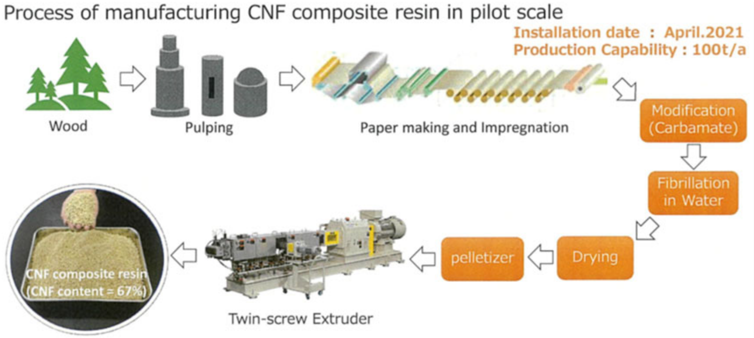
Beyond the Boundaries

Oji Holdings

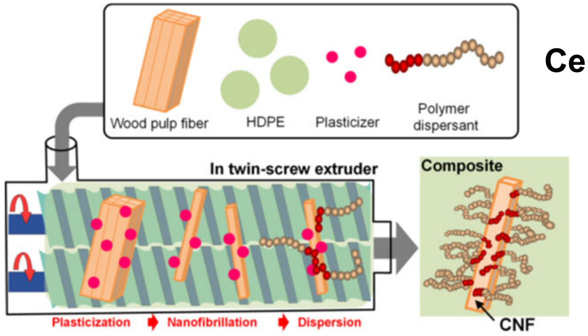


$$\text{Cellulose-O-}\overset{\overset{\displaystyle O}{\|}}{P}\text{-}(O^-\,{}^+NH_4)_x(OH)_{2-x}$$

■ **Daio Paper Co:** Carbamylated CNF/polypropylene composites (64/36 by mass)



Process of manufacturing CNF composite resin in pilot scale



Cellulose-O-C-NH_2

DAIO PAPER CORPORATION

Practical applications and developments of TEMPO-CNFs

2015： NPI Crecia started to sell TEMPO-CNF-containing super-deodorant diapers for adults to decrease helpers’ burden

2015： Mitsubishi Pencil developed TEMPO-CNF-containing ballpoint pen ink dispersants for smooth writing

2017： Taiyo Holdings developed light-weight and thermally stable electronic boards containing CNFs (news release)

2019： Sumitomo Rubber started to sell longitudinal direction-oriented TEMPO-CNF-containing eco-tires

2020： Kao developed chemically surface-modified TEMPO-CNF-containing composite materials for electronics and mobilities

2020： Toyota developed TEMPO-CNF-containing metallic silver spray coating for Lexus

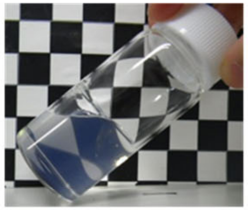
2021： Tohoku University developed TEMPO-CNF-containing supercapacitors for mobilities

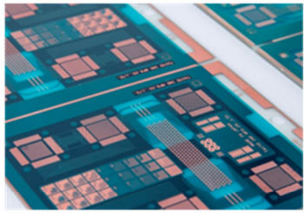
2021： Bing Hu’s group developed solid-Li butteries using TEMPO-CNFs as efficient Li ion-channels

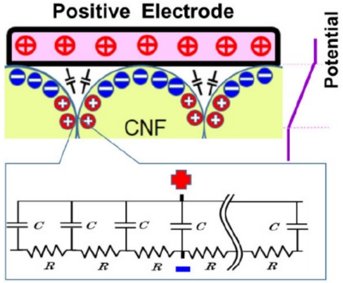
2022： Mizuno developed CNT/CNF composite golf shafts

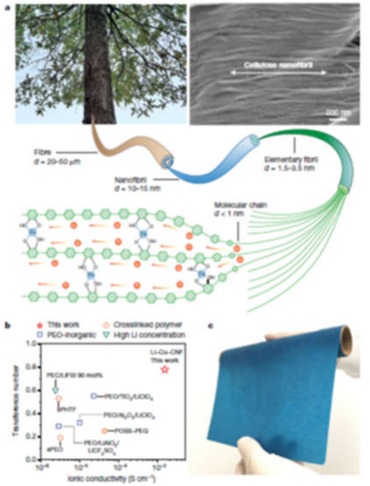
2022： NPI Crecia developed TEMPO-CNF-containing antibacterial masks for medical applications

2022： Tohoku Seiren: TEMPO-CNF-treated permanent-press clothes









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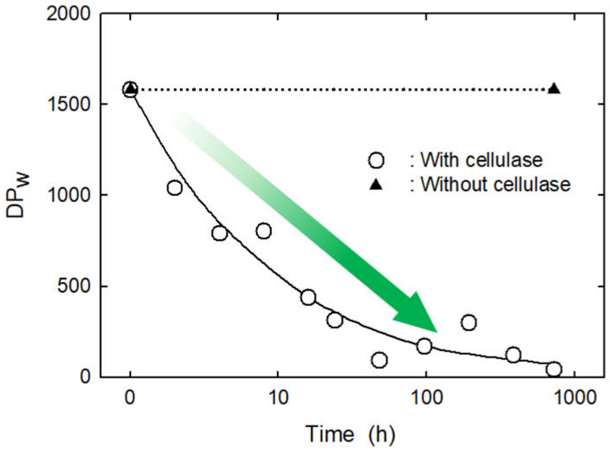
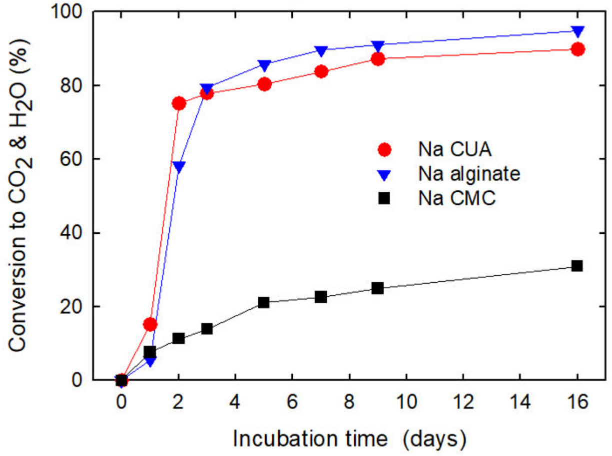
Conclusions and future challenges

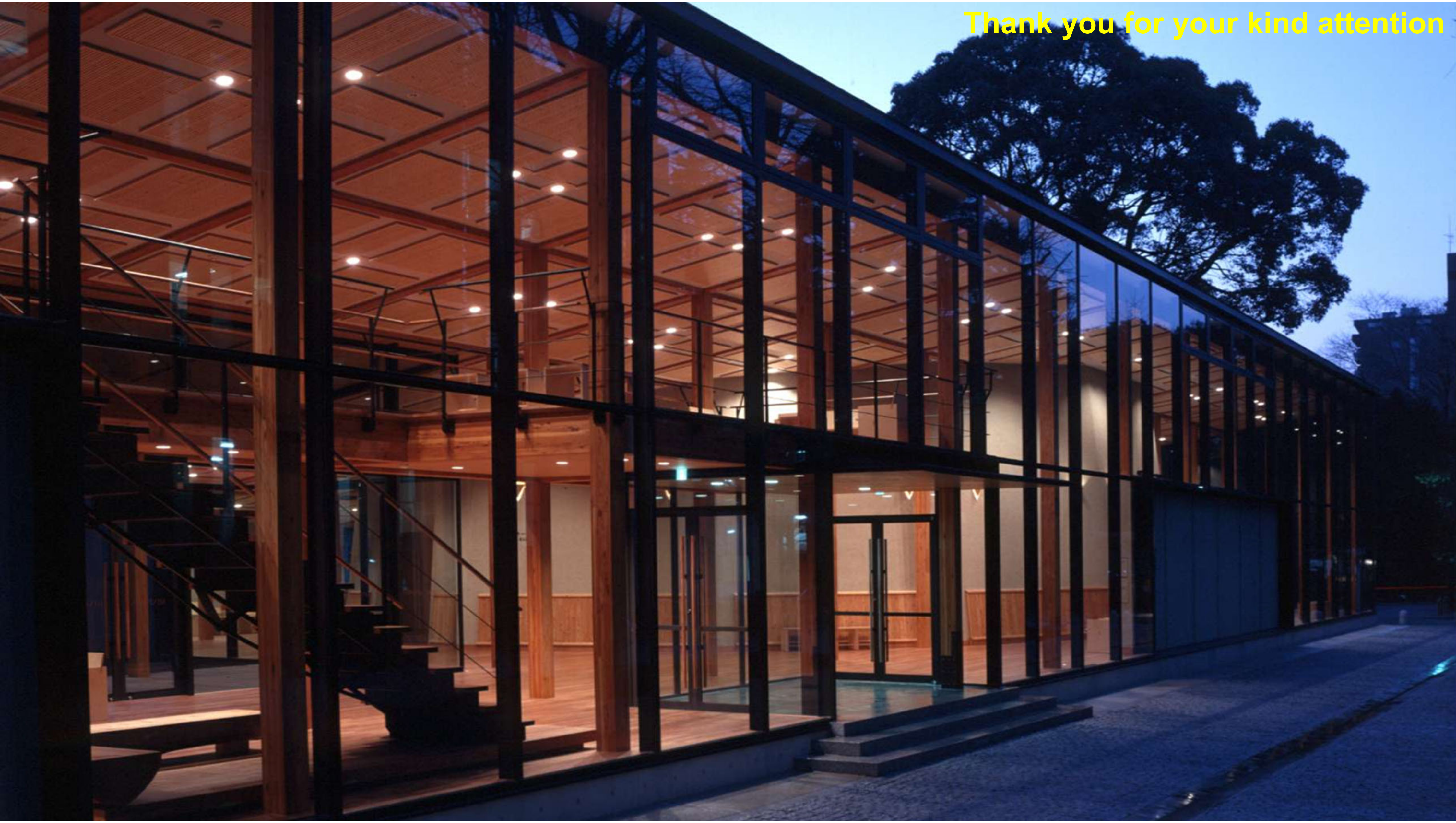
- Diverse fibers, MFC, and nanocellulose materials with abundant carboxy groups can be prepared from TEMPO-catalyzed wood cellulose fibers by controlling degrees of mechanical fibrillation
- Cellulose nanofiber/water dispersions with high aspect ratios for superior shear-thinning additives to conventional CNFs with low aspect ratios.
- Cellulose fibers or partly fibrillated cellulose fibers containing abundant carboxy groups to be converted to functional sheets in medical and electronic materials, produced by the conventional papermaking and coating facilities.
- Water-soluble sodium polyglucuronates from regenerated cellulose materials, starch, etc. for biodegradable and metabolizable polymeric builders (calcium ion-catchers in tap water to improve washing efficiency) in laundry detergents.

Biodegradability of cellourونate Na salt



Metabolizability of cellouronate Na salt





Thank you for your kind attention