Relationships between the Structures and Properties of Acid-free TEMPO-Oxidized Cellulose Nanocrystals (TEMPO-CNCs)

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PRESENTED BY:

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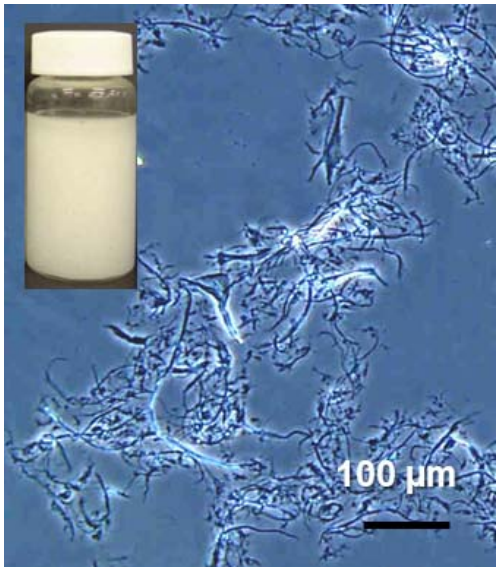
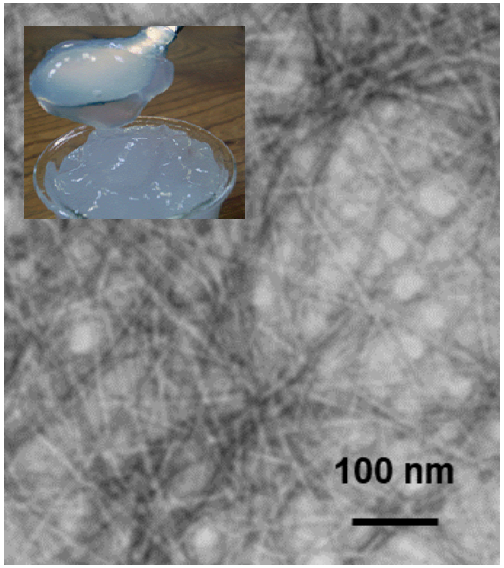
TAPPI

Categories of plant nanocelluloses and microfibrils

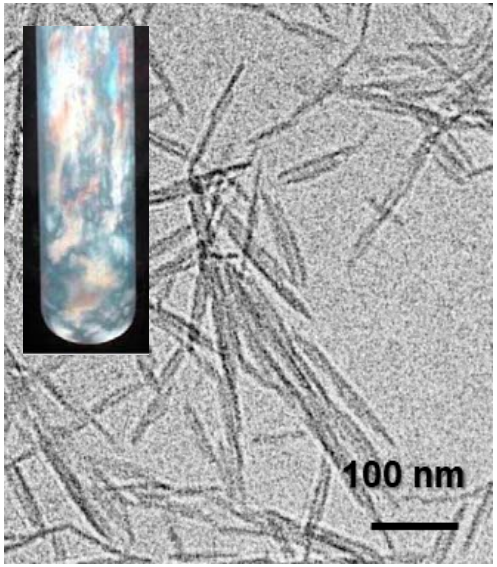
A: Microfibrillated cellulose (MFC)



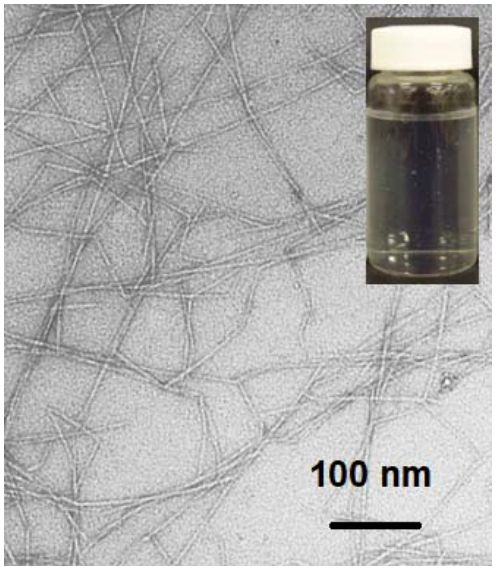
B: Mostly fibrillated cellulose nano-networks (CNNeW)

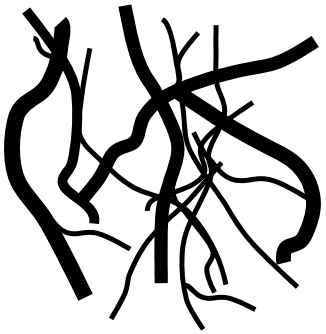


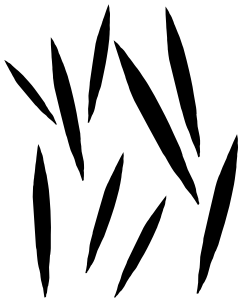
C: Mostly individualized cellulose nanocrystal (CNC)

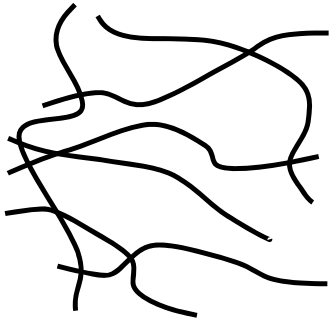


D: Mostly individualized cellulose nanofiber (CNF)









Categories of plant nanocelluloses and microfibrils

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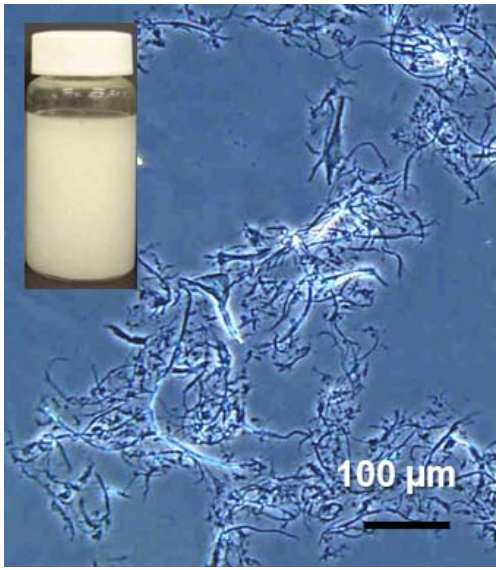
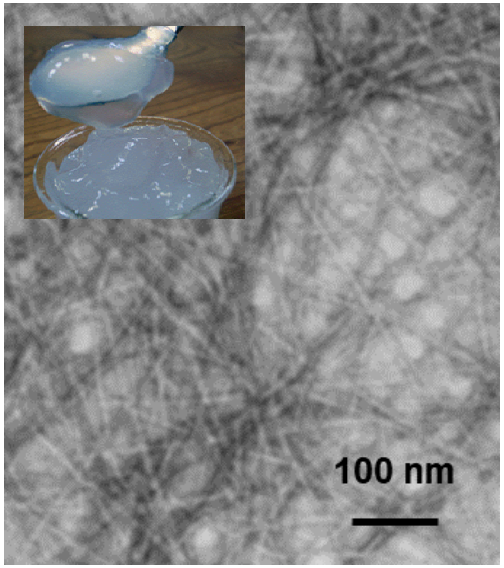


Mechanical disintegration of plant cellulose fibers in water

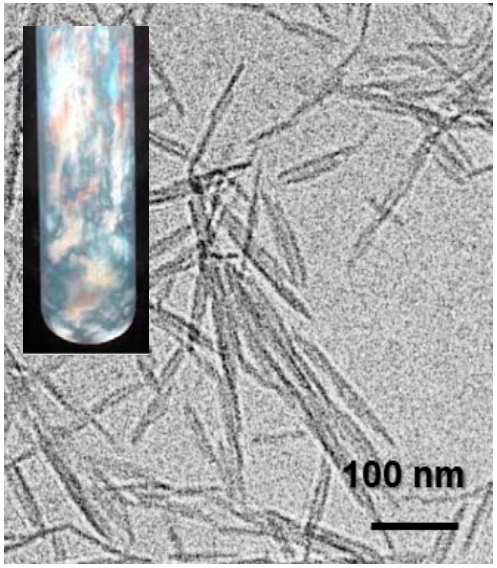
B: Mostly fibrillated cellulose nano-networks (CNNeW)



Mechanical disintegration of mildly pretreated plant cellulose fibers in water

Pretreatment:
Endo-cellulase,
Carboxymethylation,
Acetylation,
Peroxidation, etc.

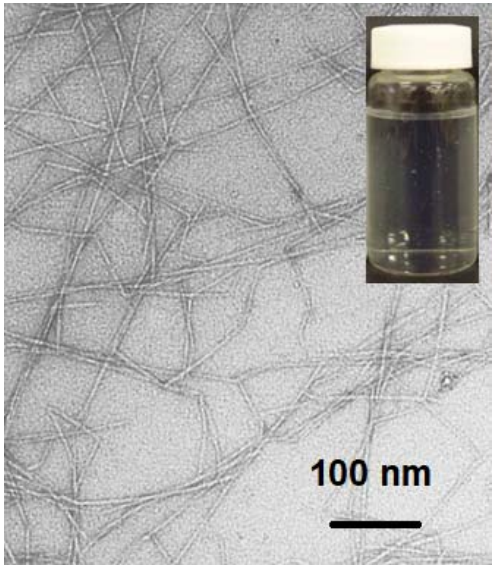
C: Mostly individualized cellulose nanocrystal (CNC)



Mechanical disintegration of acid-hydrolyzed plant cellulose fibers in water

Acid hydrolysis:
64% H_2SO_4 at 70 ºC
for 30 min
Yields ~40% in lab

D: Mostly individualized cellulose nanofiber (CNF)

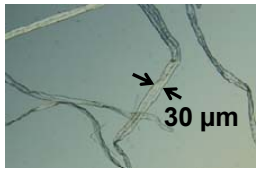


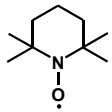
Mechanical disintegration of pretreated plant cellulose fibers in water

Pretreatment:
TEMPO-mediated oxidation at RT
Phosphorylation at 165 ºC for 10 min

Preparation of TEMPO-oxidized cellulose nanofibers (TEMPO-CNFs)

Wood cellulose fiber

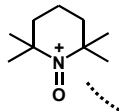




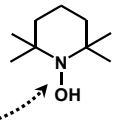
TEMPO
(2,2,6,6-tetramentylpiperidine-1-oxyl radical)

[O] [O]

Oxidized TEMPO

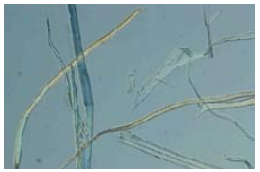


Reduced TEMPO



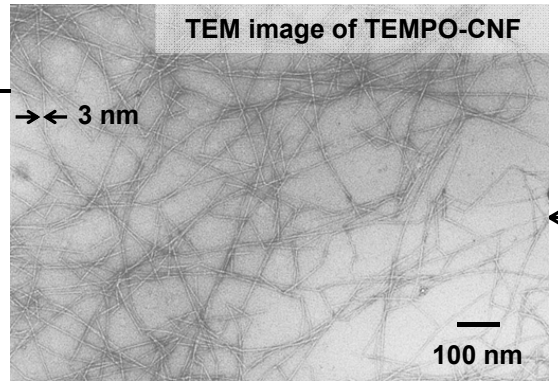
TEMPO-mediated oxidation in water at pH 10 and room temp.
for < 90 min

Fibrous TEMPO-oxidized cellulose (TOC)



Mild mechanical disintegration in water

aq. TEMPO-CNF dispersion



TEMPO-CNC

TEMPO-oxidized cellulose nanocrystals prepare from TOCN by sonication in water ?

Acid-free preparation of TEMPO-CNCs from SBKP or MCC compared with conventional acid hydrolyzed SBKP (Acid-CNC)

Softwood bleached kraft pulp (SBKP)

Microcrystalline cellulose (MCC)

↓

TEMPO/NaBr/NaClO oxidation in water at pH 10

Post-$NaBH_4$ reduction in one pot

↓

TEMPO-oxidized SBKP

TEMPO-oxidized MCC

↓

Ultrasonic treatment in water for 10−120 min (0.1% and 0.25%)

↓

SBKP-10, SBKP-30

SBKP-60, SBKP-120

MCC-10, MCC-30

MCC-60, MCC-120

↓

Control sample:

Acid-CNC (from SBKP)

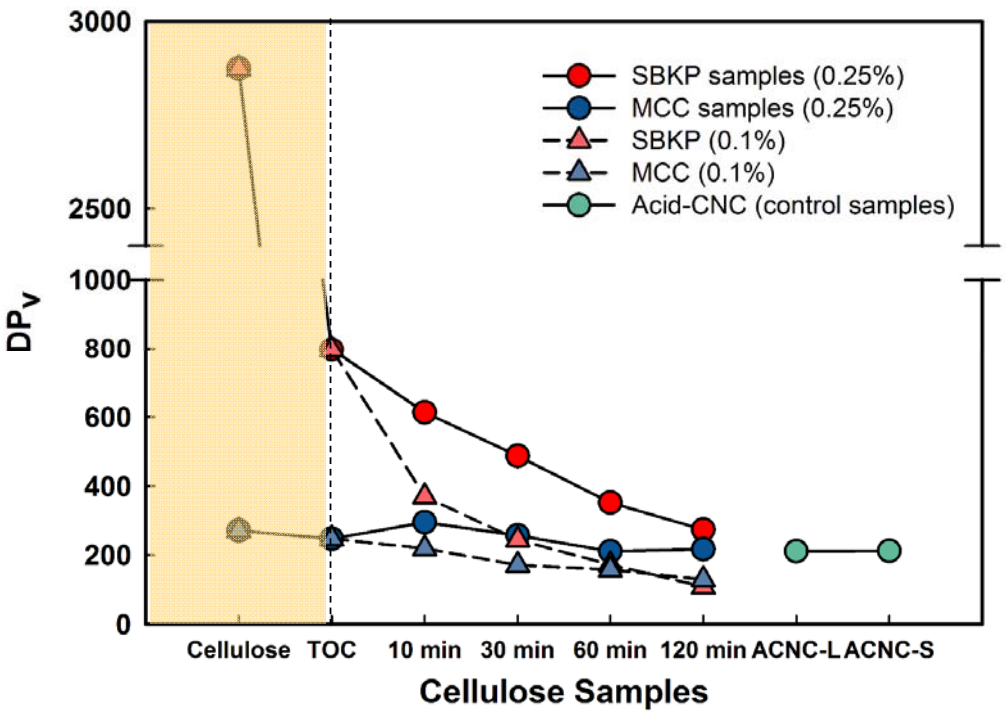
(64% H_2SO_4 at 70 ºC for 30 min)

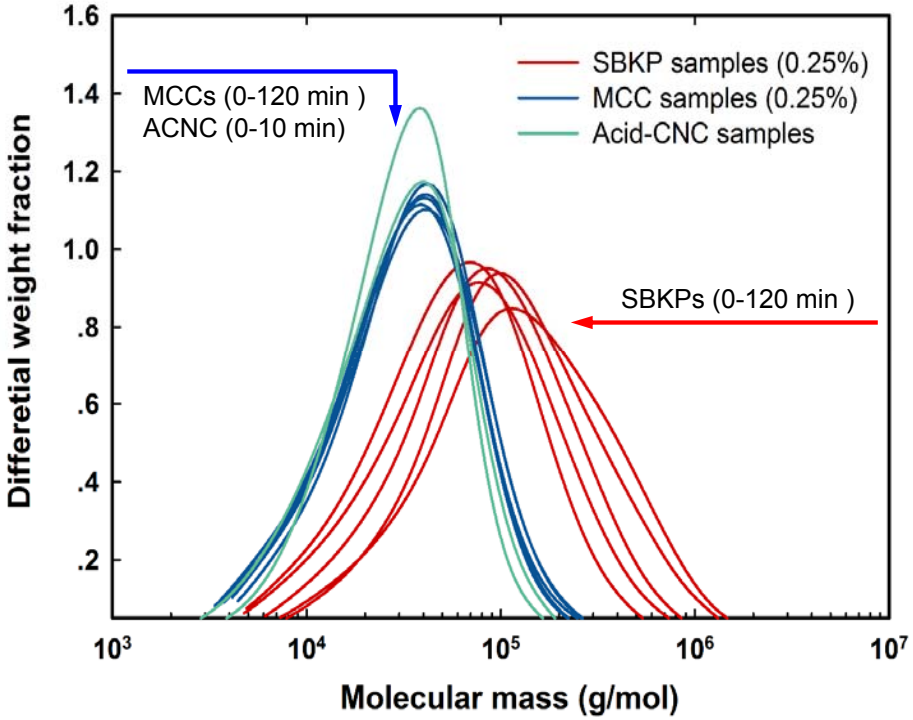
Sample	Mass recovery (%)	Carboxylate content (mmol/g)	DP_v	XRD crystallinity (%)	XRD crystal width (nm)	ξ-Potential (mV)
SBKP	–	0.01	2900	82	3.9	–
SBKP-10	94	1.74	800	81	3.6	–54
SBKP-20	93	1.57	650	83	3.6	–50
MCC	–	0.06	270	90	4.7	–
MCC-10	70	1.24	250	88	4.3	–60
MCC-20	69	1.12	240	88	4.1	–55

- Mass recovery ratios of TEMPO-oxidized SBKP are higher than MCC.
- Carboxylate content of TEMPO-oxidized SBKP are higher.
- Crystal widths of TEMPO-oxidized SBKP are smaller.

Zhou *et al.*, *Biomacromolecules* (2018)

Changes in DP_v and molecular mass of TEMPO-SBKP/MCC during sonication

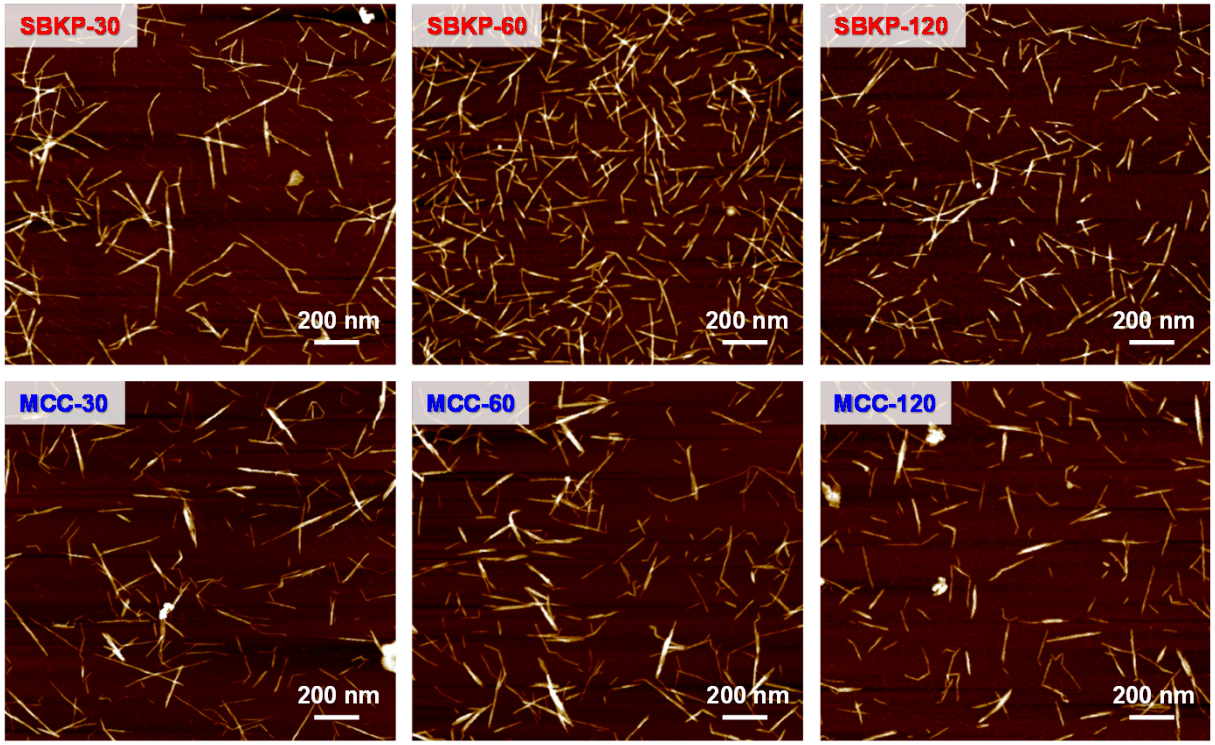


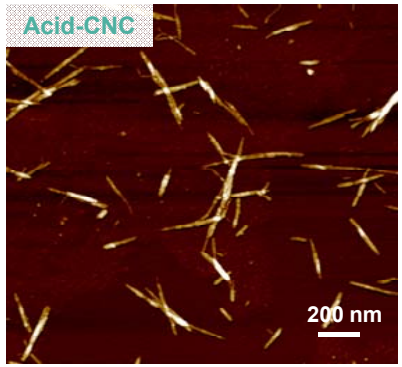


- DP_v values and molecular mass of TEMPO-oxidized celluloses decrease to ~200 by sonication in water.
- The kinetics of DP decrease are concentration-dependent during sonication, and the sonicated TEMPO-CNCs approached limiting DP values, around LODP of Acid-CNCs.

Zhou *et al.*, *Biomacromolecules* (2018)

AFM images of TEMPO-CNCs prepared from SBKP and MCC

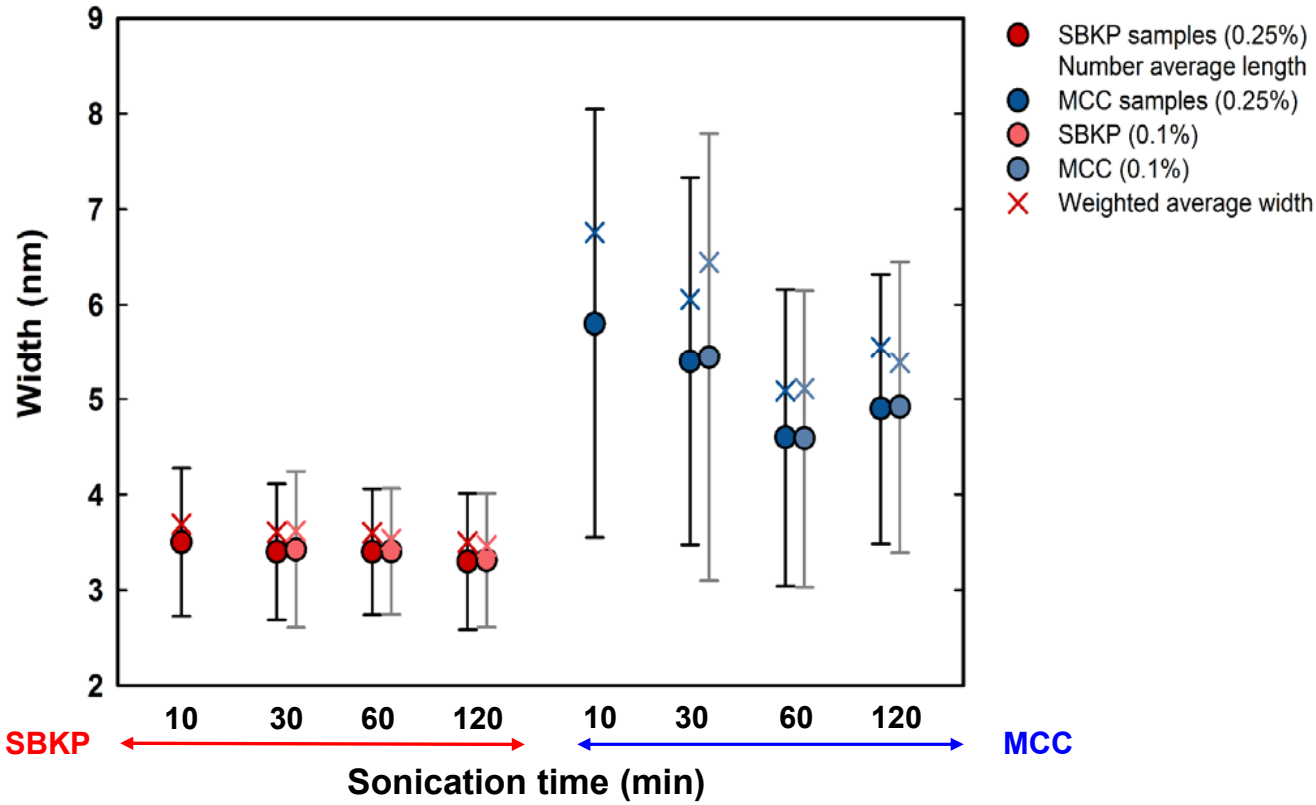


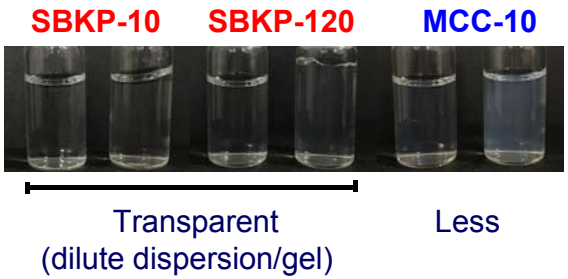


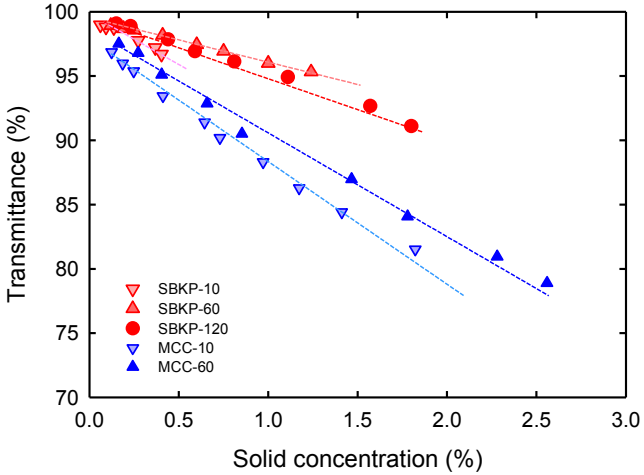
- Needle-like cellulose nanocrystals are prepared from SBKP and MCC.
- Yields of CNCs are 94% and 67% from SBKP and MCC, respectively, whereas CNCs prepared using 64% H_2SO_4 are ~40% in lab experiments.
- Sulfate ester contents are ~0.3 mmol/g, whereas TEMPO-CNCs have carboxylate contents of 1.2–1.7 mmol/g.

Zhou *et al.*, *Biomacromolecules* (2018)

Average widths of TEMPO-CNCs prepared from SBKP and MCC



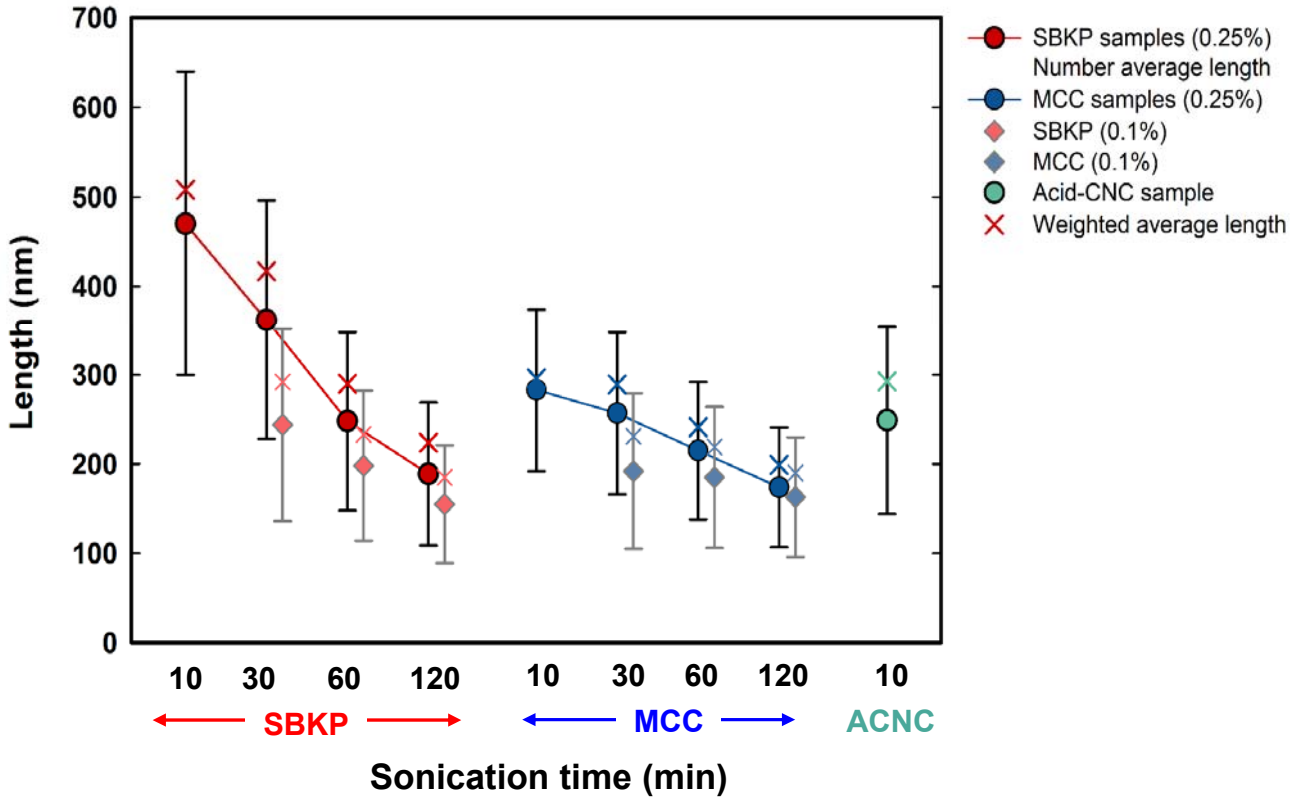




- **TEMPO-CNCs prepared from SBKP have homogeneous widths of ~3.5 nm, whereas those from MCC have heterogeneous widths of ~5 nm, which reflected in the difference in visible light transmittance of both dispersion and the following hydrogels.**

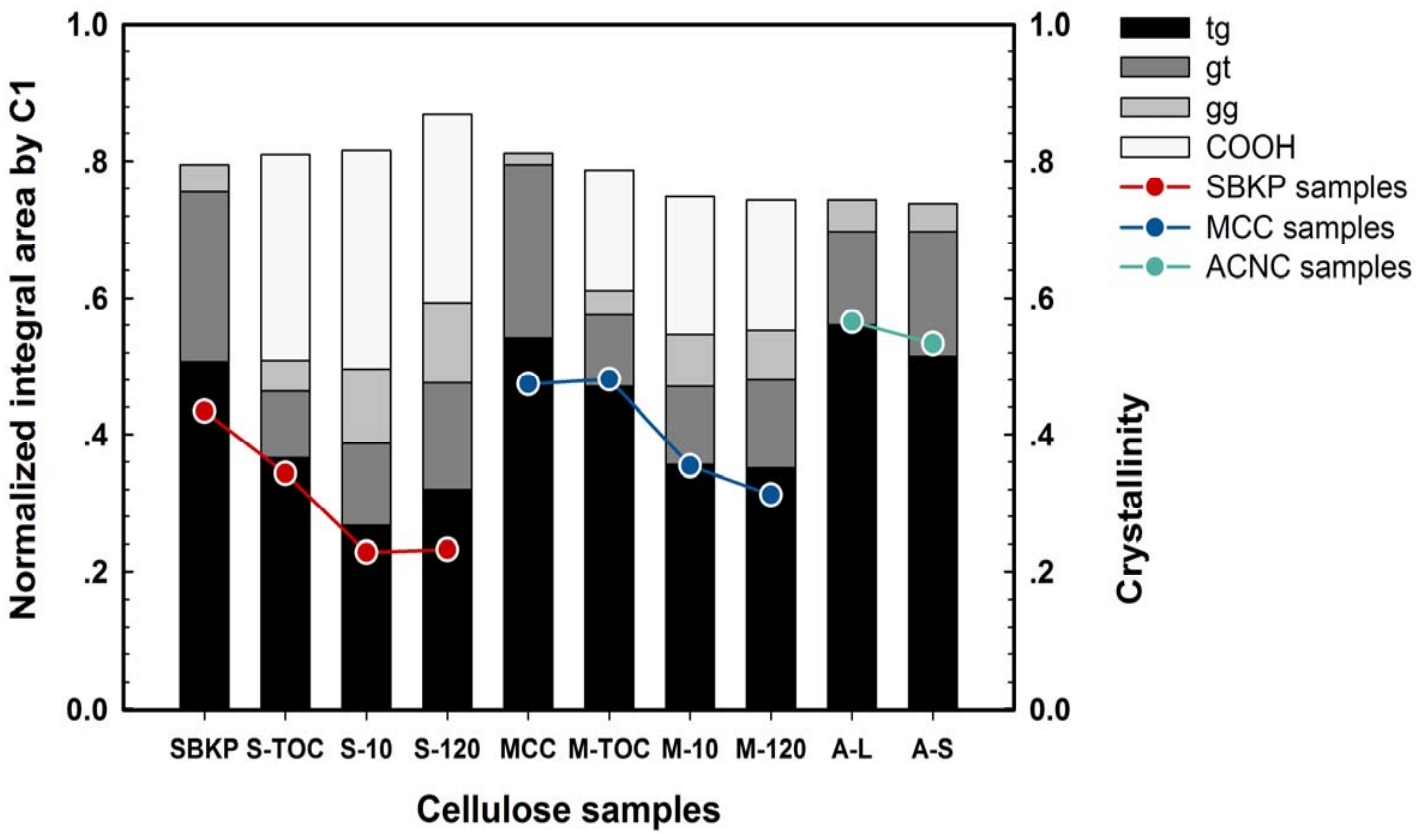
Zhou *et al.*, *Biomacromolecules* (2018)

Average lengths of TEMPO-CNCs prepared from SBKP and MCC



- TEMPO-oxidized celluloses decrease in their lengths ~200 nm in average by sonication in water.
- The scission rate of lengths are consistently with the power law relation between TEMPO-CNCs' average length and sonication time $L \sim t^{-m}$, and influenced by the concentration of the sonication.

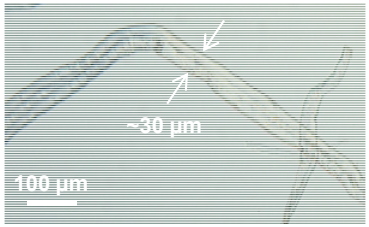
Changes in Crystallinity and C6 conformations of TEMPO-CNCs during sonication



- **Prolonging the sonication from 10 to 120 min do not decrease the crystallinity dramatically, and no surface peeling observed during extensive sonication.**

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

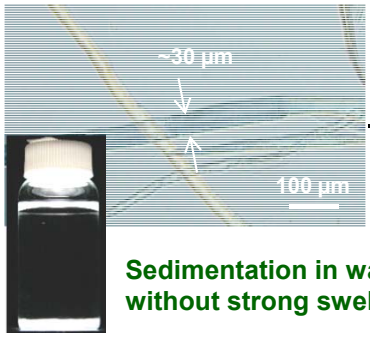
Softwood cellulose fiber



Carboxy content: ~0.01 mmol/g

TEMPO-mediated oxidation in water at pH 10

TEMPO-oxidized cellulose fiber

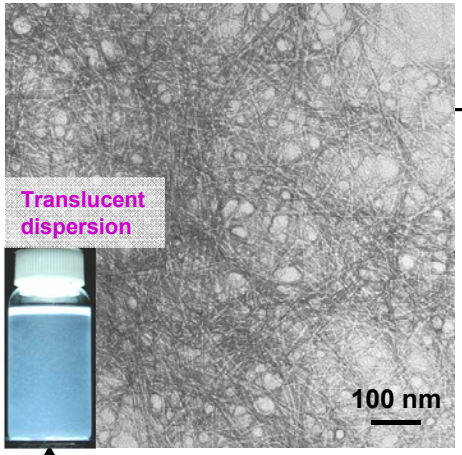


Sedimentation in water without strong swelling

Carboxy content: 0.5−1.7 mmol/g

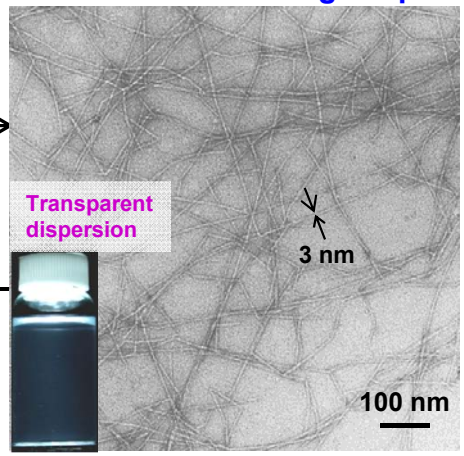
Slight disintegration in water or disintegration in water using TEMPO-oxidized cellulose fiber with low carboxylate contents

Partly nanofibrillated cellulose nanonetwork with heterogeneous structures structures



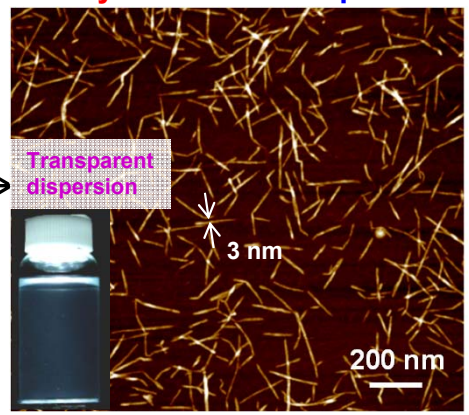
Gentle disintegration in water

Completely individualized TEMPO-oxidized cellulose nanofiber with high aspect ratio

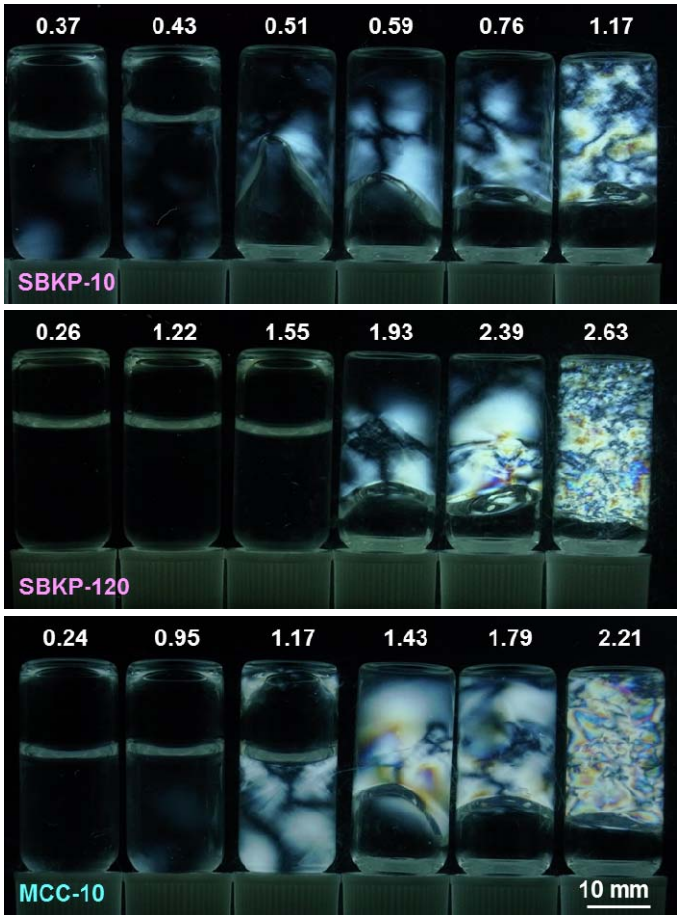


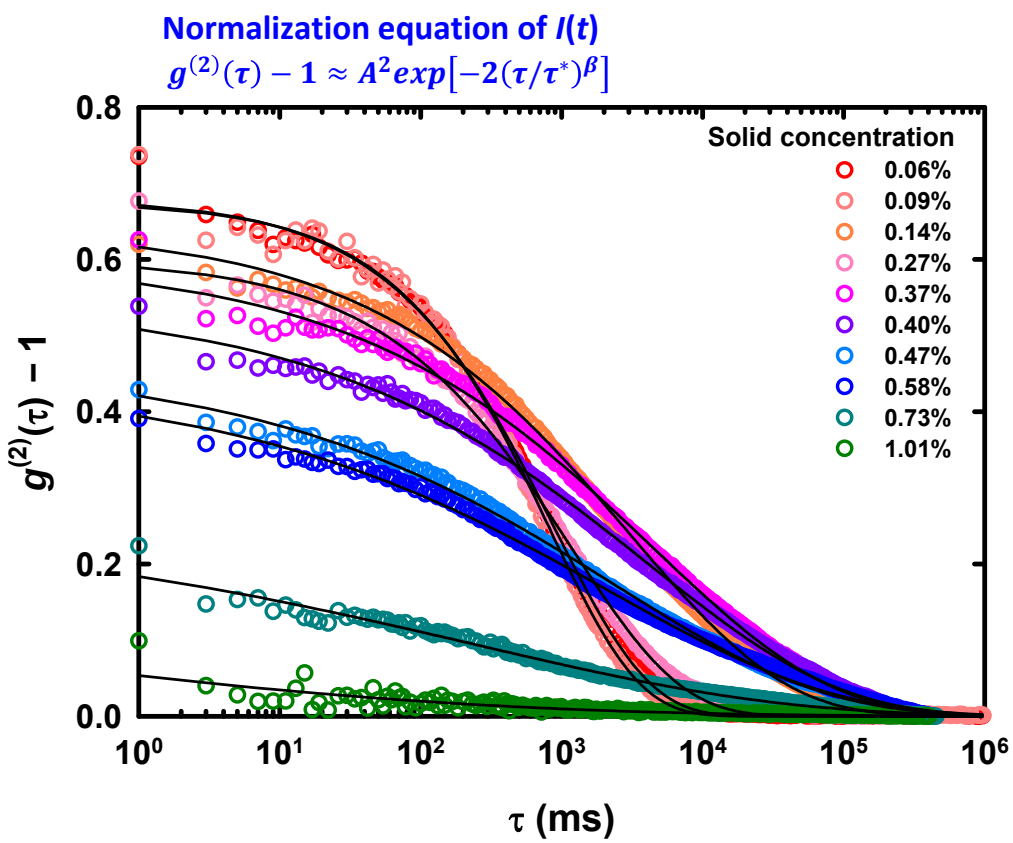
Repeated sonication in water

Needle-like TEMPO-oxidized cellulose nanocrystal with low aspect ratio



Dynamic laser-light scattering (DLS) analysis of aqueous dispersions of TEMPO-CNF and TEMPO-CNCs for characterization of concentration-dependent gelation behavior





- **All the DLS plots are fitted well to the normalization equation,**

Zhou *et al.*, *Biomacromolecules* (2019)

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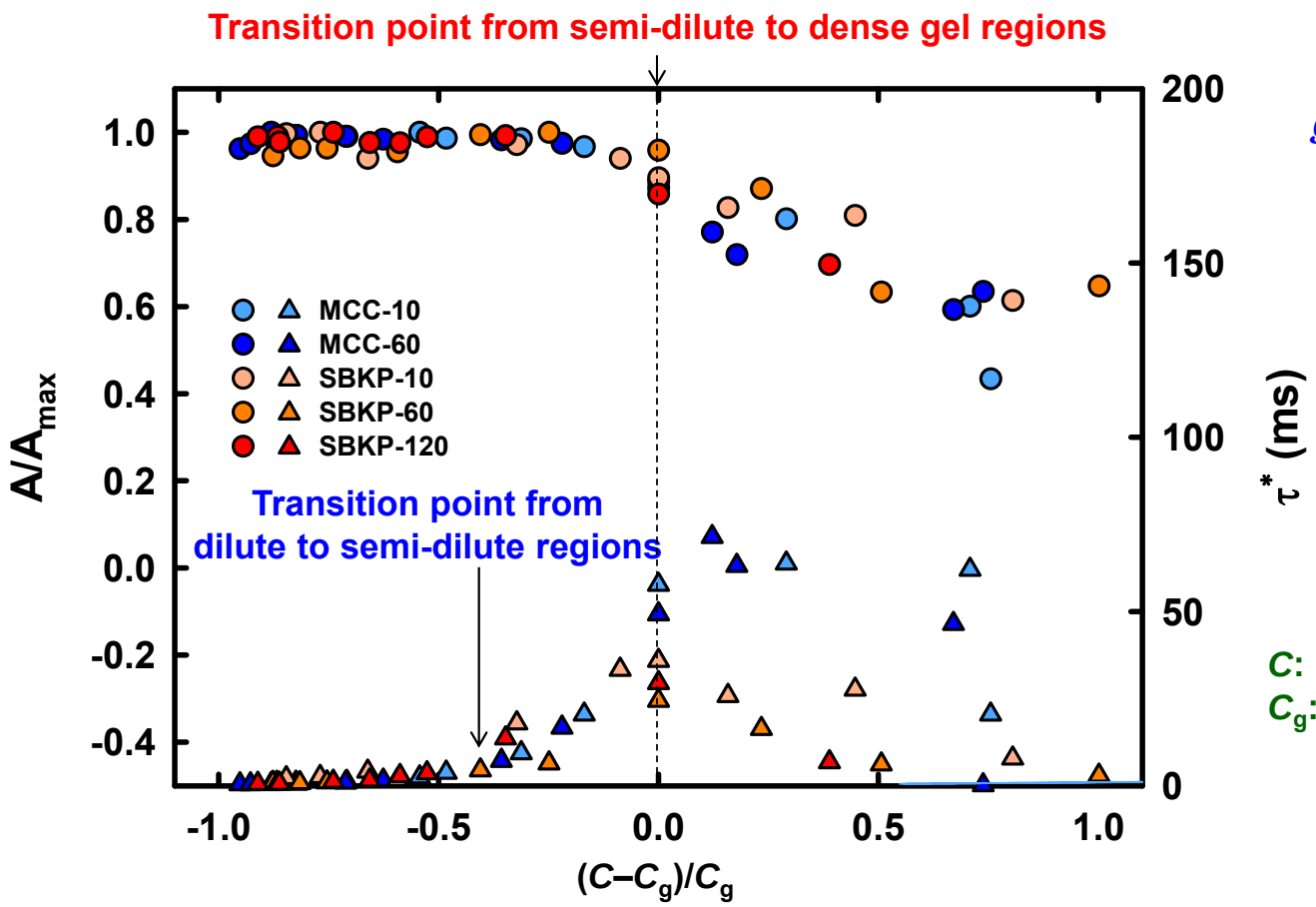


$$g^{(2)}(\tau) - 1 \approx A^2 exp\left[-2(\tau/\tau^*)^{\beta}\right]$$

A: initial amplitude

τ*: relaxation time

β: stretched exponent (disorder degree of system)

C: concentration of TEMPO-CNF or CNC

C_g: concentration of TEPO-CNF or CNC at gelation point

- **DLS data provide information about transition concentrations between dispersed, initial cluster-formed, and gel-formed states of TEMPO-CNC/water systems.**

Dynamic laser-light scattering (DLS) analysis of aqueous dispersions of TEMPO-CNF and TEMPO-CNCs for characterization of concentration-dependent gelation behavior

Theoretical calculation: Effective-medium theory (EMT)

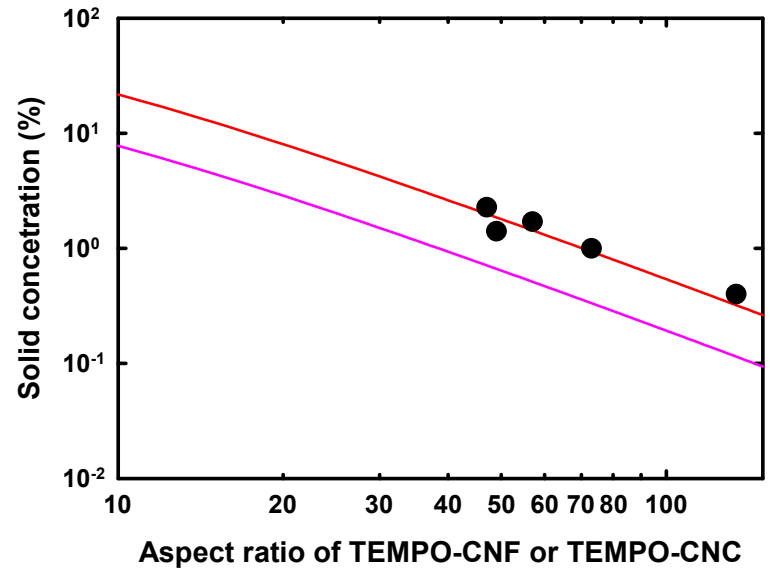
$$\Phi_c = \frac{9L_c(1-L_c)}{2+L_c(15-9L_c)}, \quad \Phi_r = 4\Phi_c$$

$$L_c = \frac{1-e^2}{2e^3}\left[\ln\frac{1+e}{1-e} - 2e\right], \quad e = \sqrt{1-(1/p)^2}$$

Φ_c: Gelation concentration of TEMPO- CNC (%)

Φ_r: Dilute region → semi dilute regtion transition concentrationof TEMPO- CNC (%)

p: Aspect ratio of TEMPO- CNC

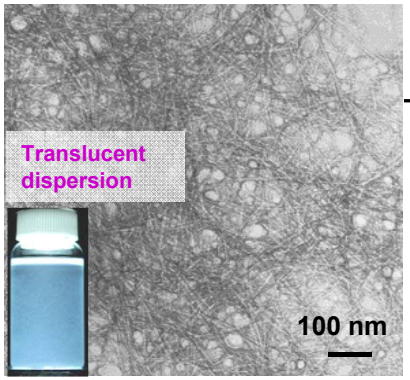


	Sample	Length (nm)	Width (nm)	Aspect ratio	Solid concentration at gel-point determined or calculated by Flow behavior (C_g %)	DLS (C_g %)	EMT ((C_g %))
TEMPO-CNF	SBKP-10	470	3.5	134	~0.5	0.40	0.32
TEMPO-CNC	SBKP-60	248	3.4	73	~1.0	1.00	0.94
	SBKP-120	189	3.3	57	~1.9	1.71	1.42
	MCC-10	283	5.8	49	~1.4	1.41	1.87
	MCC-120	215	4.6	47	~2.3	2.28	2.01

- **TEMPO-CNCs with low aspect ratios can increase in solid concentration in aqueous dispersions.**

Diverse nanocelluloses can be prepared from the same TEMPO-oxidized cellulose fiber: Nano-networks, nanofibers, and nanocrystals with different gelation boundaries

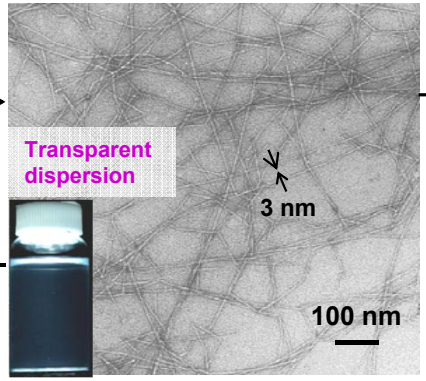
Partly nanofibrillated cellulose nanonetwork with heterogeneous structures structures



Slight disintegration in water or disintegration in water using TEMPO-oxidized cellulose fiber with low carboxylate contents

Gentle disintegration in water

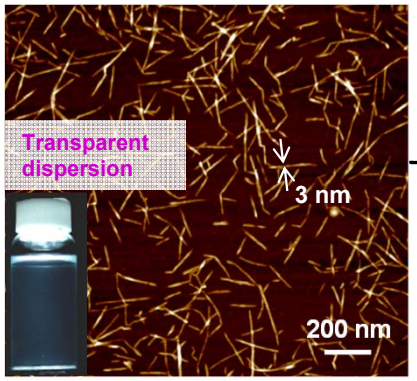
Completely individualized TEMPO-oxidized cellulose nanofiber with high aspect ratio

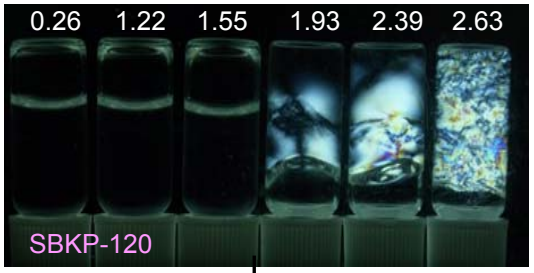


Continuous evaporation

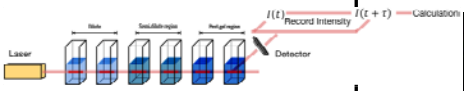
Repeated sonication in water

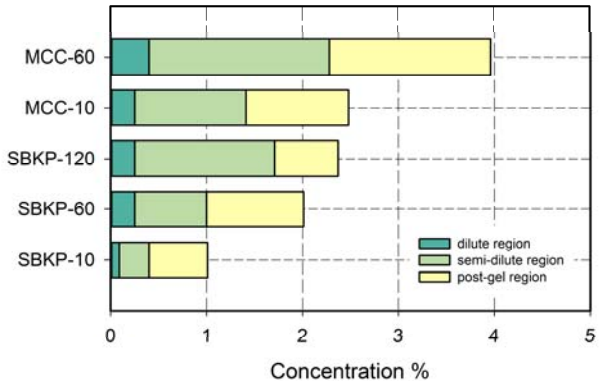
Needle-like TEMPO-oxidized cellulose nanocrystal with low aspect ratio





Dilute dispersion/ gel





	Aspect ratio		Gelation concentration	
TEMPO-CNF	134	x 1/2	0.4%	x 4
TEMPO-CNC	57		1.7%	

Zhou *et al.*, *Biomacromolecules* (2019)

Conclusions

- Diverse nanocelluloses can be prepared from the same TEMPO-oxidized wood cellulose fibers: nano-networks, nanofibers, and nanocrystals
- Solid concentrations at the gelation point can be increased from 0.4% for TEMPO-CNF to 1.7% for TEMPO-CNC, while their aspect ratios decreased from 134 to 57, respectively.
- TEMPO-CNCs are categorized as new nanocelluloses different from conventional CNC.
- Because these TEMPO-nanocelluloses of nano-networks, nanofibers, and nanocrystals have abundant sodium carboxylate groups on microfibril surfaces, they can be used as scaffolds of further functionalization with simple ion-exchange from sodium to other metal ions and alkylammonium ions.
- TEMPO-mediated oxidation of crystalline native celluloses can individualize cellulose microfibrils with less damage, and therefore can visualize them by TEM or AFM.

Thank you

PRESENTED BY:

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