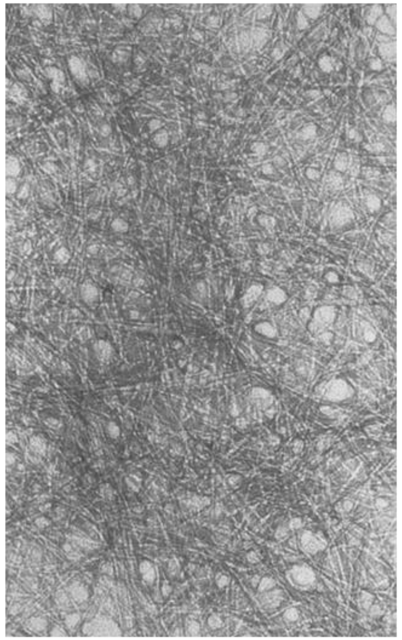
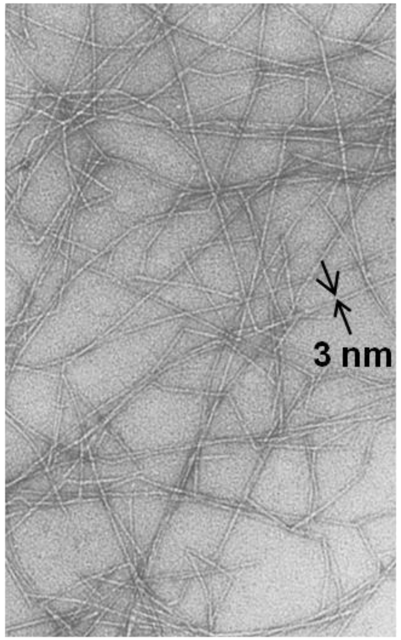
Preparation and characterization of plant cellulose nanofibers, and their applications as new bionanomaterials to functional and commodity materials

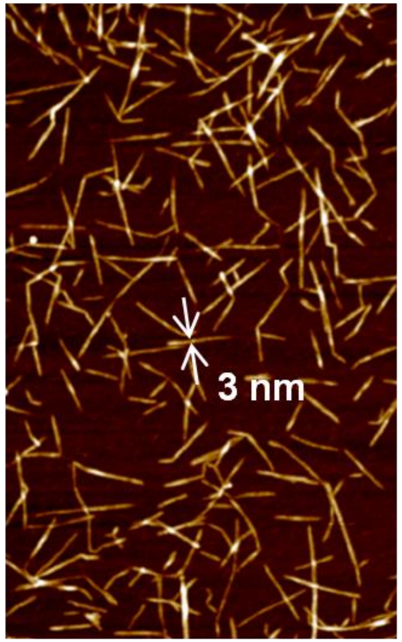
Cellulose nano-network



cellulose nanofiber



cellulose nanocrystal



Tohoku Forum for Creativity - International Symposium on Designing Foods for the Future -

September 20th, 2024, Aobayama Commons, Tohoku University, Sendai, Japan

Akira ISOGAI

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The University of Tokyo, Japan

Outline

- Background of biomass and nanocellulose utilization for creation of sustainable society and for circular economy
- Fundamentals and application of TEMPO-mediated oxidation to cellulose and polysaccharides
- Characteristics of TEMPO-oxidized fibers, nanomaterials, and films
- Application of TEMPO-CNFs
- Summary

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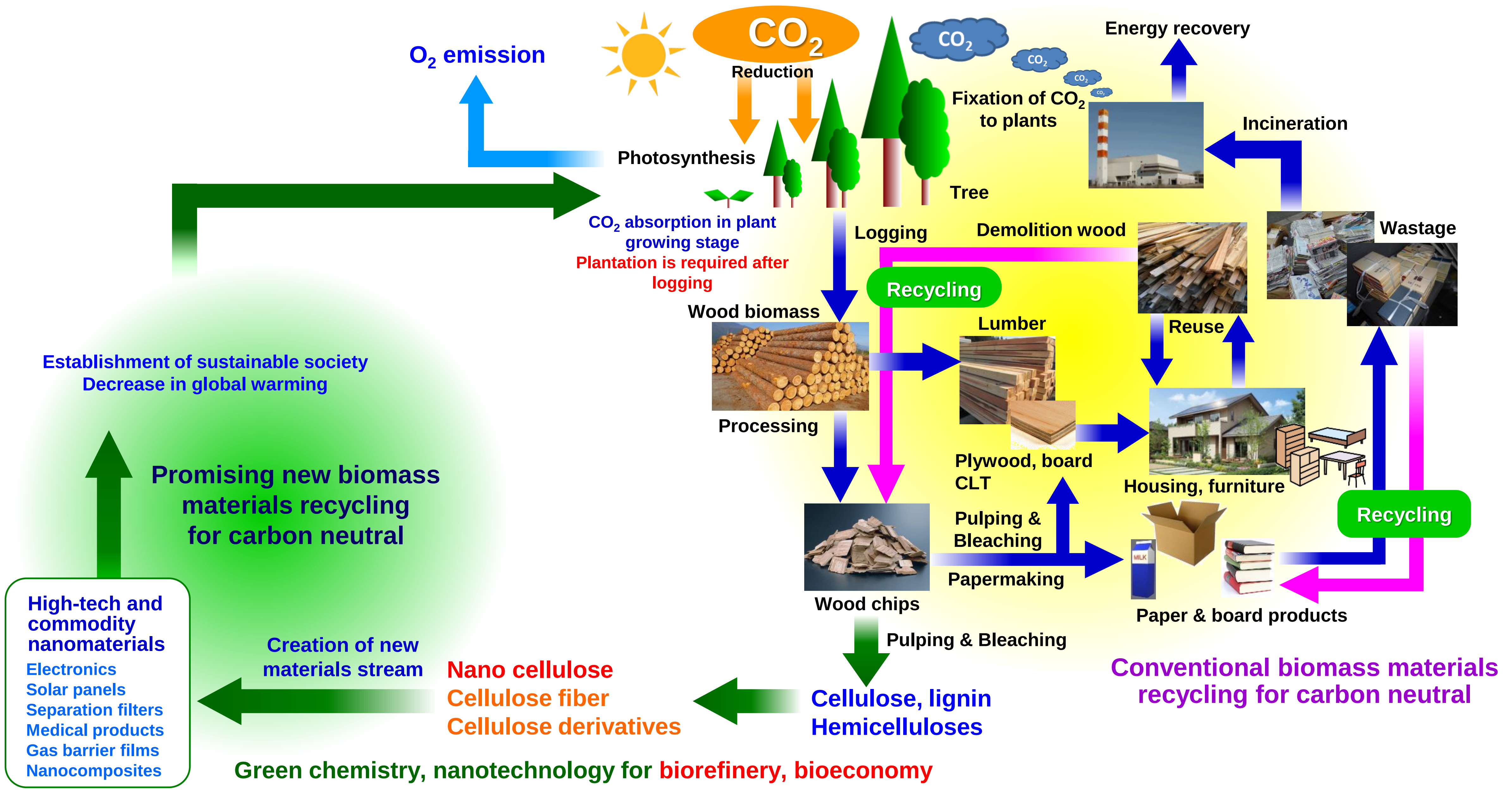
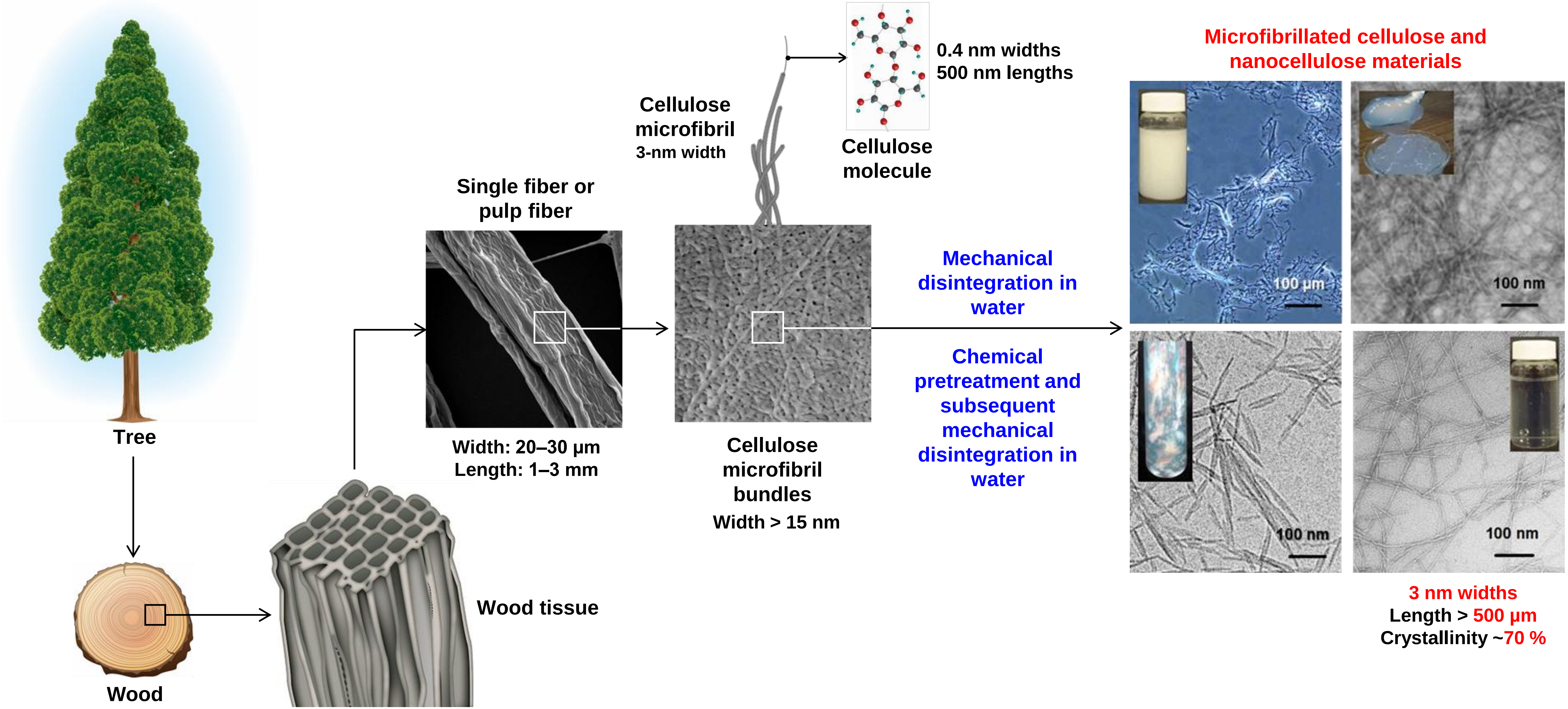
Creation of sustainable society based on renewable biomass utilization



Hierarchical structures of crystalline cellulose microfibrils

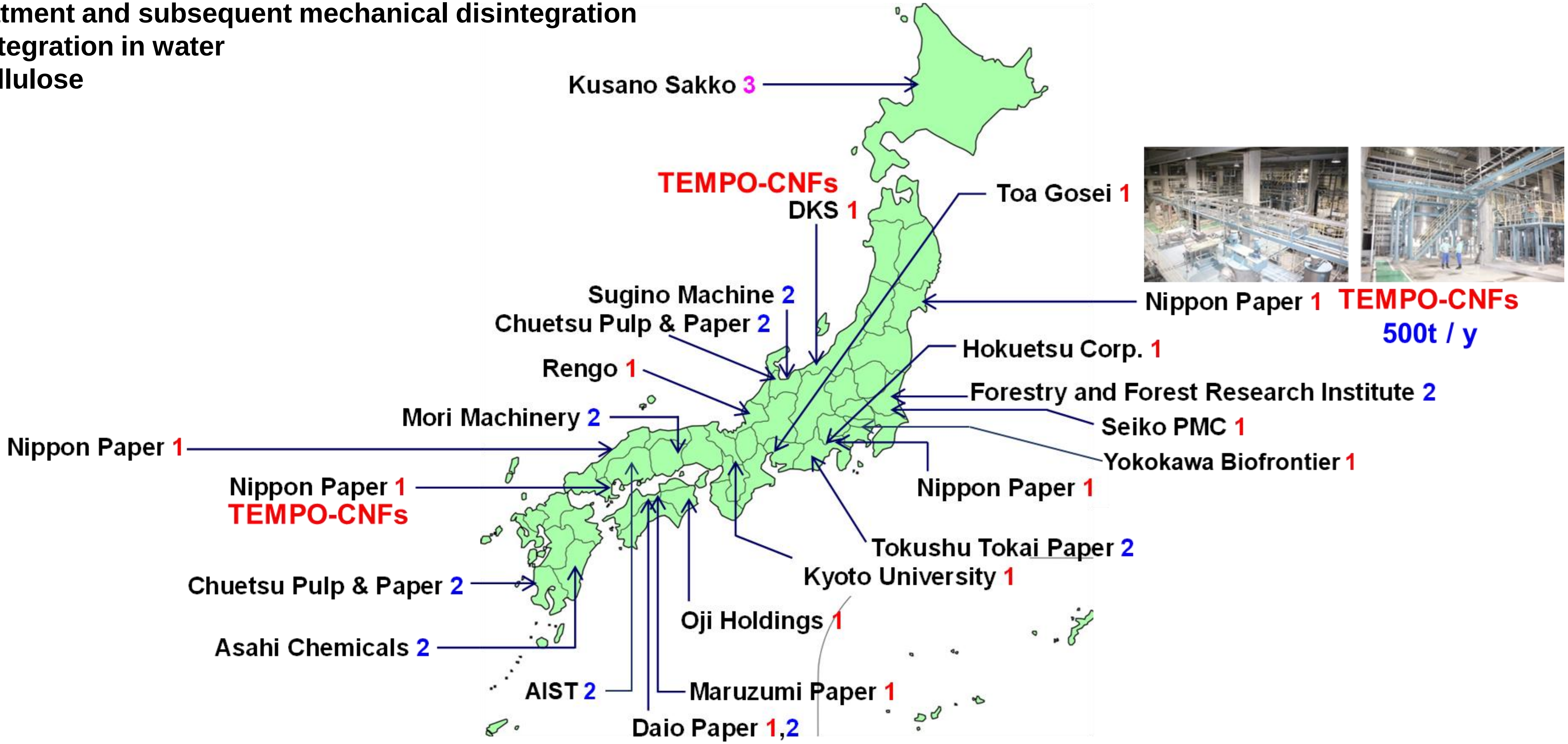


- Cellulose microfibrils are renewable and CO_2-accumulated bio-nanofibers most abundantly present in plants and most abundantly increased annually.

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

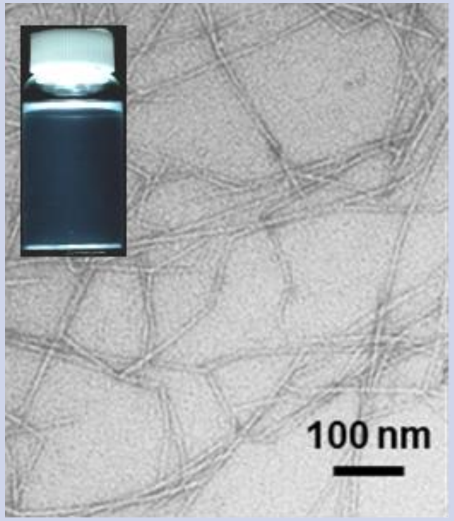
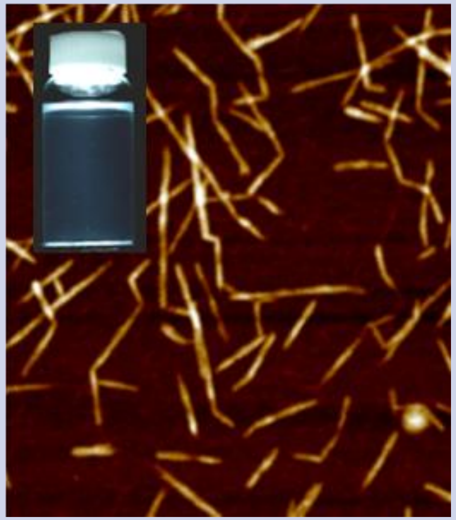
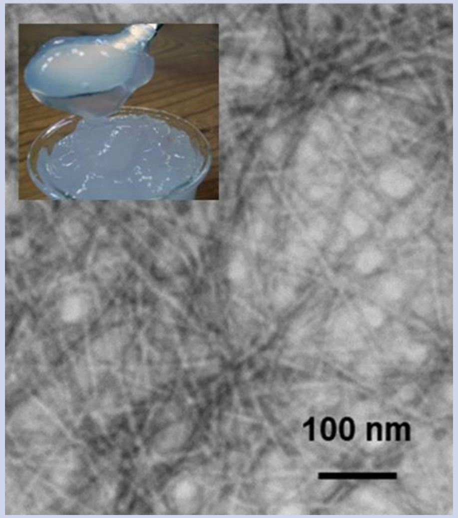


- **TEMPO-CNFs have been produced at the industrial level from 2013.**
- **We have decided separation of roles; R&D in industry for applications and production technologies, while our lab for fundamental research and advising.**

Categories of CNFs: Introduction of charged groups to pulp fibers in pretreatment

Raw material	Pretreatment	Chemicals	Production company	Charged groups of CNF surface	Safety
Agricultural wastes, etc.	None	–	–	Hemicellulose-COO$^-$ Lignin phenolic-O$^-$	☺
Non-wood pulp, etc.	None	–	Asahi Chemical, etc.	Hemicellulose-COO$^-$	☺
Chemical wood pulp	None	–	Daio Paper, Mitsubishi Paper, Tokushu Tokai Paper, etc.	Residual hemicellulose-COO$^-$	☺
	C6-TEMPO-oxidation	TEMPO/NaBr/NaClO/ Water	Nippon Paper DKS, ITT Leyonier, FPL, etc.	C6-carboxylate cellulose-COO$^-$	😐
	Phosphorylation	$H_2(NH_4)PO_4$/urea/water	Oji Holdings	Phosphorylate ester cellulose-OP(=O)O_2^{2-}	😐
	Phosphite esterification	$H(NH_4)PO_3$/urea/water	Daio Paper	Phosphite ester cellulose-OP(=O)O$^-$	😐
	Carboxymethyl etherification	$ClCH_2COONa$/NaOH/water	Nippon Paper	Carboxymethylcellulose-OCH_2COO^-	☺
	Endo-type cellulase treatment	Endo-type cellulase/water	FFRI (Forest Agency)	Residual hemicelluloses-COO$^-$	☺
	Xanthate esterification	CS_2/NaOH/water	Rengo	Xanthate ester cellulose-OCSS$^-$	😐
	Alkenylsuccinate esterification	ASA/KCO_3/NMP	Seiko PMC	Alkenylsuccinate ester cellulose-$OCOCH_2CRHCOO^-$	😐
	Sulfate esterification	Na sulfamate/urea/water	Maruzumi Paper	Sulfate ester cellulose-OSO_3^-	😐
	C2,3-Dicarboxylation	$NaClO \cdot 5H_2O$/water	TOA Chemical	C2,3-dicarboxylate cellulose-$(COO^-)_2$	😐

Differences between chemically pretreated CNFs and mechanically fibrillated CNFs

	CNFs prepared by chemical pretreatment and disintegration in water	Mechanically fibrillated CNFs
Chemical pretreatment	TEMPO-mediated oxidation $\rightarrow$ C2/C3-oxidation, phosphorylation, sulfate esterification, carboxymethyl etherification, etc.	N/A
Surface charge	CNF-COO^-, CNF-O-PO_3^{2-}, CNF-O-PO_2^-, CNF-OSO_3^-, CNF-OCS_2^-, CNF-OCH_2COO^-	Hemicellulose-COO^-
CNF content in water	< 2%	> 10%
Width	3 nm or 3–100 nm, depending on disintegration conditions	10–200 nm
Morphology	homogeneous ~3 nm width  	heterogeneous branched/network structures  

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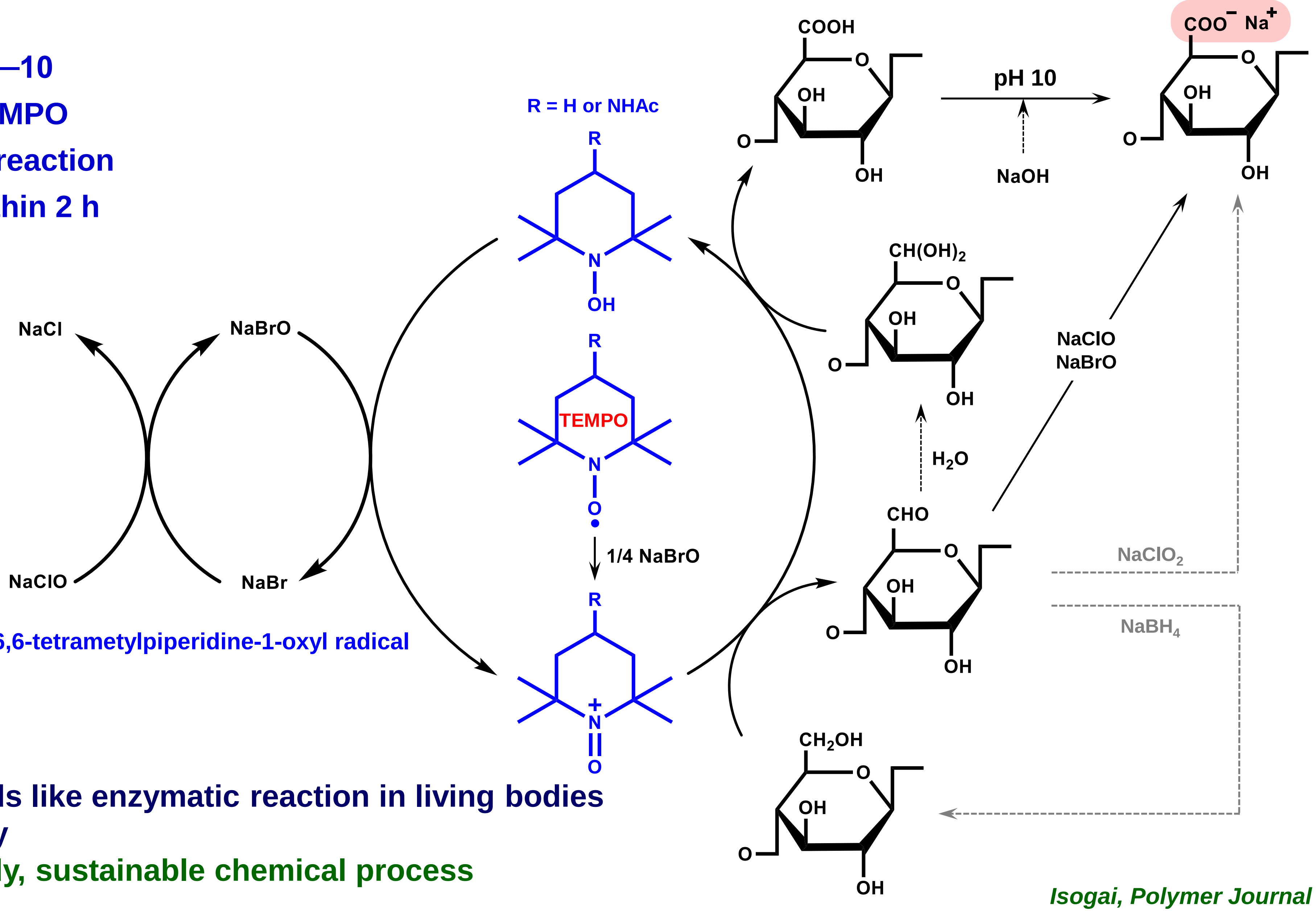
TEMPO-catalyzed oxidation of polysaccharides

Advantages:

- **Aqueous systems at pH 6–10**
- **Catalytic reaction with TEMPO**
- **Highly position-selective reaction**
- **Mild conditions at R.T. within 2 h**

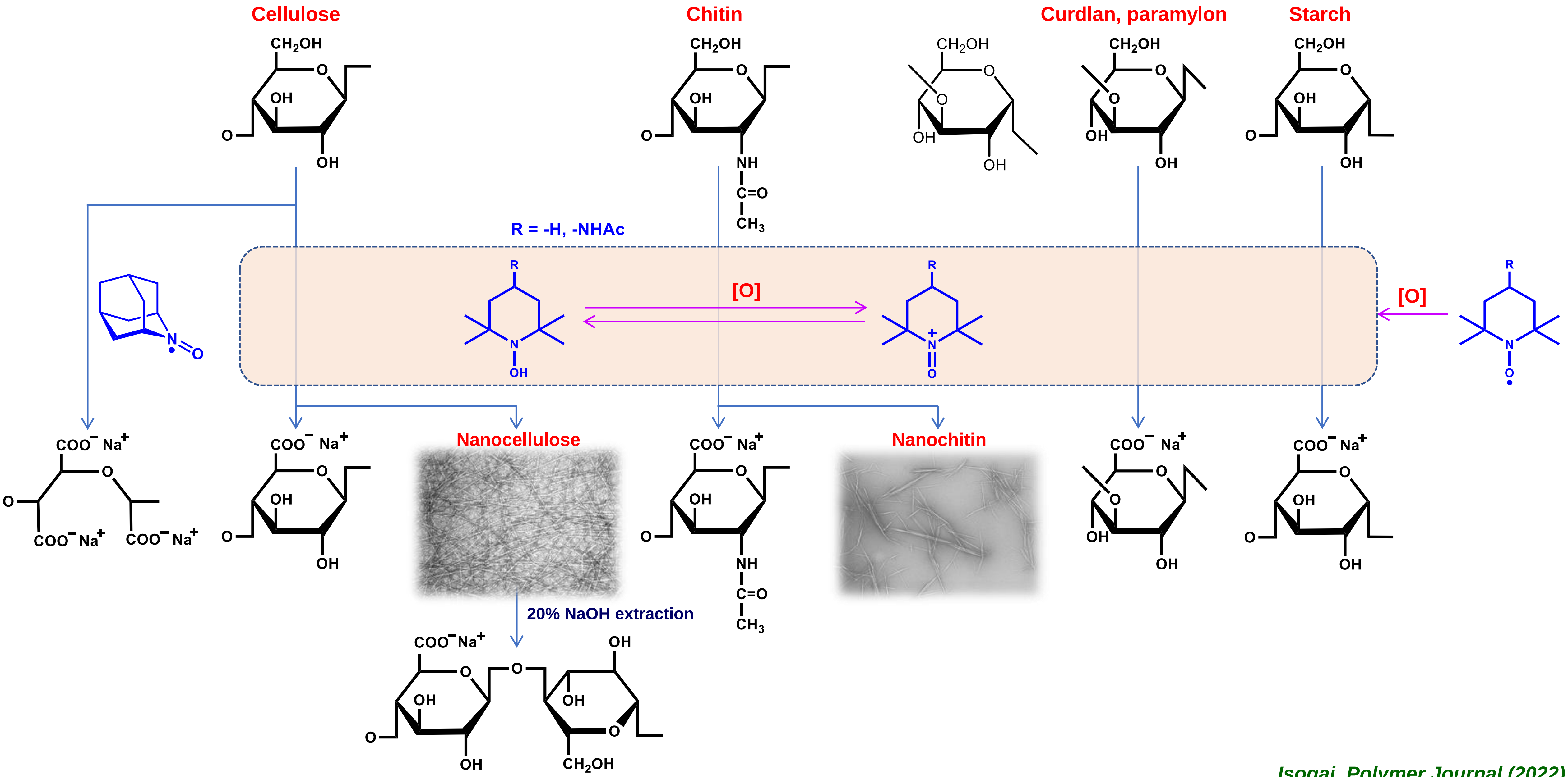


TEMPO: 2,2,6,6-tetrametylpiperidine-1-oxyl radical

- **TEMPO-oxidation proceeds like enzymatic reaction in living bodies but proceeds more rapidly**
  → Environmentally friendly, sustainable chemical process

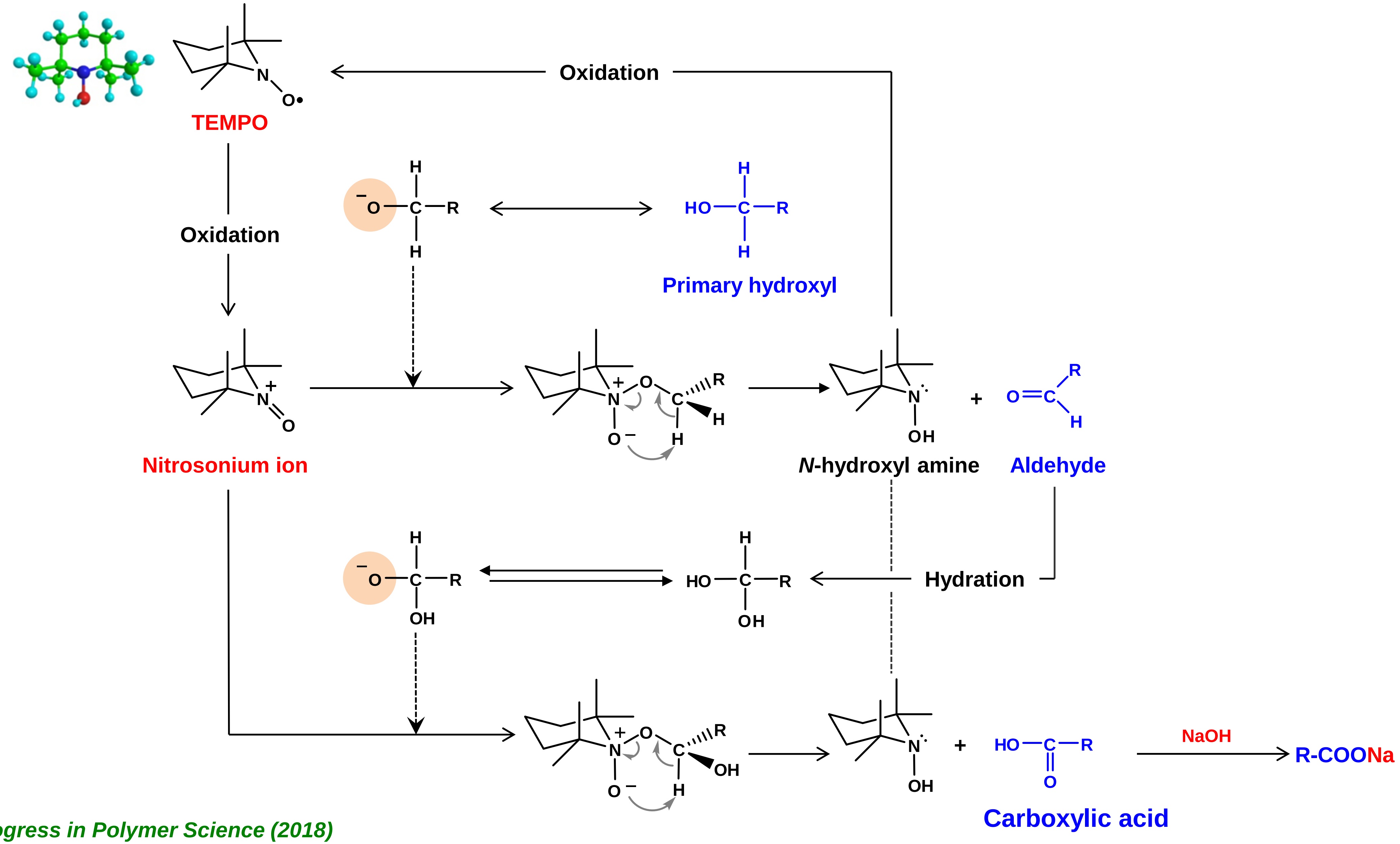
Isogai, Polymer Journal (2022)

TEMPO-catalyzed oxidation of various polysaccharides, starting from 1996



Isogai, Polymer Journal (2022)

Position-selective conversion mechanism of primary OH groups to carboxy groups by TEMPO-mediated oxidation

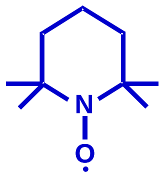


Isogai et al., Progress in Polymer Science (2018)

TEMPO-catalyzed oxidation process of plant, BC, tunicate, & algal cellulose fibers

Wood cellulose fibers (1 g)

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



Recycling

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

TEMPO
NaCl
NaBr

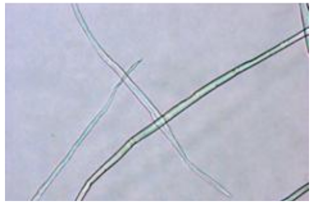
Washing effluent

Desalting

Fibrous TEMPO-oxidized cellulose

Carboxy content: 0.01 mmol/g

Carboxylate content: 1.7 mmol/g

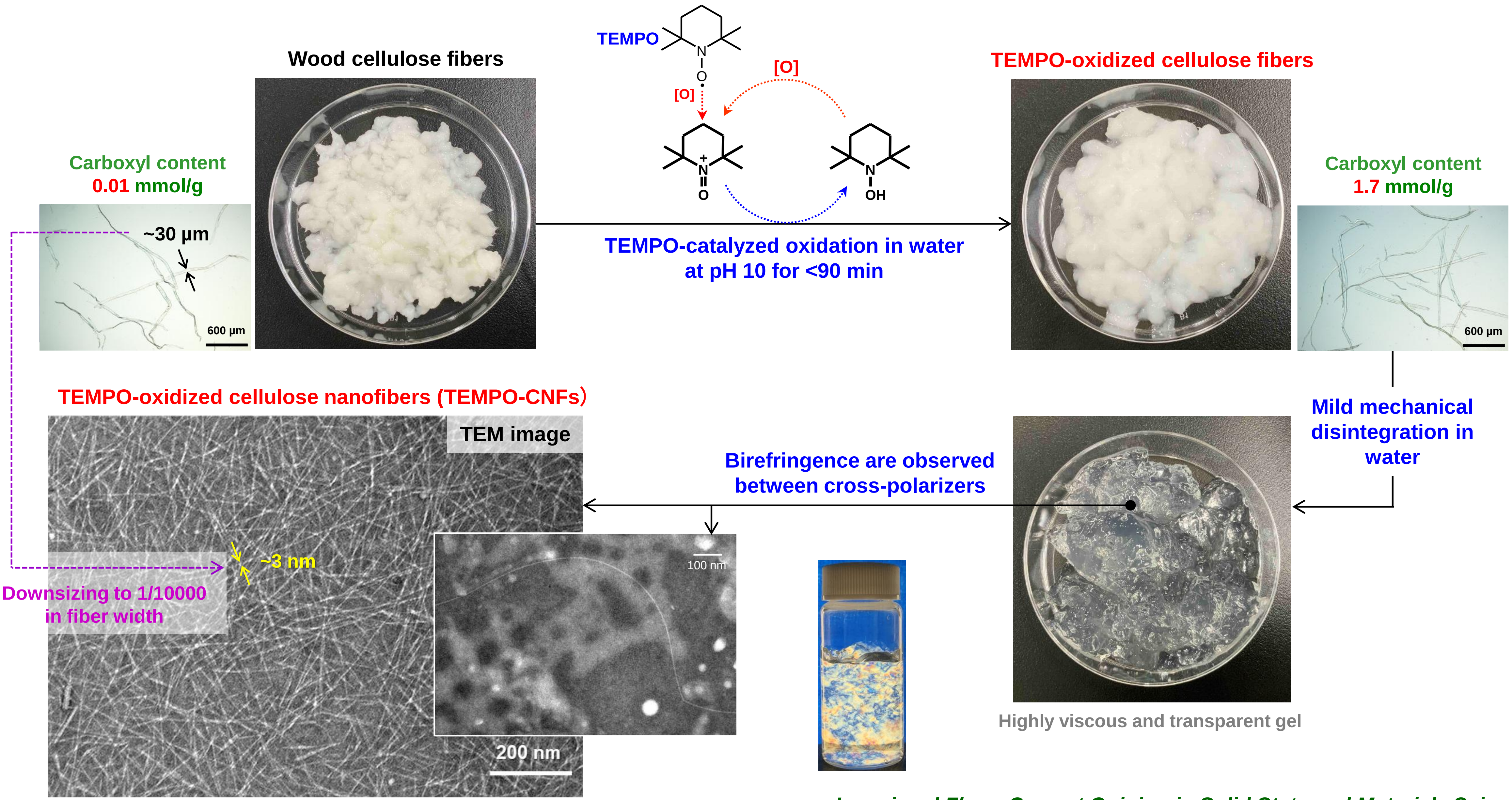


Fibrous morphologies are unchanged before and after oxidation.

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

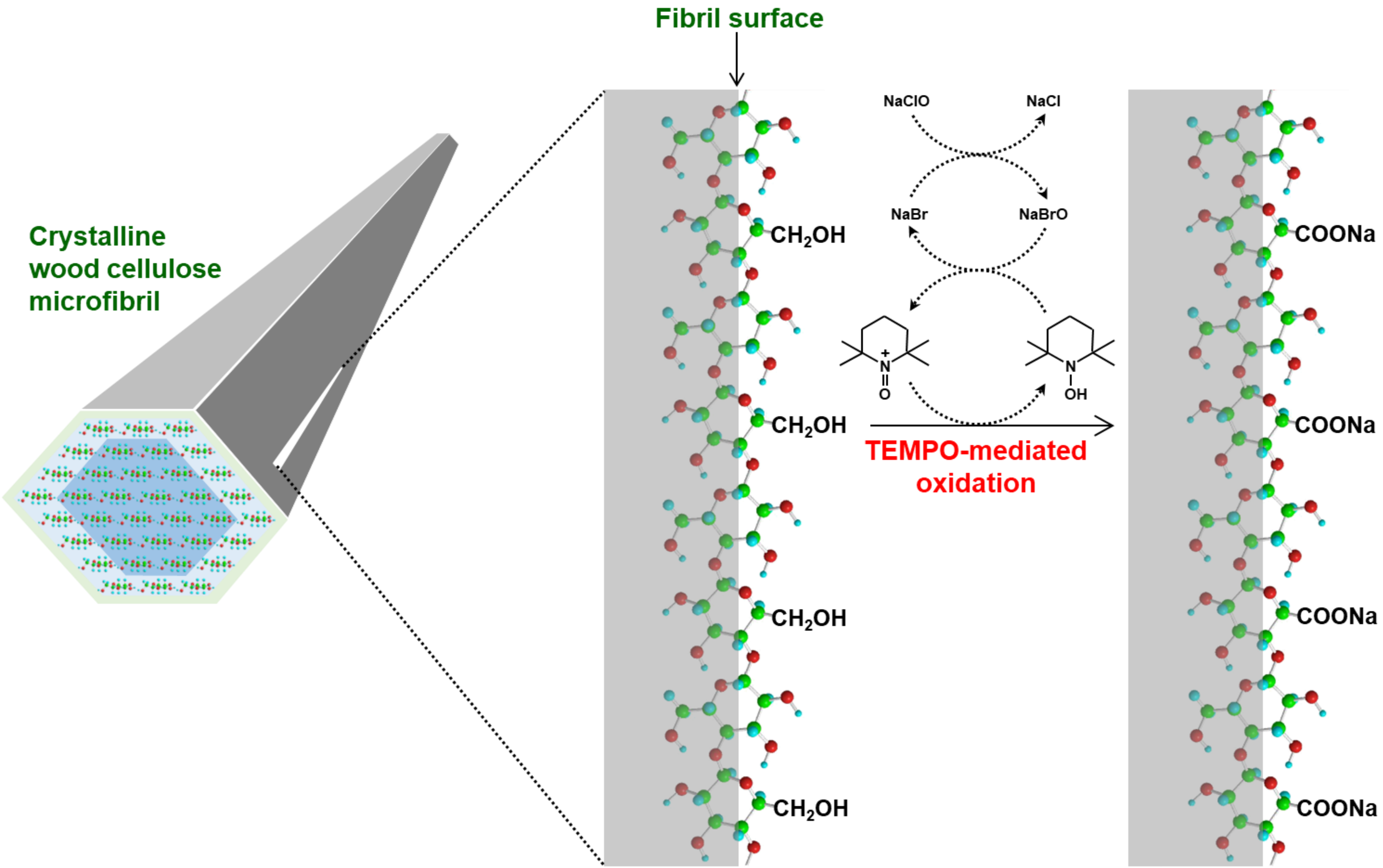
Shinoda et al., Biomacromolecules (2012)

Conversion of wood cellulose fibers to TEMPO-oxidized cellulose nanofibers (TEMPO-CNFs)



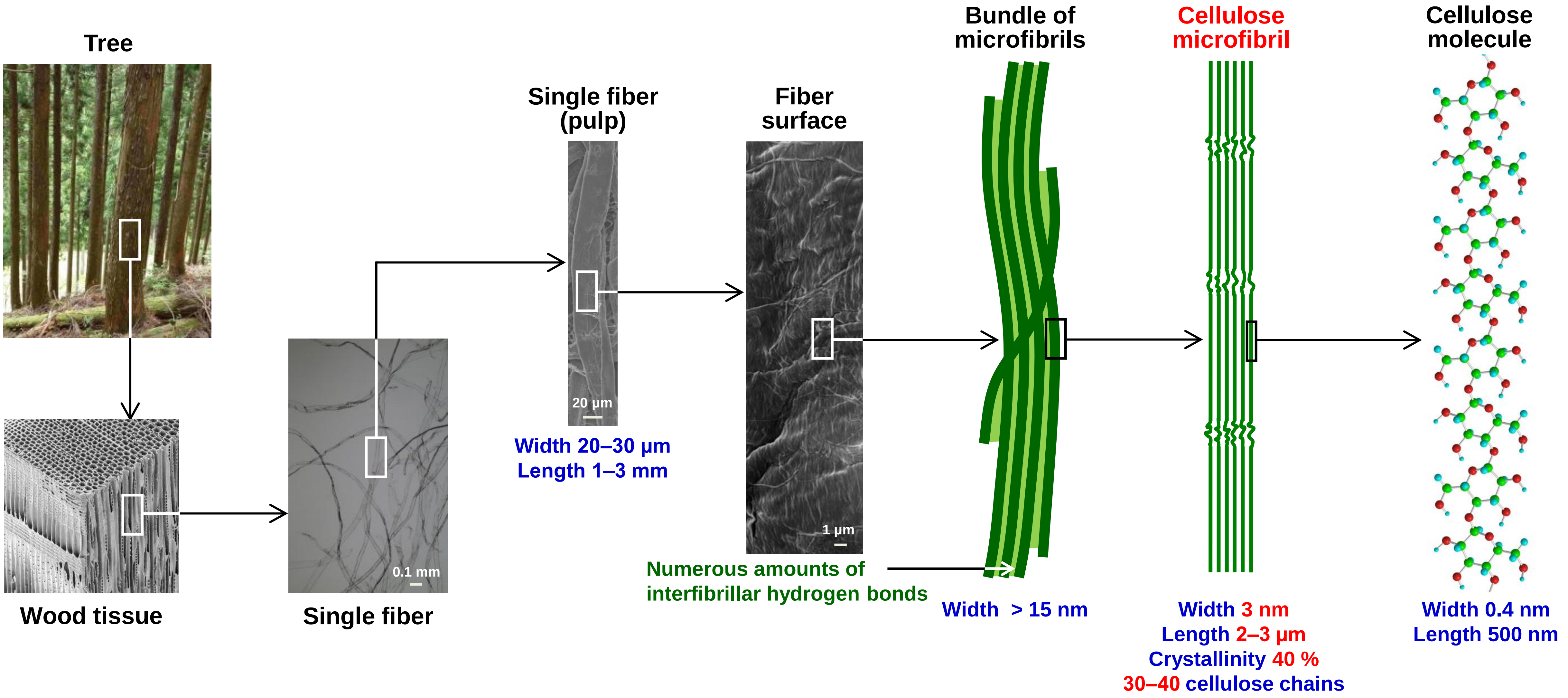
Isogai and Zhou, Current Opinion in Solid State and Materials Science (2019)

Distribution of carboxyl groups in TEMPO-oxidized wood cellulose microfibril



Okita et al., Biomacromolecules (2010)

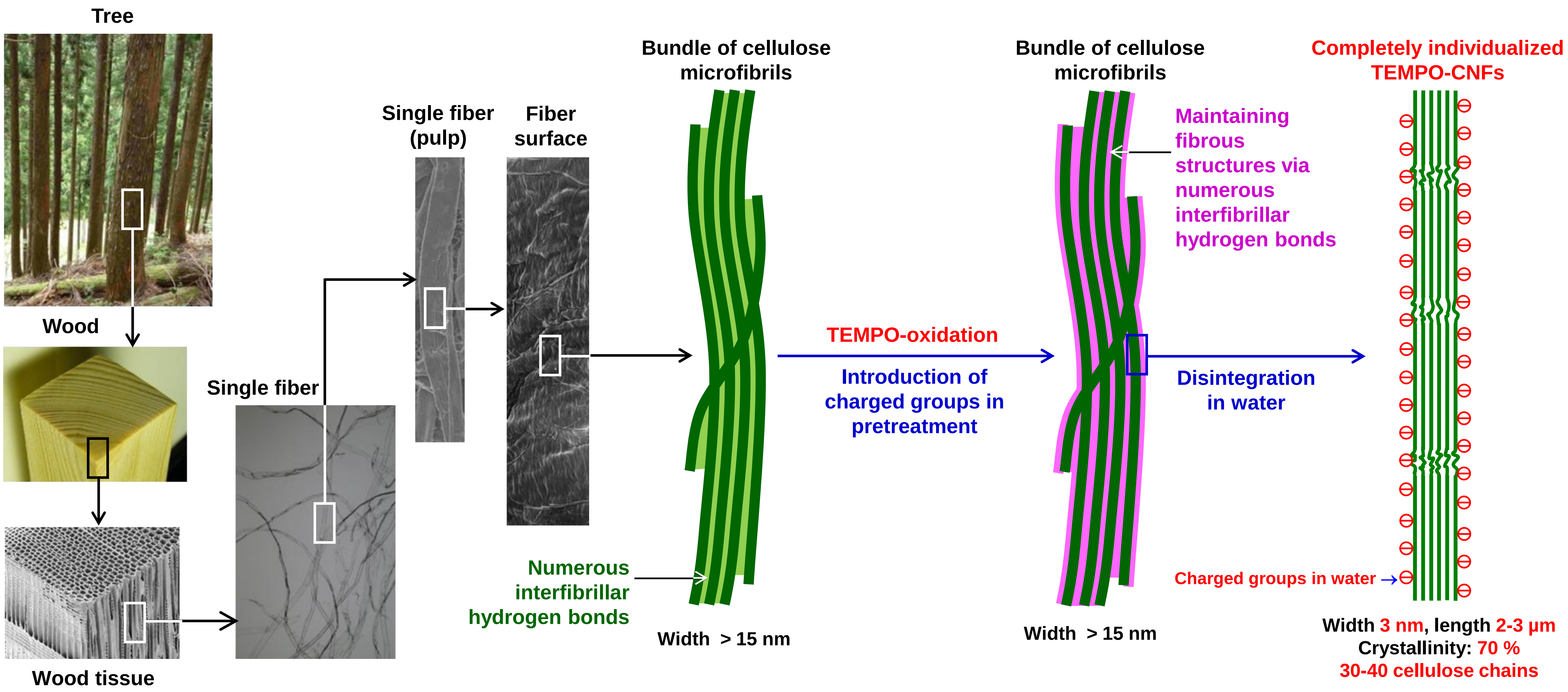
Hierarchical structure of wood cellulose



- **Cellulose microfibrils are the most abundantly present bio-based nanomaterials on Earth.**

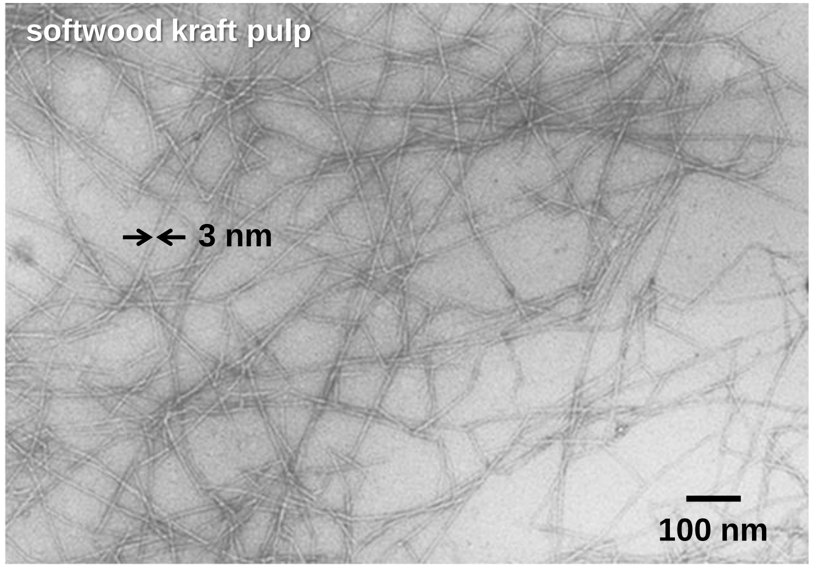
Isogai et al., Nanoscale (2011); Prog. Polym. Sci. (2018)

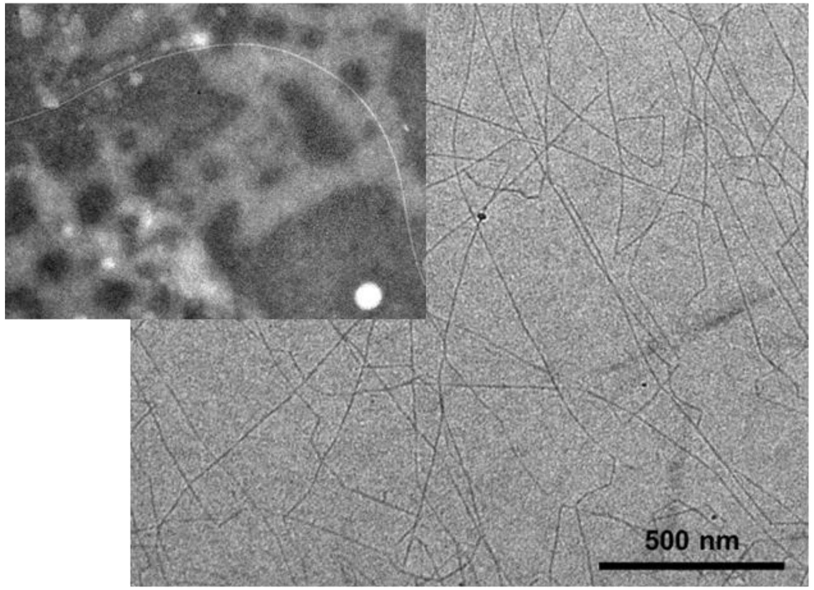
Mechanism to convert completely nano-dispersed CNFs from wood cellulose fibers

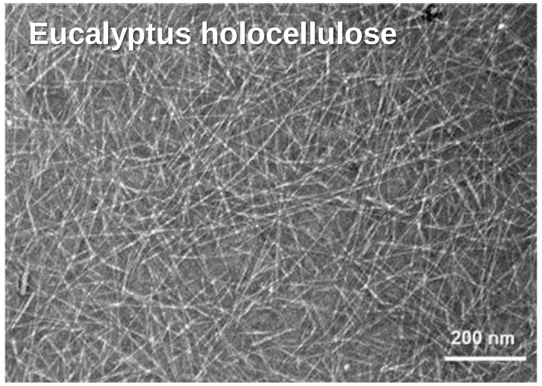


- **Osmotic effect and electrostatic repulsion efficiently work between surface-charged cellulose microfibrils in water.**

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



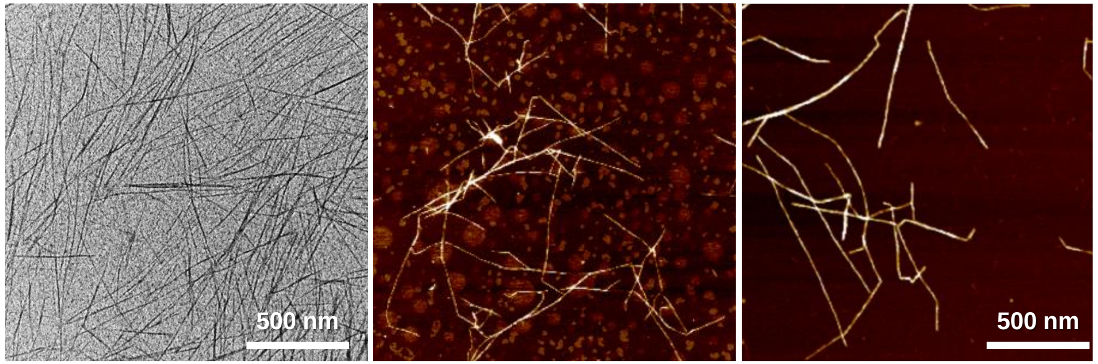


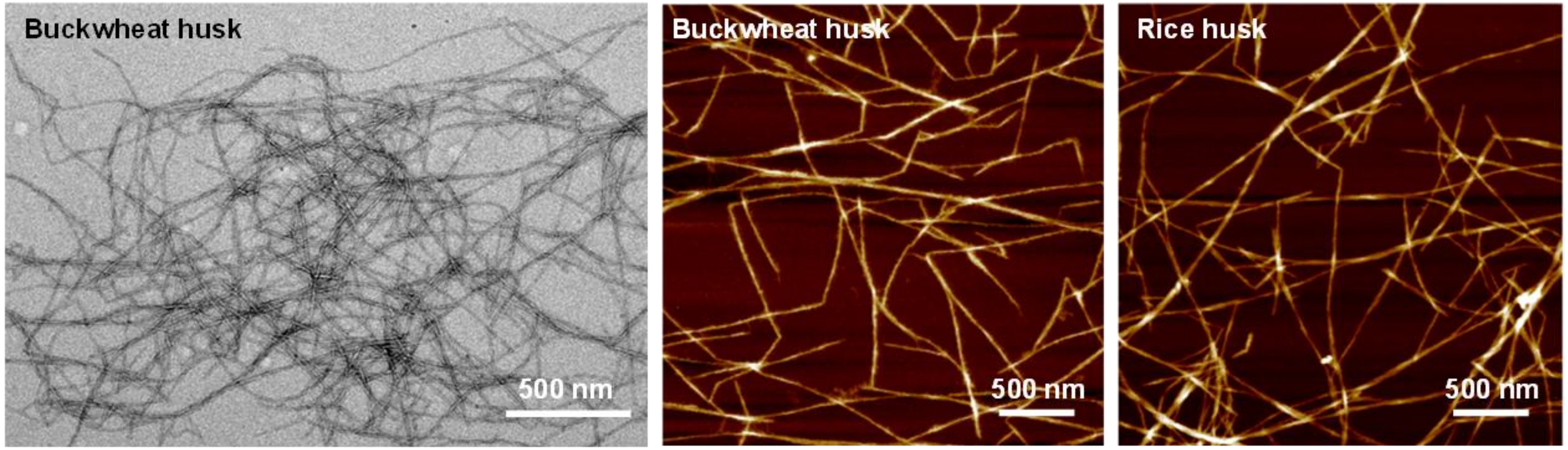


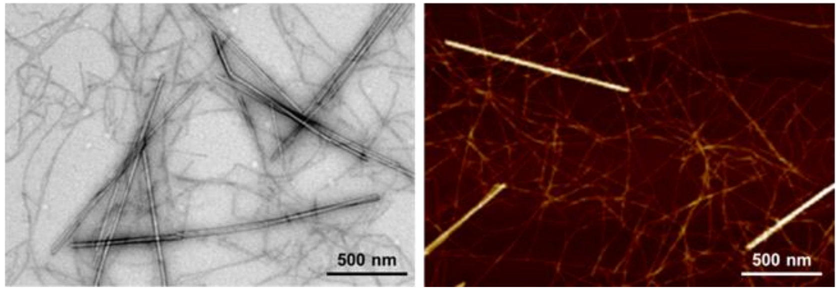
Chara TO-CNFs

Haircap moss TO-CNFs

Adiantum TO-CNFs







Needle-like cellulose microfibril bundles in buckwheat husk

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

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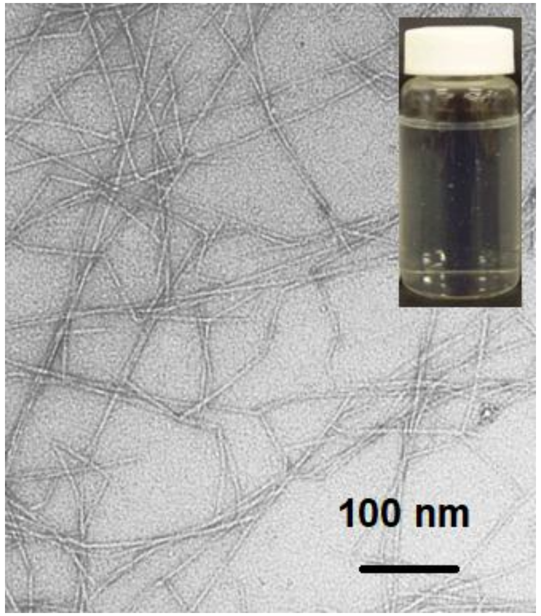
Diverse counterion exchanges of charged groups of CNFs

TEMPO-oxidized cellulose-COONa fibers, nanofibers ⟶ Cell-COOM or Cell-COONR$_4$ fibers, nanofibers

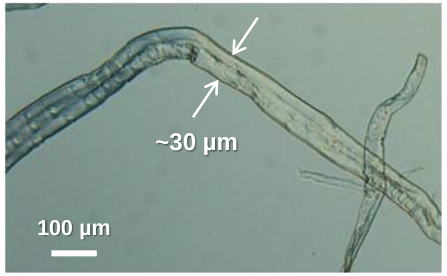
- **Switching of hydrophilicity/hydrophobicity**
  - Gas barrier/gas separation
  - Biodegradability/stability
  - Electrical conductivity/electric insulation
  - Thermal conductivity/thermal insulation
- **Scaffolds for catalytic performance**
  - Super deodorant performance
  - Metal organic frameworks
- **Air filter performance**



- **Resistance to high humidity or water, or increase in thermal stability**
- **Highly strong, light weight, transparent, and thermally stable composites with individually nano-dispersed CNF elements in polymer matrices are possible to be prepared, according to high aspect ratios of charged CNFs.**

Diverse nanocellulose can be prepared from the same TEMPO-oxidized cellulose fiber: Nano-networks, nanofibers, and nanocrystals

Softwood cellulose fiber



Carboxy content: ~0.01 mmol/g

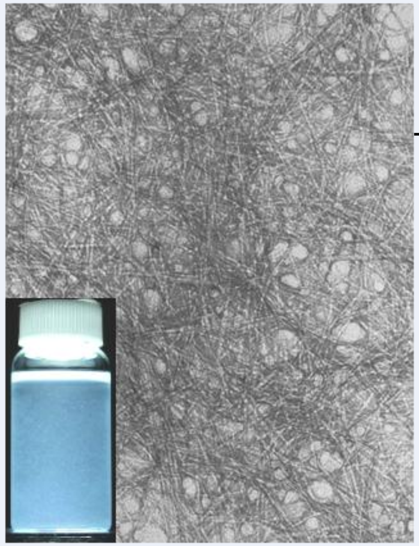
TEMPO-mediated oxidation in water at pH 10

TEMPO-oxidized pulp fibers (TOPFs)

Carboxy content: 0.5-1.7 mmol/g

Very gentle mechanical disintegration in water

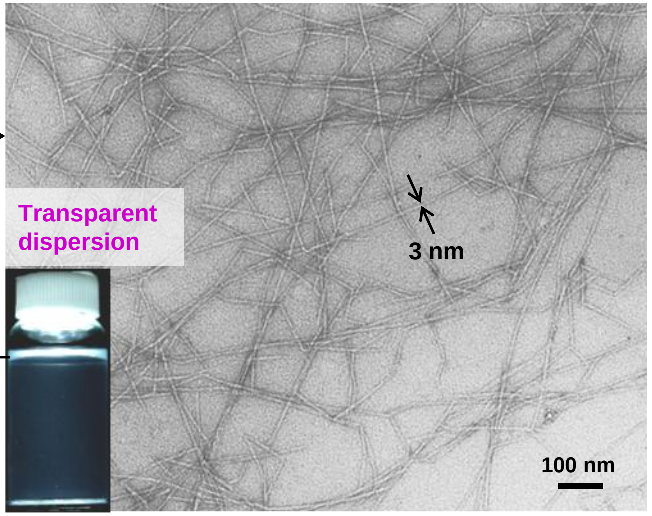
TEMPO-cellulose nano-networks, CNNeWs



Carboxy content: 0.5-1.7 mmol/g

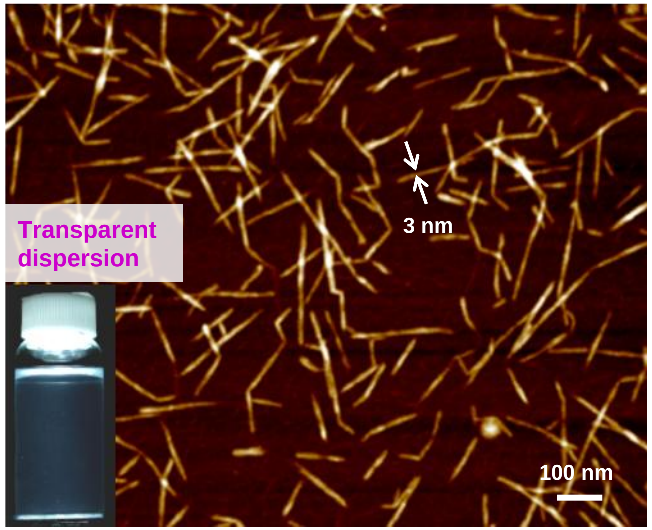
Gentle mechanical disintegration in water

TEMPO-cellulose nanofibers, CNFs



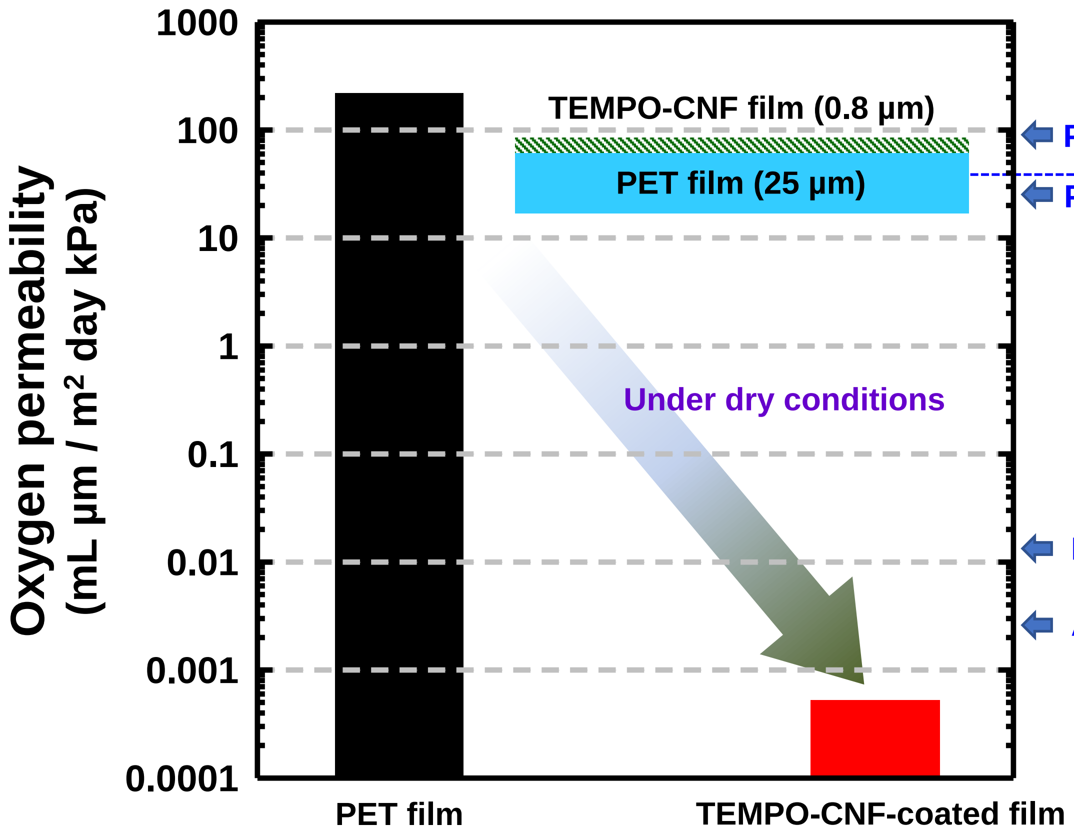
Repeated sonication in water

TEMPO-cellulose nanocrystals, CNCs



Zhou et al., Biomacromolecules (2018)

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

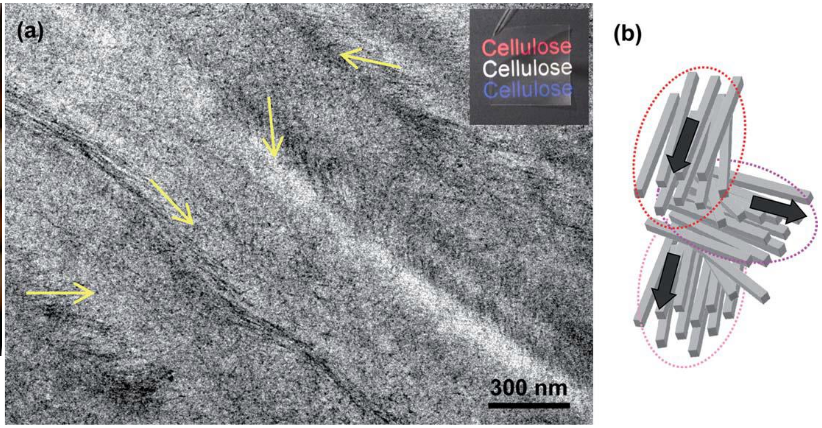


PE film

PET film

EVOH film for food/medicine package film

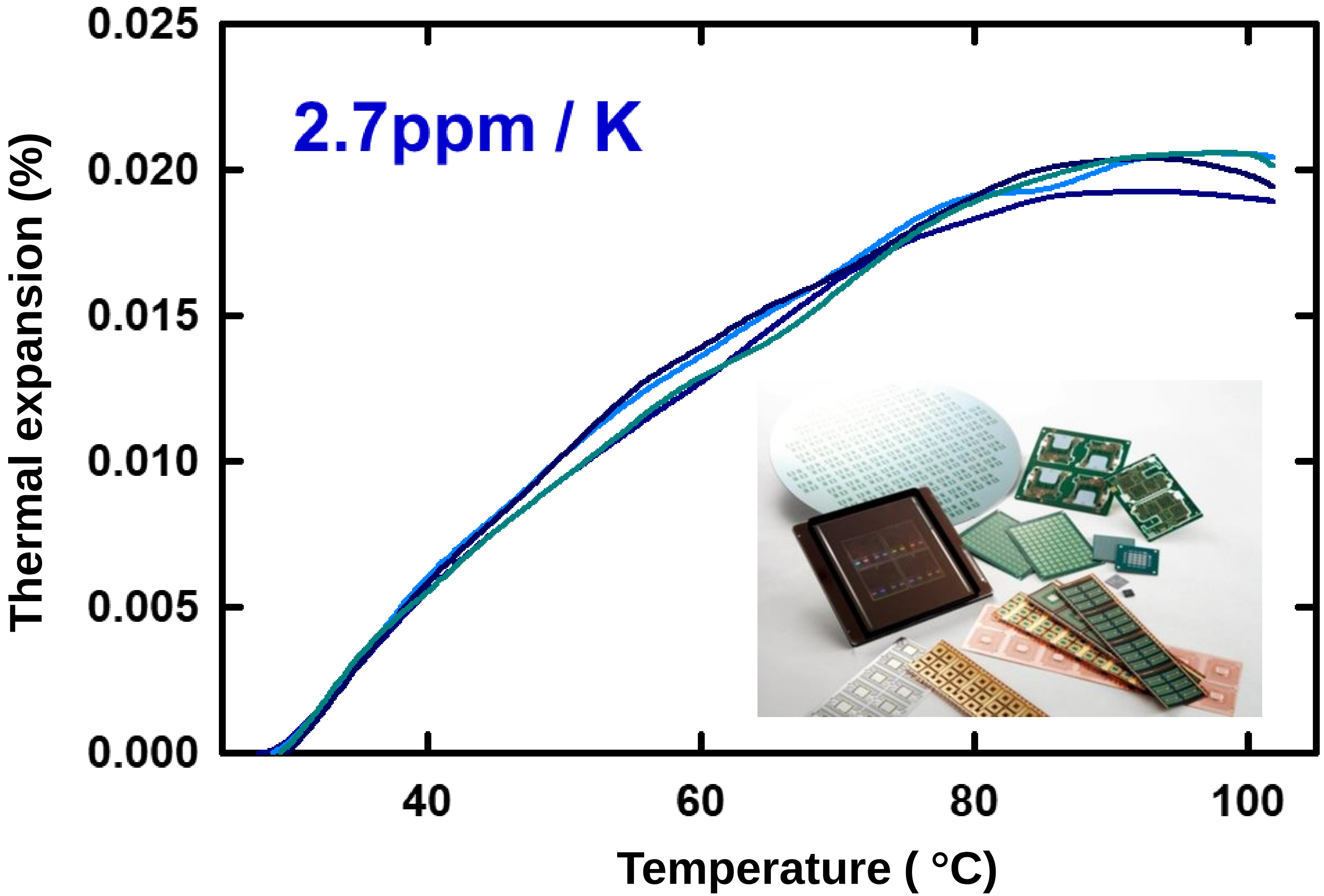
Aluminum vapor deposited film



Saito et al., Soft Matter (2011)

- **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.**

Quite low coefficient of thermal expansion of TEMPO-CNF films



- Low coefficient of thermal expansion or thermal dimensional stability → required for electronics, flexible display, etc.

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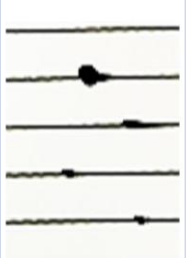
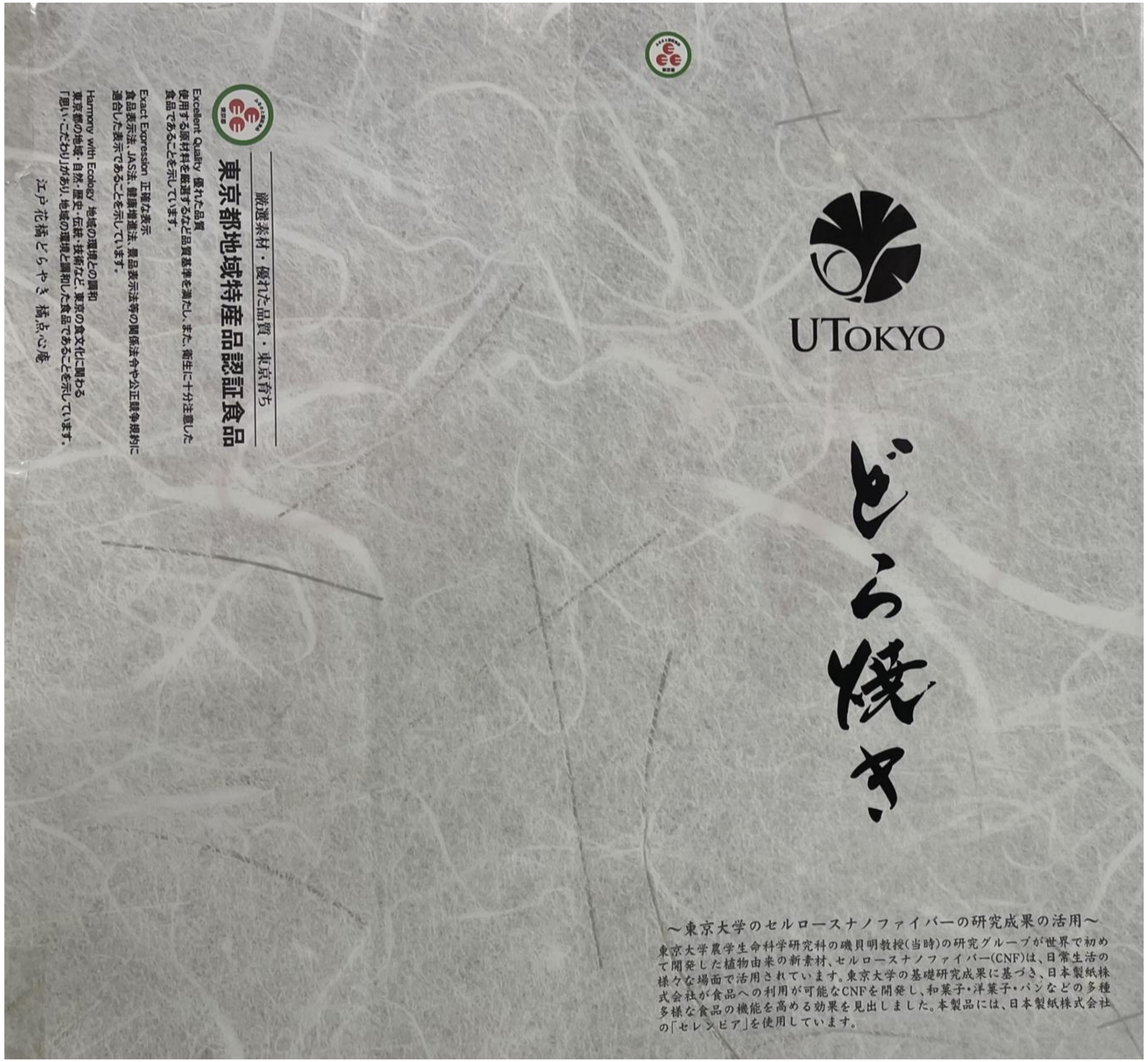
Ballpoint pen ink containing TEMPO-CNFs as dispersant for smooth writing

		Conventional gel ink	TEMPO-CNF-containing ink
Ink viscosity (mPa • s)	A 25 °C, 38/s	250	90
	B 25 °C, 380/s	90	22
A/B		2.8	4.1
Writing quality	Vertical crack		
	Lump		

DORA-YAKI containing CNFs of University of Tokyo Brand



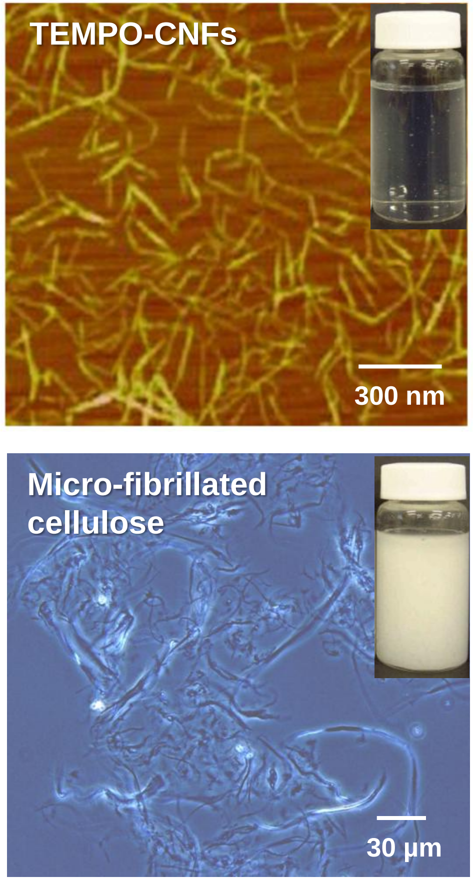
東京大学のセルロースナノファイバーの研究成果を活用したどら焼き

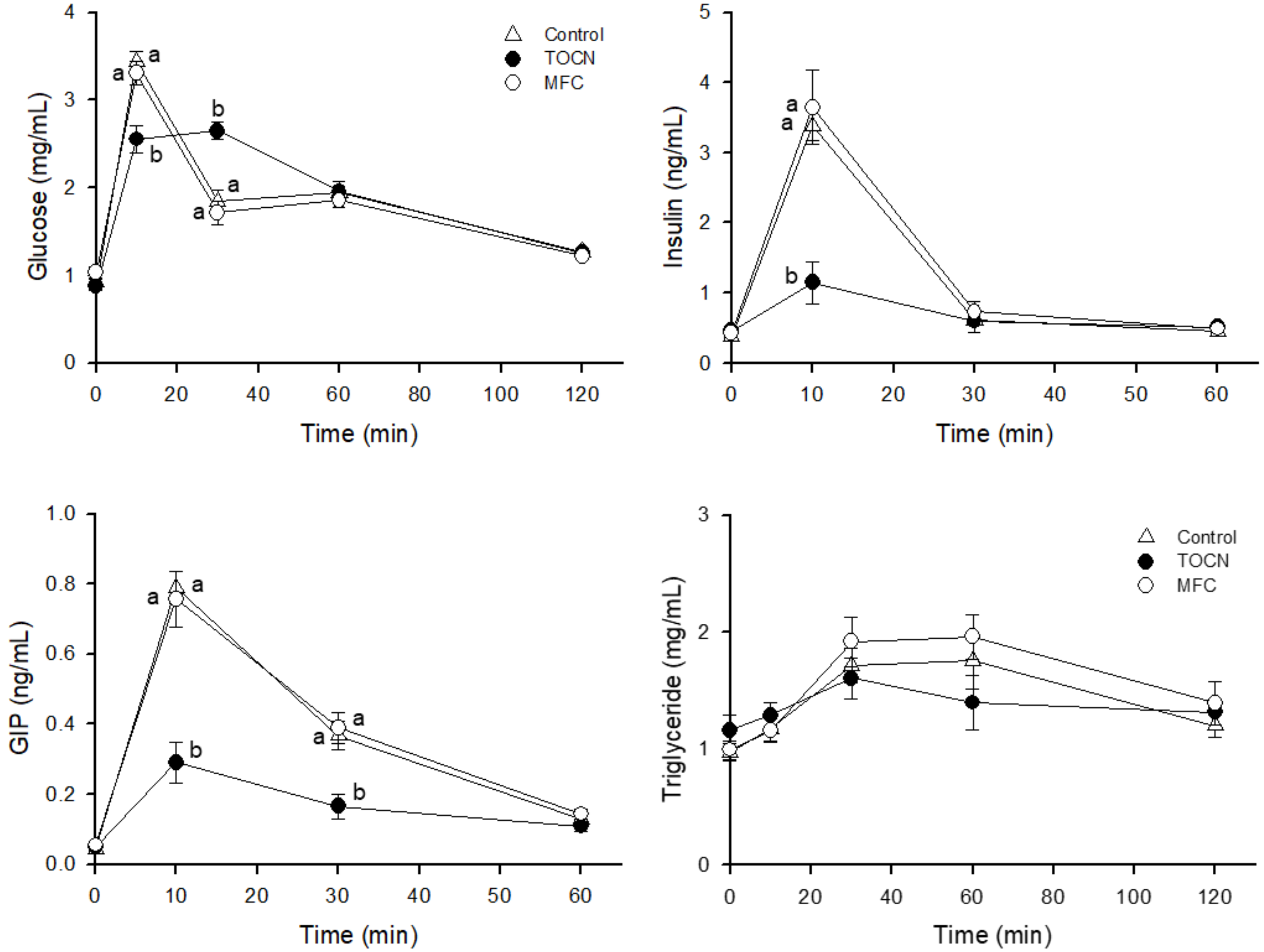
東京大学農学生命科学研究科の磯貝明教授(当時)の研究グループが世界で初めて開発した植物由来の新素材、セルロースナノファイバー(CNF)は、日常生活の様々な場面で活用されています。東京大学の基礎研究成果に基づき、日本製紙株式会社が食品への利用が可能なCNFを開発し、和菓子・洋菓子・パンなどの多種多様な食品の機能を高める効果を見出しました。

このどら焼きの皮に、日本製紙株式会社の「セレンピア」を使用しています。

[発 売 元] **国立大学法人 東京大学**
[お問い合わせ] 東京大学コミュニケーションセンター
東京都文京区本郷7-3-1 東京大学本郷キャンパス内赤門北隣

Regulation of postprandial blood metabolic variables by CNFs: bioactivity studies



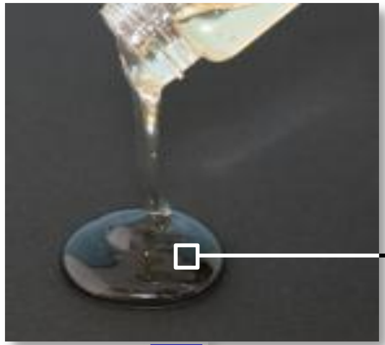


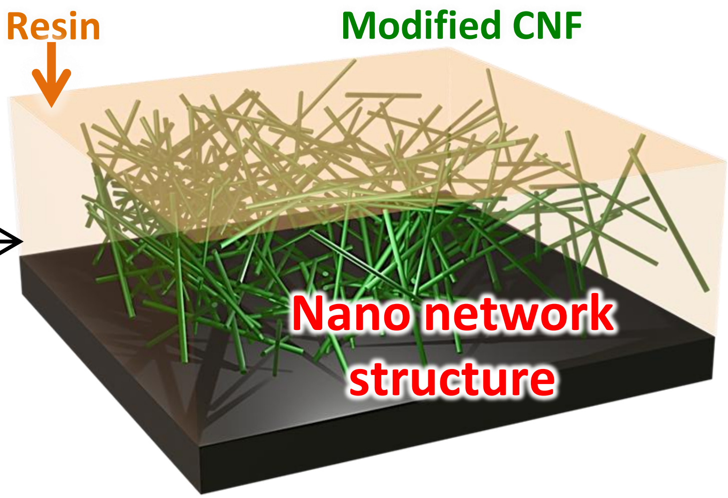
- **Clear reduction of blood glucose, insulin, GIP concentrations after oral administration of glucose and triglyceride with TOCN**

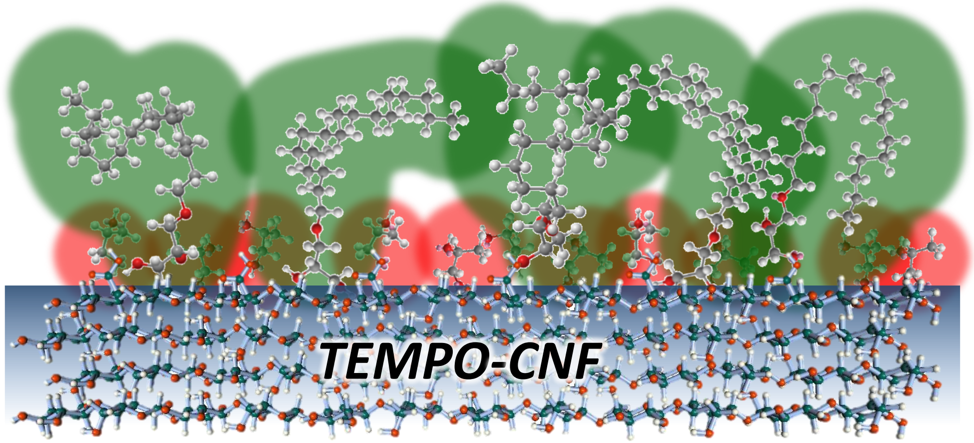
GIP: glucose-dependent insulinotropic polypeptide

Shimotoyodome et al., Biomacromolecules (2011)

TEMPO-CNF/epoxy composites prepared by surface dual chemical modifications



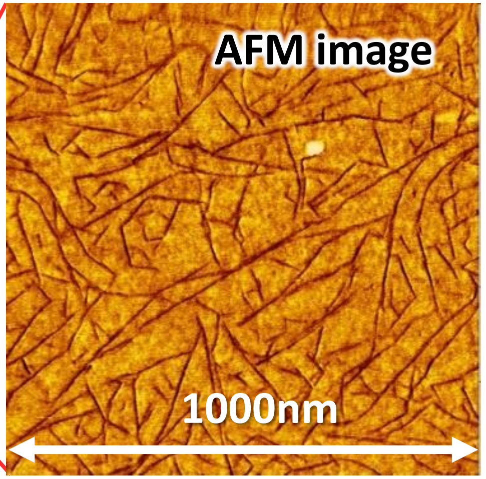




Curing/molding

Improved organic solvent affinity by introducing a large amount of benzene ring compound into the surface

Introduction of small amounts of long chains improves nano-dispersion of TEMPO-CNFs in plastic substrates

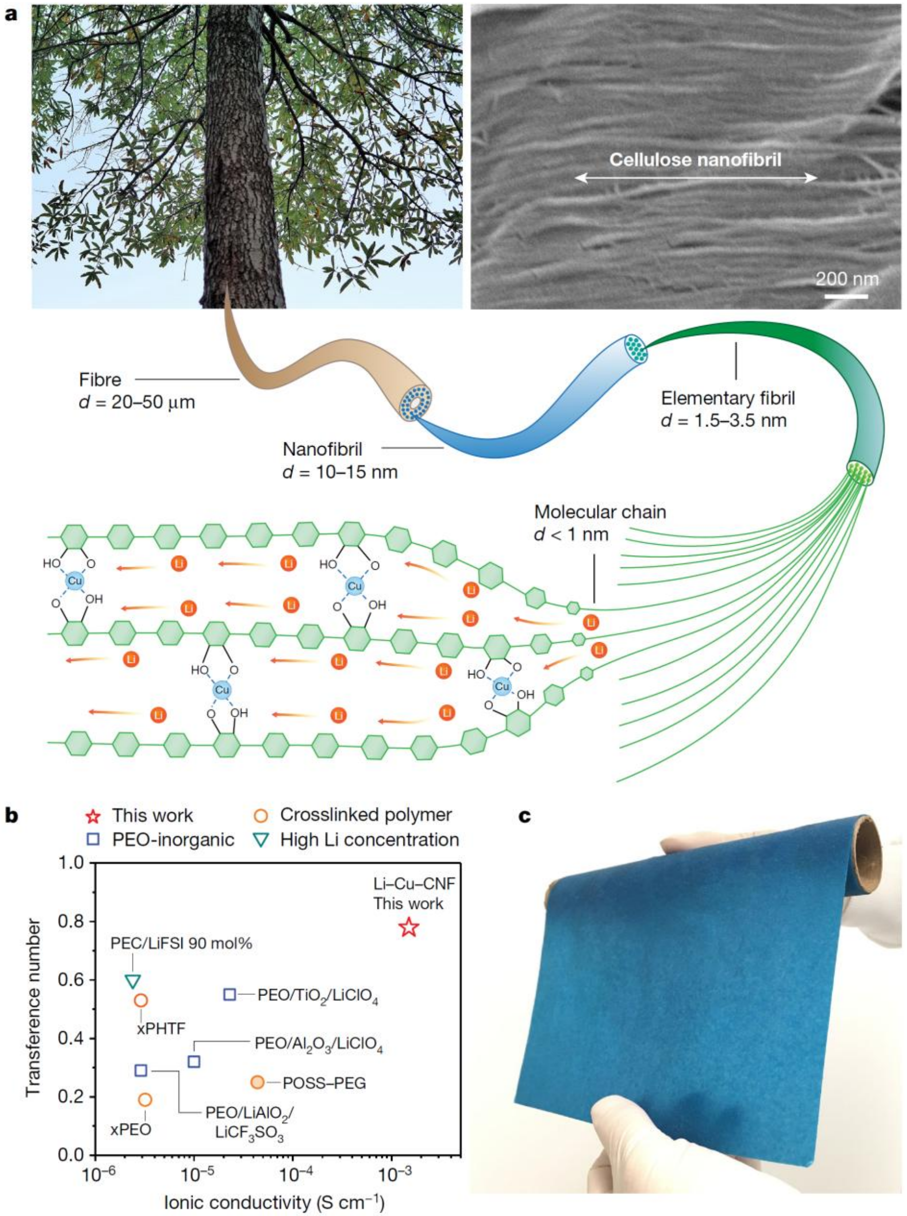


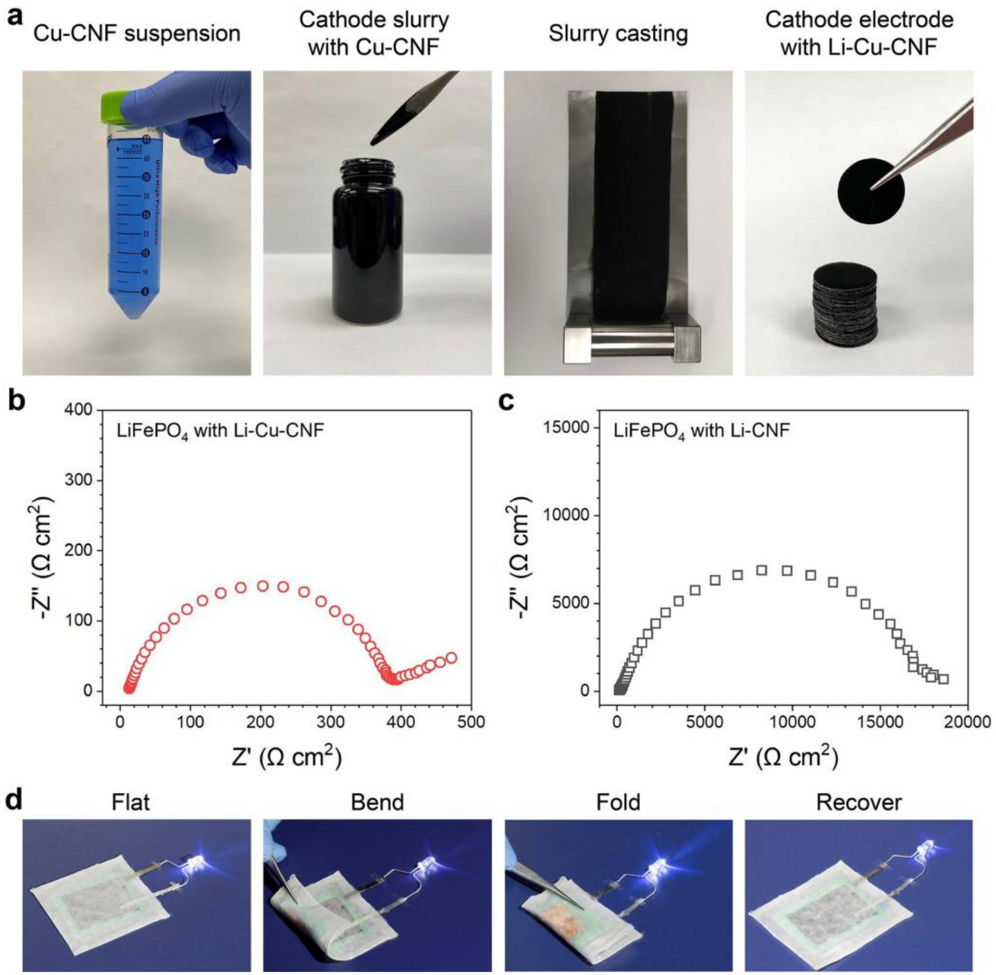
https://www.youtube.com/watch?v=8Qgn0HuHgmY

- **Compounding a small amount of surface-modified TEMPO-CNFs with plastics improves the elastic modulus and linear thermal expansion coefficient.**

Yamato et al., Cellulose (2021)

Copper-coordinated cellulose ion conductors for solid-state batteries:
Cu/TEMPO-CNF complex material





Cu^{2+}/TEMPO-CNF ion conductors have high Li^{+} conductivity, high transference number, and wide window of electrochemical stability , and are suitable for safe solid-state batteries.

Yang et al., Nature, (2021）

Practical applications and developments of TEMPO-CNFs

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

2015: Mitsubishi Pencil developed 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 CNF-containing eco-tires for automobiles

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

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

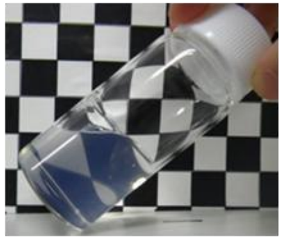
2021: Tohoku University developed CNF-containing supercapacitors for automobiles

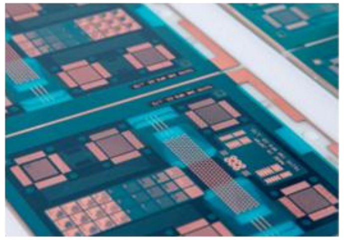
2021: Maryland University developed solid-Li butteries using CNF as efficient Li ion-channels

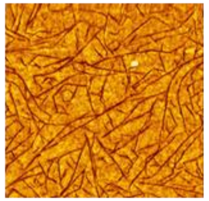
2022: Mizuno developed CNT/CNF composite golf shafts

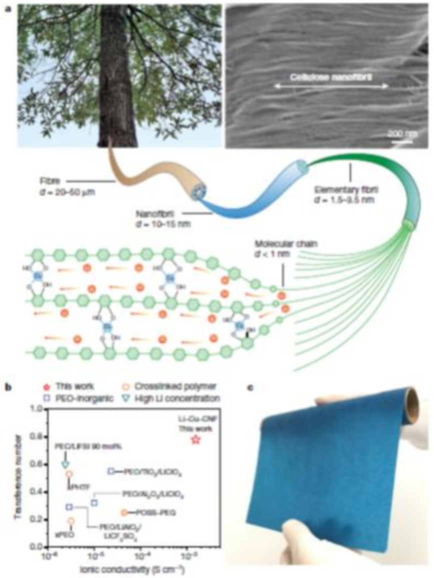
2022: NPI Crecia developed CNF-containing antibacterial masks for medical applications

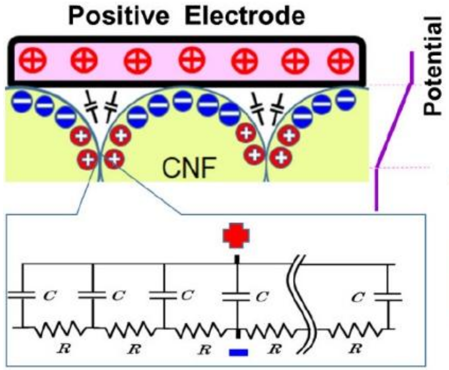
2022: Tohoku Seiren: TEMPO-CNF-treated permanent-press clothes



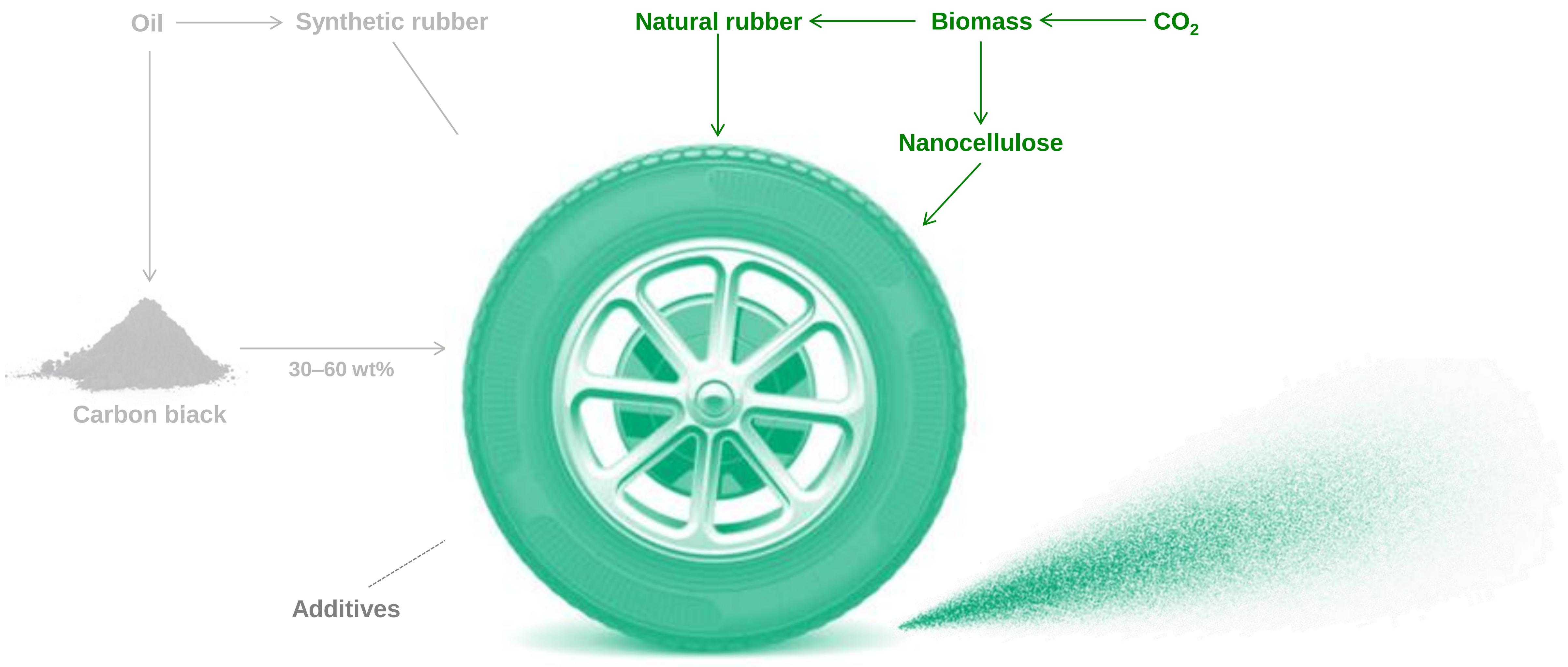








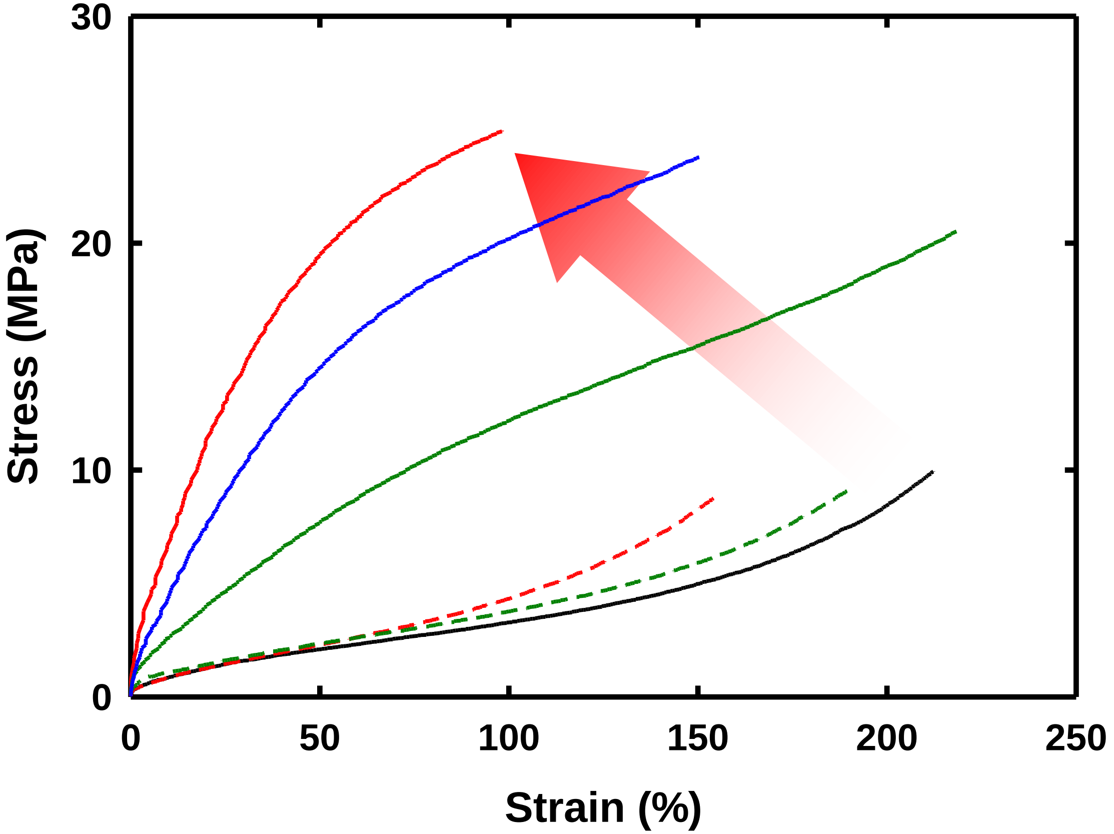
From petroleum-based rubber composites for mobilities to partly nanocelluose-containing elastomers for sustainable society



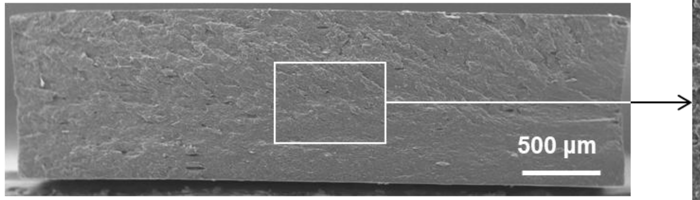
- Long-term safety, high durability, dry/wet strength, toughness, and low hysteresis loss are required for applications.

Third step: Preparation of oven-dried TEMPO-CNF/resorcinol resin/rubber composites

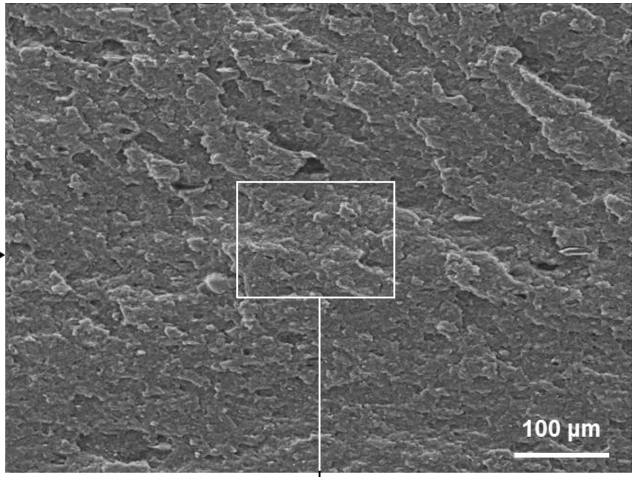
	Weight per 100 X-NBR							Vol%
	X-NBR	NBR latex	Resorcinol resin	TEMPO-CNF	Peroxide	ZnO	Anti-aging agents	TEMPO-CNF
	100	150	25	50	8	7.5	7.5	10.2
	100	150	25	0	8	7.5	7.5	0
	100	60	10	20	5.1	4.8	4.8	6.7
	100	30	5	10	4.2	3.9	3.9	4.4
	100	30	5	0	4.2	3.9	3.9	0
	100	0	0	0	3.2	3	3	0

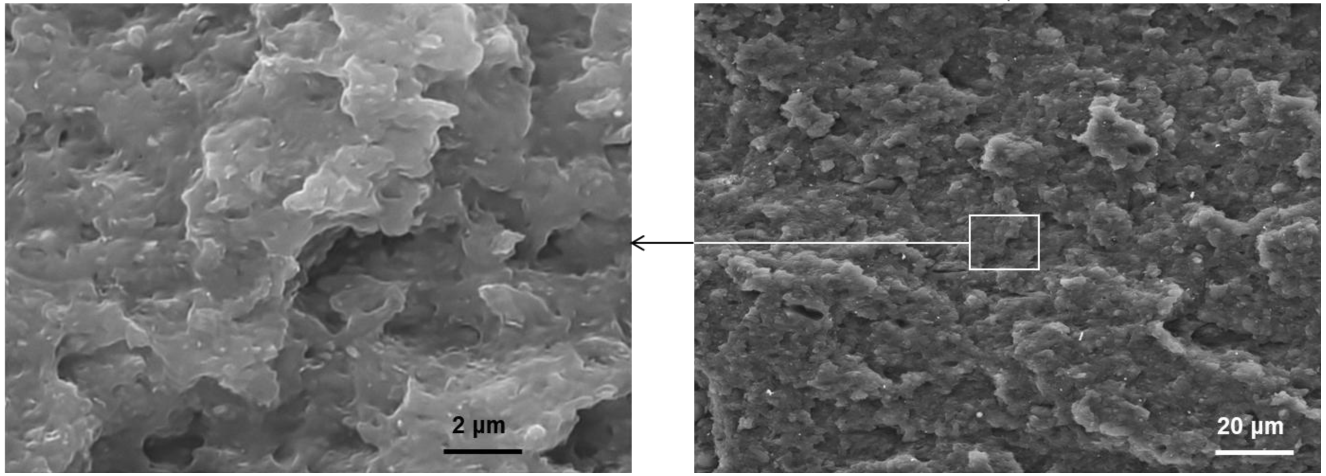


- Tensile properties are improved by adding the oven-dried TEMPO-CNF/resorcinol resin.
- No TEMPO-CNF aggregates are formed in the composite.



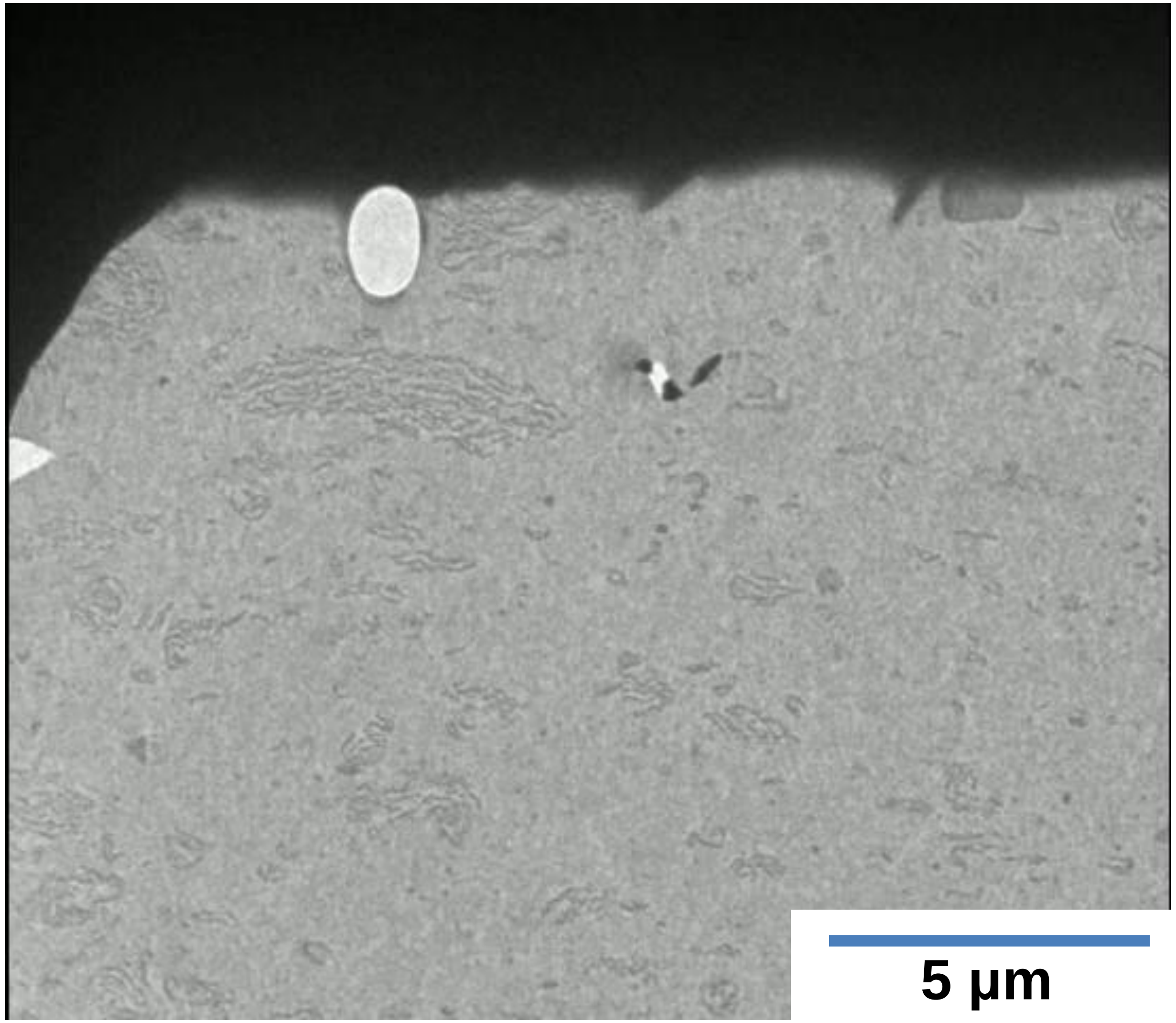
Cross section of rubber composite containing 10 vol% TEMPO-CNF

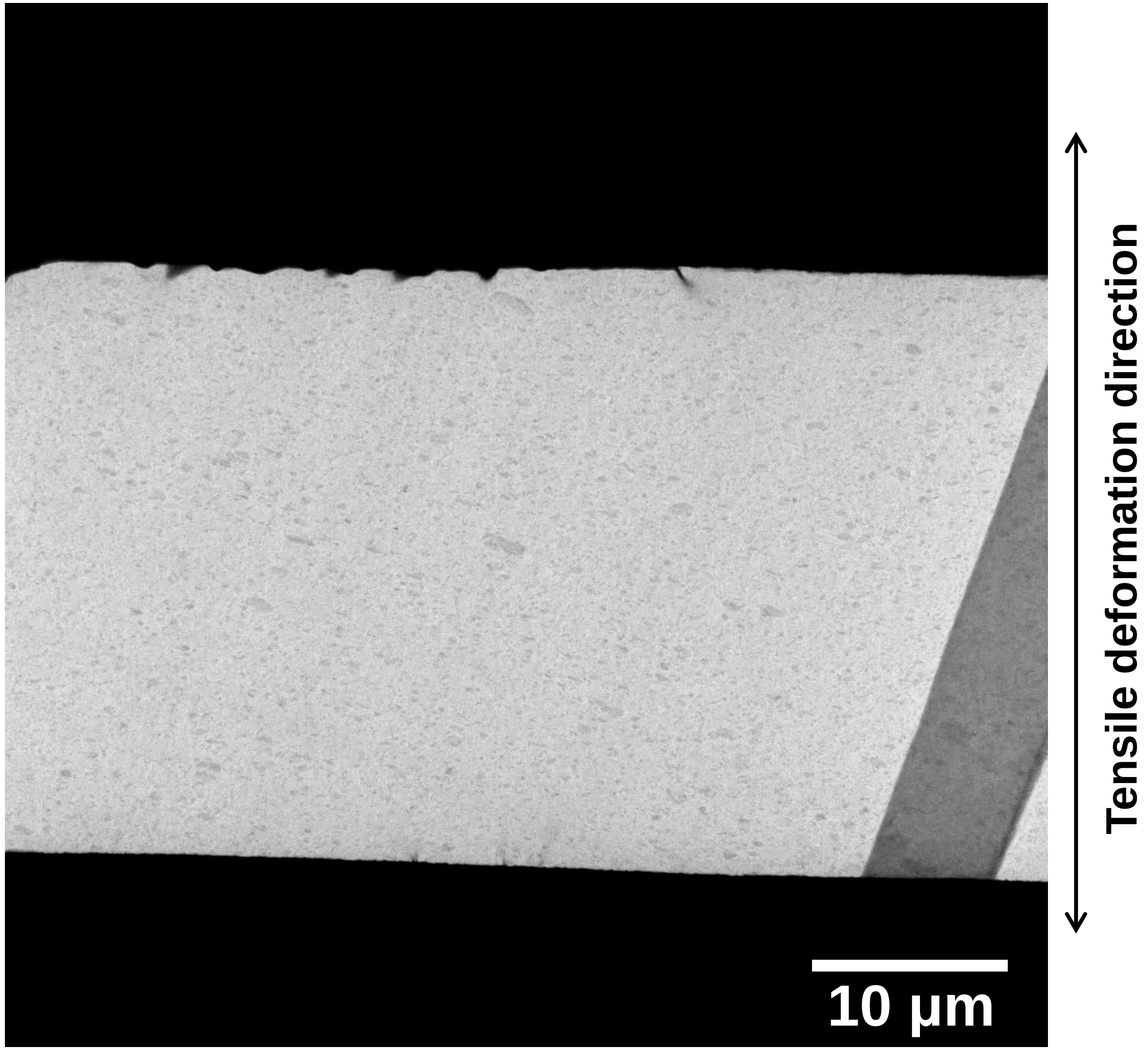




Noguchi et al., Macromolecular Materials & Engineering (2021)

Real-time observation of microcrack growth in TEMPO-CNF/rubber composites, during tensile deformation





- Structures and distributions of TEMPO-CNFs in rubber matrix influence the resultant deformation behavior during tensile deformation process.

Jinnai et al., Polymer Composites (2022)

Outline

- Background of biomass and nanocellulose utilization for creation of sustainable society and for circular economy
- Fundamentals and application of TEMPO-mediated oxidation to cellulose and polysaccharides
- Characteristics of TEMPO-oxidized fibers, nanomaterials, and films
- Application of TEMPO-CNFs
- **Summary**

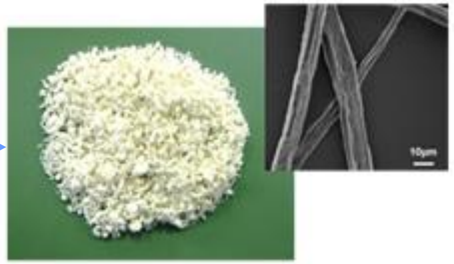
Creation of new material stream from forest resources to high-tech materials with cellulose nanofibers

Forest biomass resources

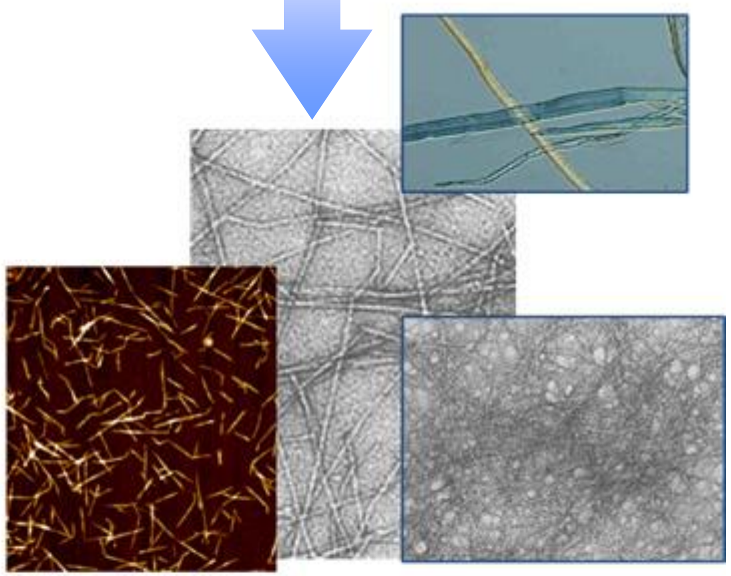
Biomass power generation

Conventional kraft pulping/bleaching technology

Plant cellulose fibers



Chemical pretreatment/mechanical fibrillation



Charged group-containing new cellulose fibers and nanofibers

Unique technology for creation of a sustainable society

Surface-modification, compounding, molding, casting, film-formation

Carbon neutral

Isogai, Bergström, Curr. Opin. Green Sus. Chem. (2018)

Conclusions

- Diverse fibers, microfibrils, and nanocellulose materials can be prepared from the same TEMPO-oxidized pulps.

- TEMPO-CNCs are categorized as new nanocellulose materials different from conventional CNCs, and available by spray-drying to be stored, delivered, and compounded with hydrophobic polymers.

- Because these TEMPO-oxidized cellulose fibers, nano-networks, nanofibers, and nanocrystals have abundant sodium carboxylate groups on fibril surfaces, they can be used as new scaffolds for further functionalization with simple ion-exchange from sodium to other metal and alkylammonium cations or stable amidation.

- Natural and synthetic rubber/CNF composites prepared by mixing once-dried CNFs with rubber sheets or emulsions have high toughness, wet/dry strength, and low hysteresis loss, applicable first to various rubber materials.

Future challenges

- Because the production quantities of CNFs are limited at present, the prices of CNFs are expensive, even though the starting pulps are inexpensive, resulting in limited application products.

- Thus, the present CNF production does not contribute to low-carbon society.

- Replacement of presently used petroleum-based materials with CNFs is not easy in terms of cost, performance, etc.

- Installation of new CNF production facilities in forest areas is not realistic, but the present pulp/paper industry should produce CNFs based on the long-term accumulated technologies for efficiency, cost, and environmental aspects

- Long-term evaluations of CNFs and CNF/polymer composites in terms of safety, durability, wet/dry strength, toughness, hysteresis loss behavior are further required.

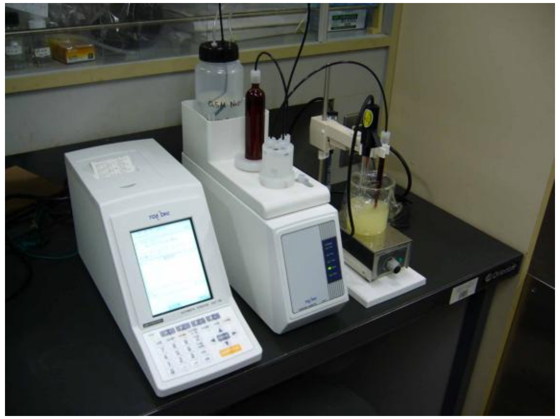
Acknowledgements

The University of Tokyo
Biomaterials Science
Cellulose Chemistry Lab

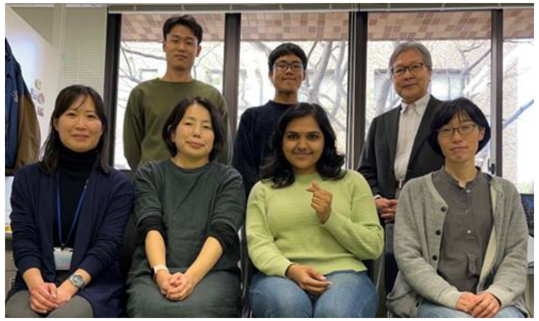
- **Cellulose Chemistry Lab has started from 2020, belonging to the University President Division**
- **Leader/Management of nano-SIMS Analytical Division of the ARIM Project, the University of Tokyo (MEXT Project)**

NanoSIMS

SEC/MALLS for determination of molar mass distributions of polymers



TEMPO-oxidation system



- **Lab member**

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2 Postdocs, 1 Office manager
5 Ph.D-course students
4 Visiting researchers

- **Others**

Project Professor, Shinshu University
Advisers of AIST, Shizuoka Prefecture, etc.
Collaborating with Prof. Hashida's Group of Tohoku University for NEDO project

NEDO 新エネルギー・産業技術総合開発機構 New Energy and Industrial Technology Development Organization
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東北大学 TOHOKU UNIVERSITY
Shizuoka Prefecture
Fuji City


Thank you for your kind attention