Aalto University
School of Chemical
Technology

Modern applications of cellulose-based fibres and nanofibres

CHEM-E2140

Cellulose-based fibres

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Learning outcomes

After this lecture, the student will be able to:

- List the most prominent (potential) application areas of nanocellulose
- Describe the main challenges in utilizing nanocellulose
- Be aware of the contemporary case studies of nanocellulose and applications

Outline

(1) Nanocellulose: recap from the previous lecture
(2) Nanopaper and other materials from nanofibrillar cellulose
  - Gas separation
  - Transistor supports
(3) Cellulose nanocomposites
  - Cellulose nanofibre (CNF) composites
  - Cellulose nanocrystal (CNC) composites
(4) CNF hydrogels
  - Biomedical applications
  - Solid-state cell factories

Basic types of nanocellulose

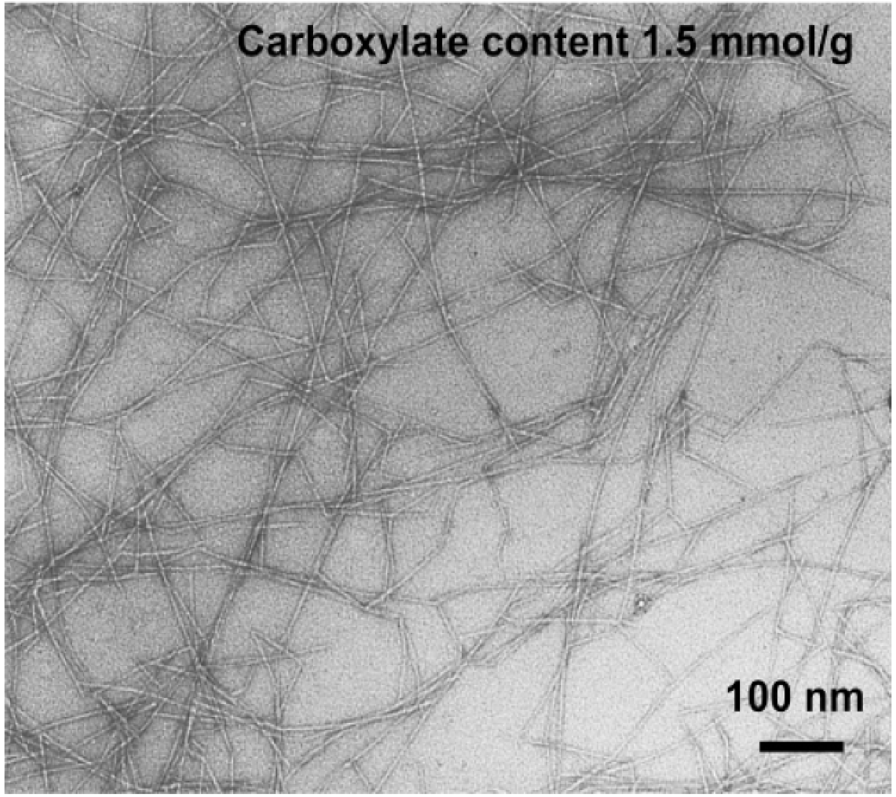
(1) Cellulose nanofibres (CNFs)

- Mechanically isolated microfibrils
- Chemically isolated microfibrils (TEMPO-oxidation)
- Cacterial cellulose

(2) Cellulose nanocrystals (CNCs)

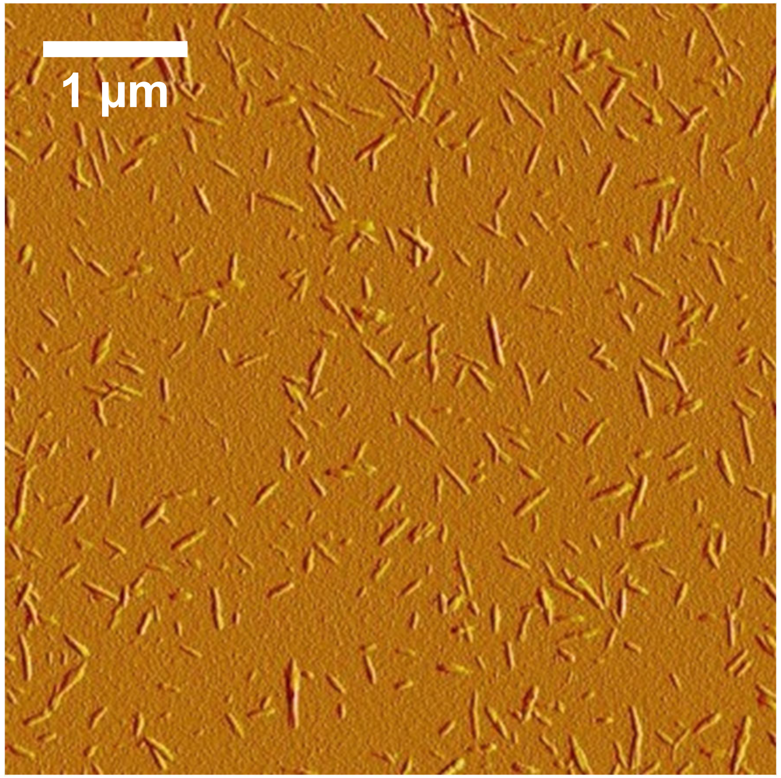
- Rods of highly crystalline cellulose, isolated by acid hydrolysis

Nanofibrillar cellulose (NFC)



- Long threads of isolated cellulose microfibrils
- Very high aspect ratio
- Length: 0.5-5 µm
- Width: 3-50 nm
- Highly charged when prepared by chemical isolation with TEMPO-oxidation
- Low charge density when prepared with mechanical isolation

Cellulose nanocrystals (CNCs)



- Rigid rods of crystalline cellulose
- Length: 50-1000 nm
- Width: 3-20 nm
- Usually charged with sulphate groups on the crystal surface
- Suspensions form spontaneously chiral nematic liquid crystal phases

Existing commercial applications of nanocellulose

Adult diapers
(nanofibres, Japan)

Viscosity control in
oil drilling
(nanocrystals,
Canada)

Ink dispersing in
ball point pens
(nanofibres, Japan)

Existing commercial applications from nanocellulose

Hydrogels for tissue growth applications (nanofibres, Finland)

Nanopaper
(networks of cellulose nanofibres)

Films from cellulose nanofibres

- Prepared by casting a film of cellulose nanofibres (CNF) by getting rid of the water in CNF suspension / gel in one way or another

- The resulting film (a.k.a. ***nanopaper***) is often unusually tough and strong

- The CNF film is often aimed at being optically transparent

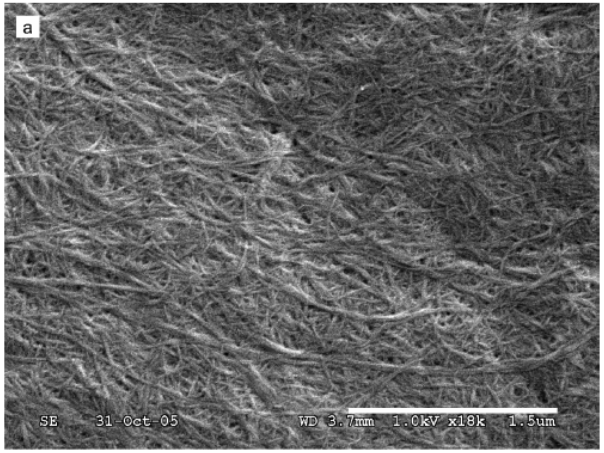
- High density of nanopaper results in good gas barrier properties

- Maintaining strength, barrier properties etc. under humid conditions is a current research challenge with nanopaper

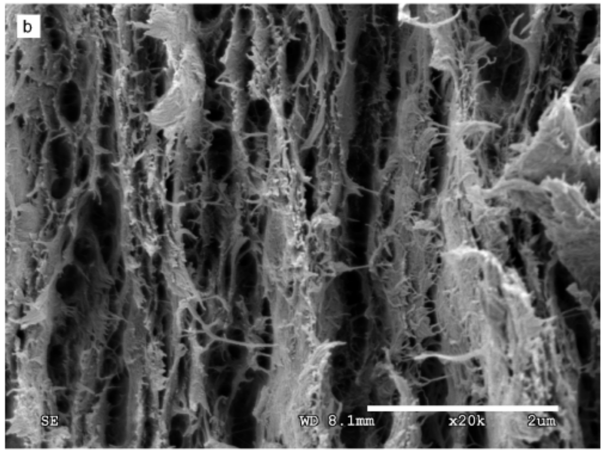
Nanopaper

Nanofibres obtained mechanically from bleached sulphite pulp after enzymatic pretreatment

The first nanopapers were prepared simply by vacuum filtration.



SEM image of the nanopaper surface

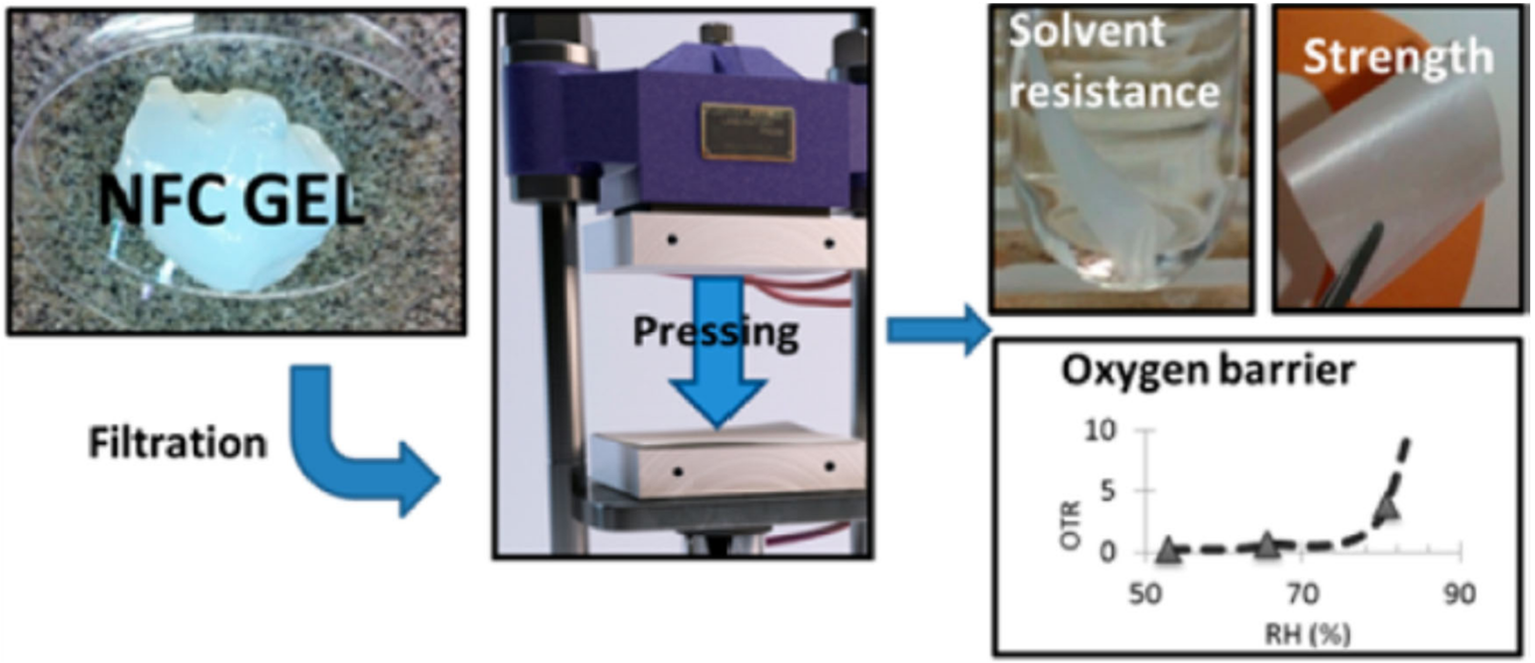


SEM image of the nanopaper fracture surface, exposing a layered structure.

Henriksson et al. *Biomacromolecules* **2008**, *9*, 1579.

Nanopaper preparation

- Generally prepared by a batch process with filtering
- Hot pressing is applied to squeeze residual water out of the CNF network

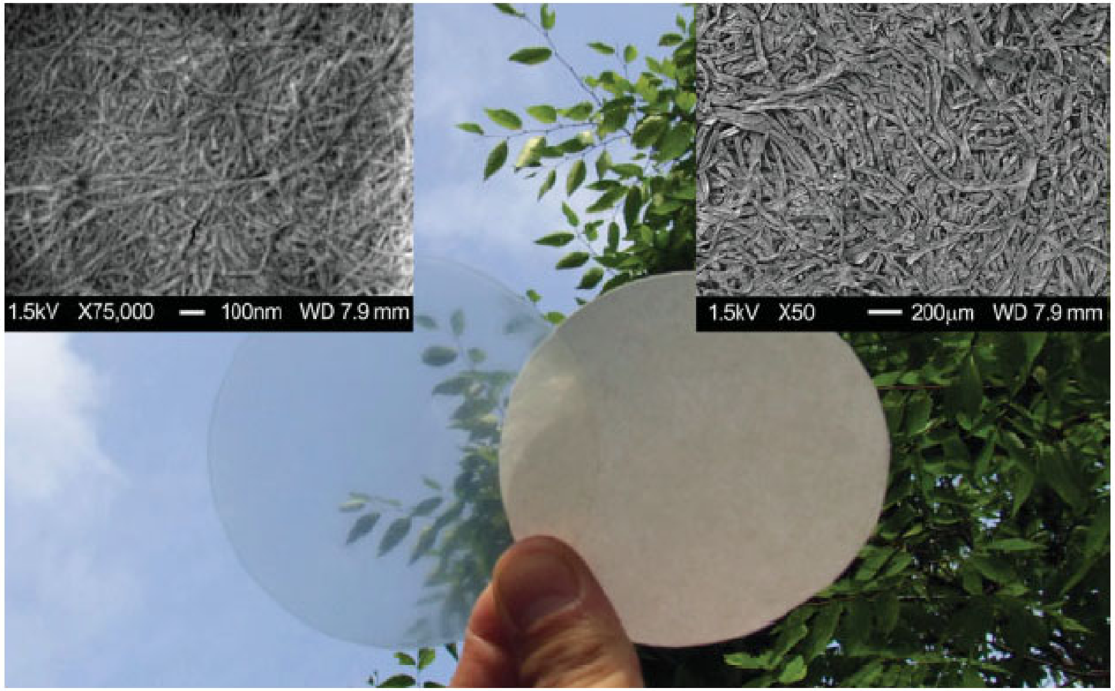


Österberg et al. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4640.

Nanopaper

Nanofibers obtained mechanically from wood fibres after chlorite delignification

Nano-
paper

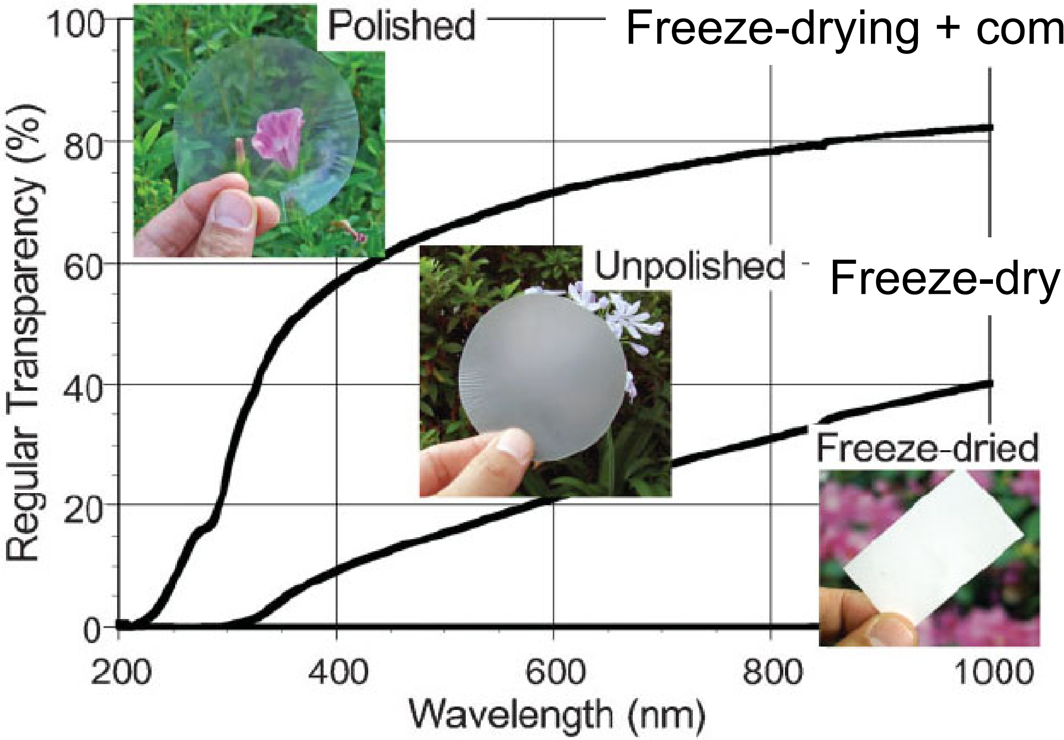


Paper

Figure 1. Optically transparent nanofiber paper (left) composed of 15 nm cellulose nanofibers (upper left, scale bar in inset: 100 nm) and conventional cellulose paper (right) composed of 30 μm pulp fibers (upper right, scale bar in inset: 200 μm).

Nogi et al. *Adv. Mater.* **2009**, *21*, 1595.

Nanopaper



Freeze-drying + compression + polishing

Freeze-drying + compression

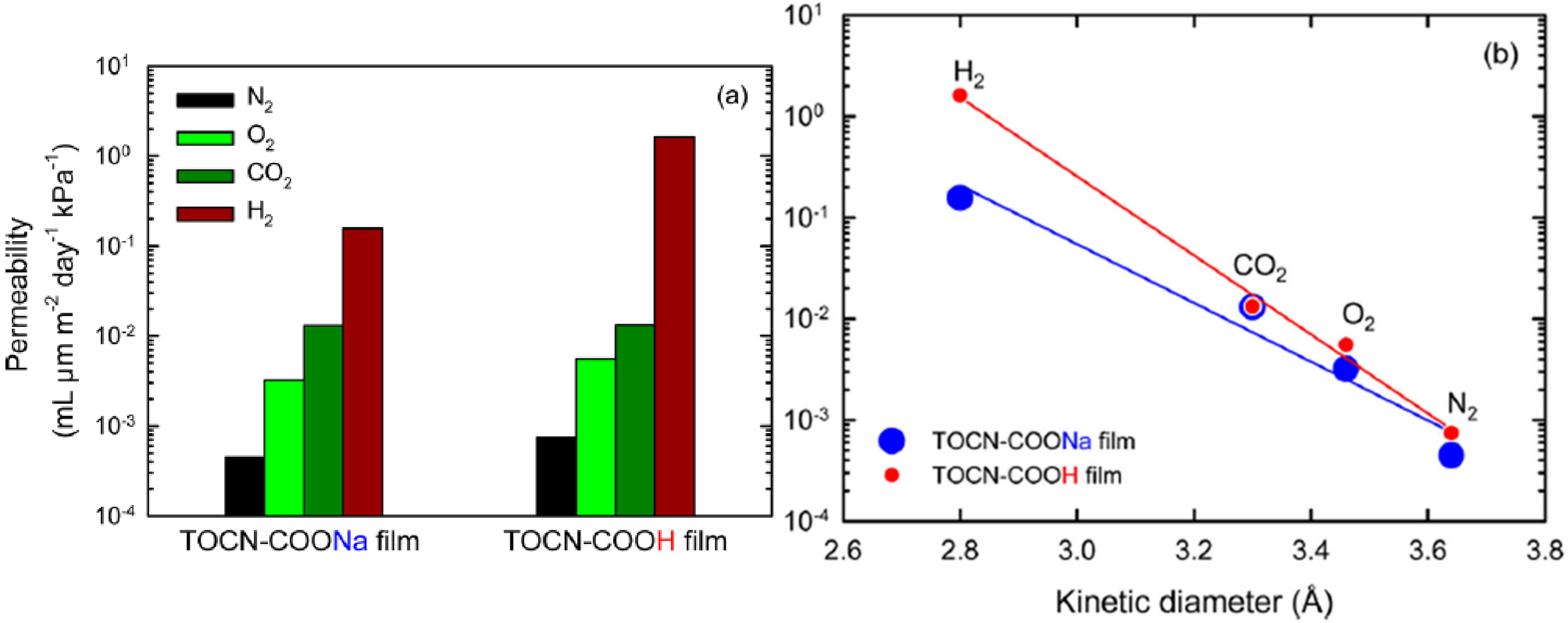
Freeze-drying
an NFC suspension

Surface roughness leads to light scattering
→ removed by polishing

Nogi et al. *Adv. Mater.* **2009**, *21*, 1595.

Selective gas permeability of nanopaper

- NFC prepared by TEMPO-mediated oxidation (TOCN)
- The counter ion of carboxylic groups makes a difference, either a proton (TOCN-COOH) or sodium (TOCN-COONa)



→ Closer packing of fibrils in with Na^+ counterion (TOCN-COONa)

Fukuzumi et al. *Biomacromolecules* **2013**, *14*, 1705.

Selective gas permeability of nanopaper

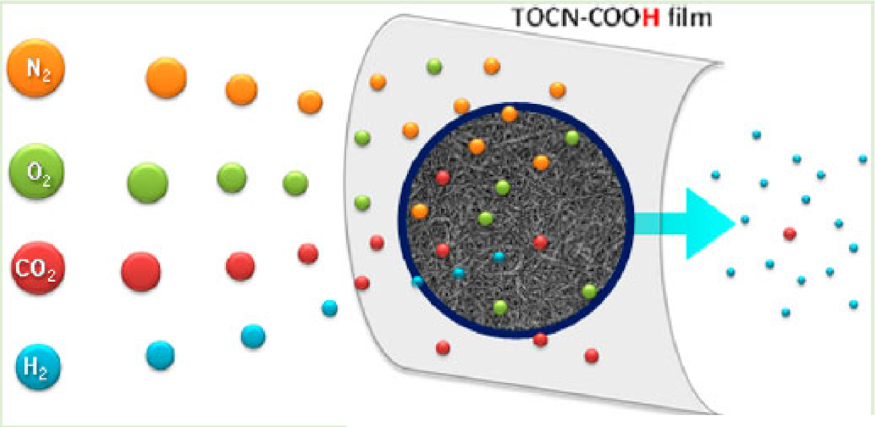
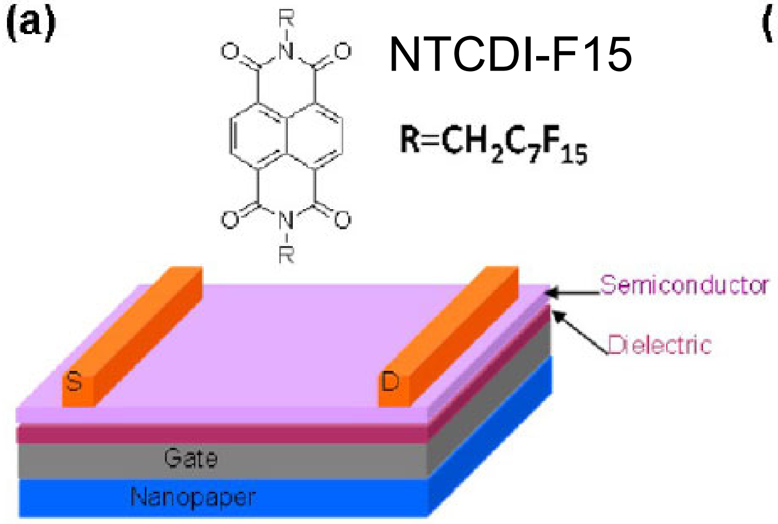


Table 1. Relative Gas Permeability Ratios of TOCN and Commercial Films

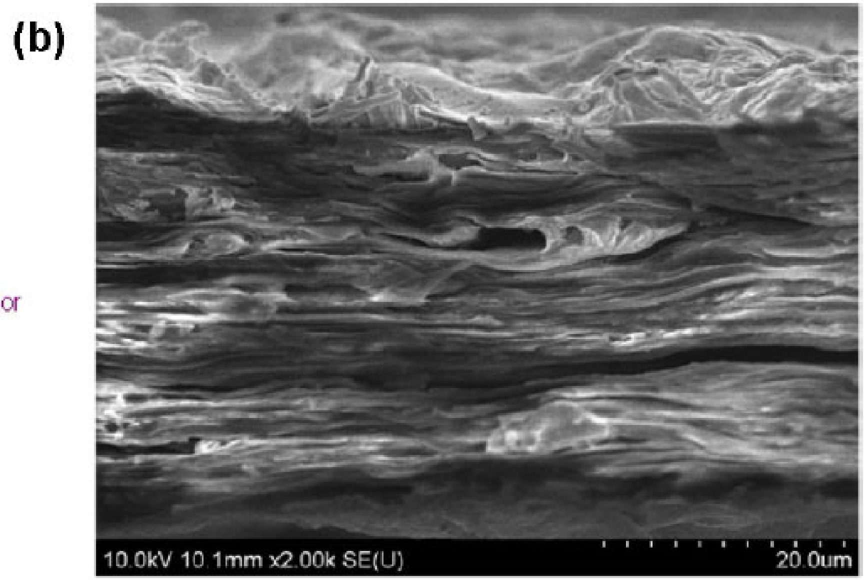
	H_2/N_2	H_2/CO_2	H_2/O_2	O_2/N_2	CO_2/N_2
TOCN-COONa	350	12	49	7.2	29
TOCN-COOH	2200	24	290	7.4	92
cellophane	220	14	39	5.6	16
PET	190	5.3	30	6.2	35
PE	8.5	0.58	3.0	2.8	15

Fukuzumi et al. *Biomacromolecules* **2013**, *14*, 1705.

Nanopaper as a transistor support



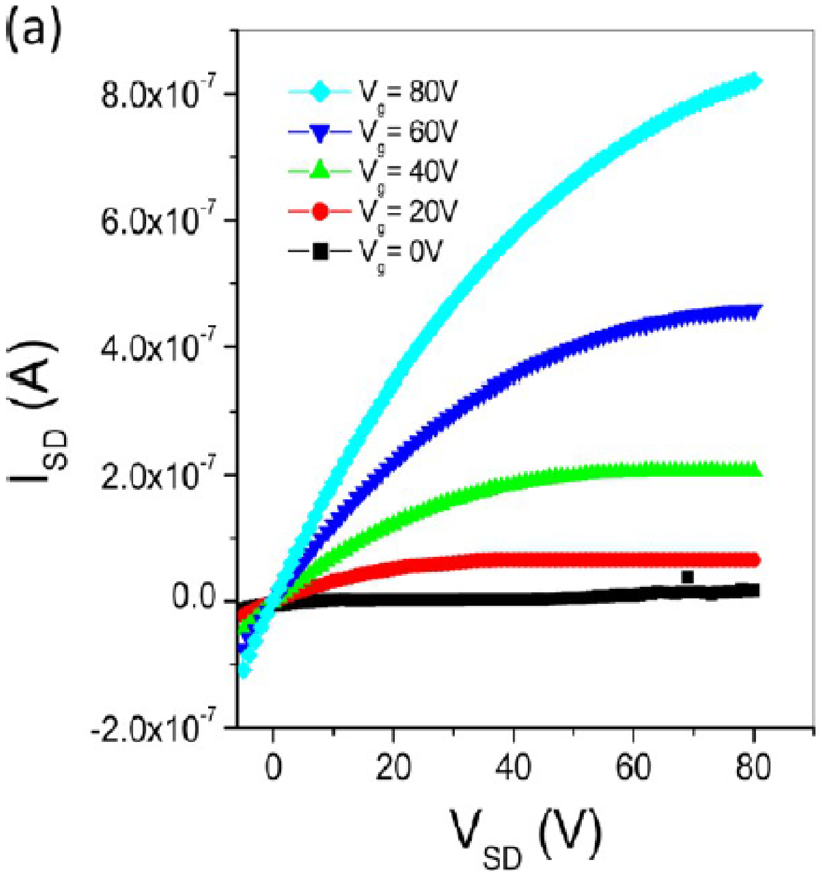
Cross sectional SEM from transistor



Semiconductor: NTCDI-F15 semiconductor film
Dielectric: poly(methyl methacrylate) film
Gate electrode: single-walled carbon nanotubes
Nanopaper: film from TEMPO-oxidized NFC

Huang et al. *ACS Nano* **2013**, *7*, 2106.

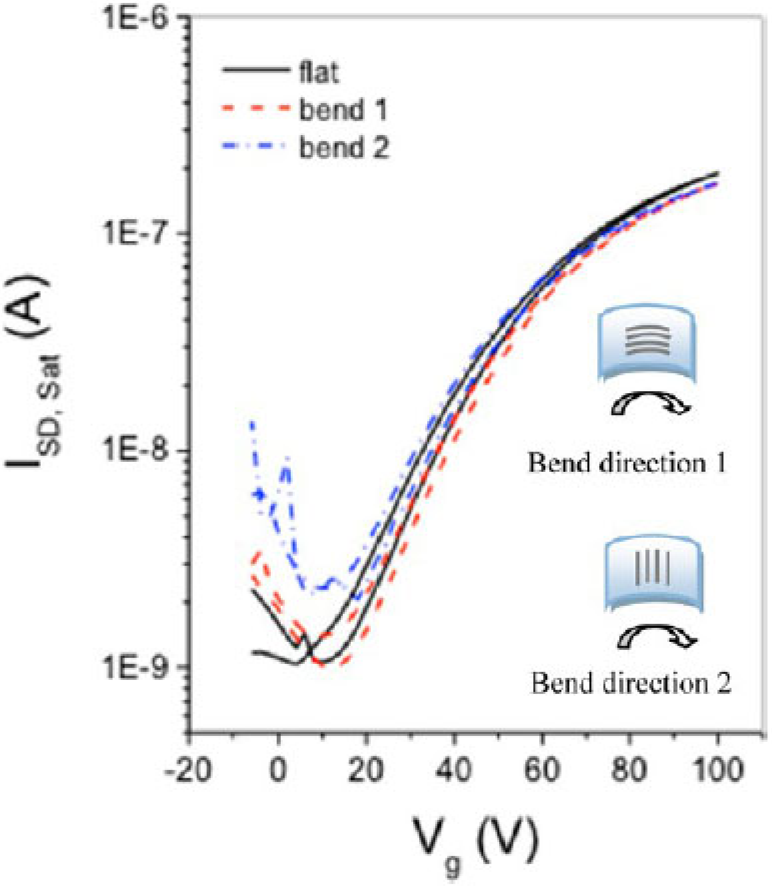
Nanopaper as a transistor support



- The constructed multilayer material works well as a field-effect transistor

Huang et al. *ACS Nano* **2013**, *7*, 2106.

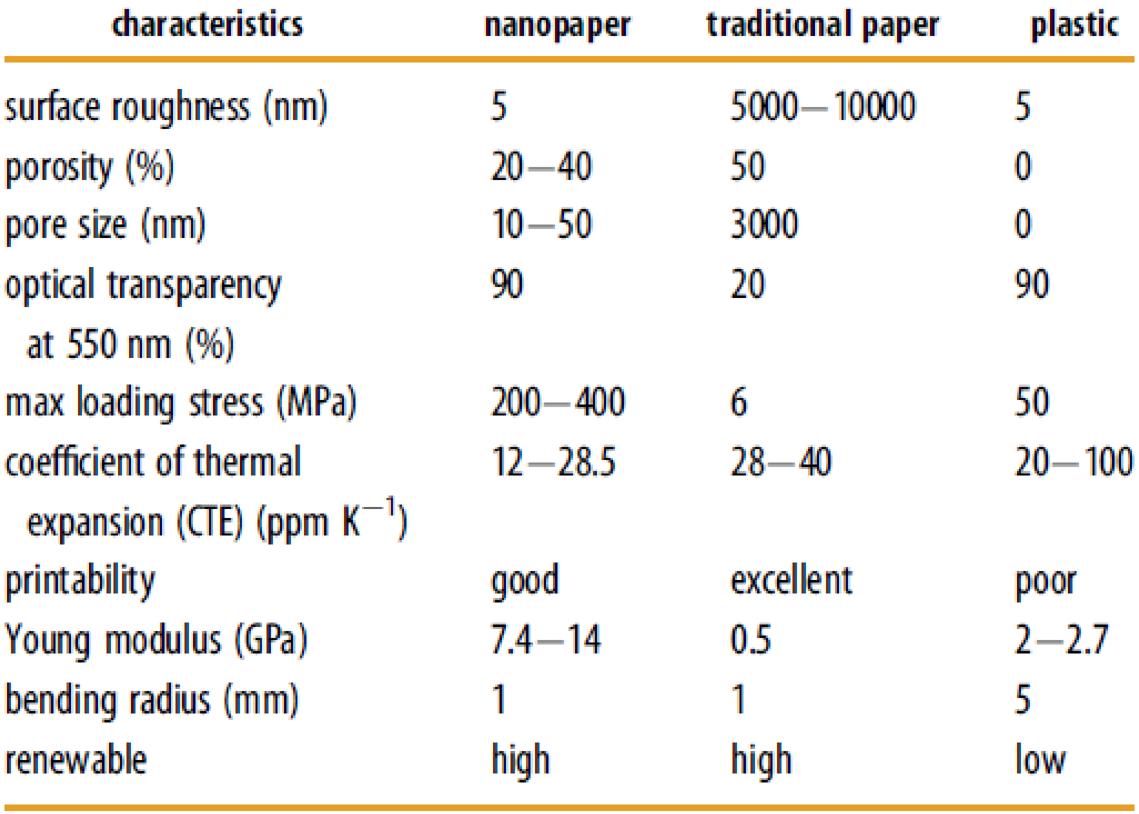
Nanopaper as a transistor support



- Bending has little effect on the transistor performance of the material

Huang et al. *ACS Nano* **2013**, *7*, 2106.

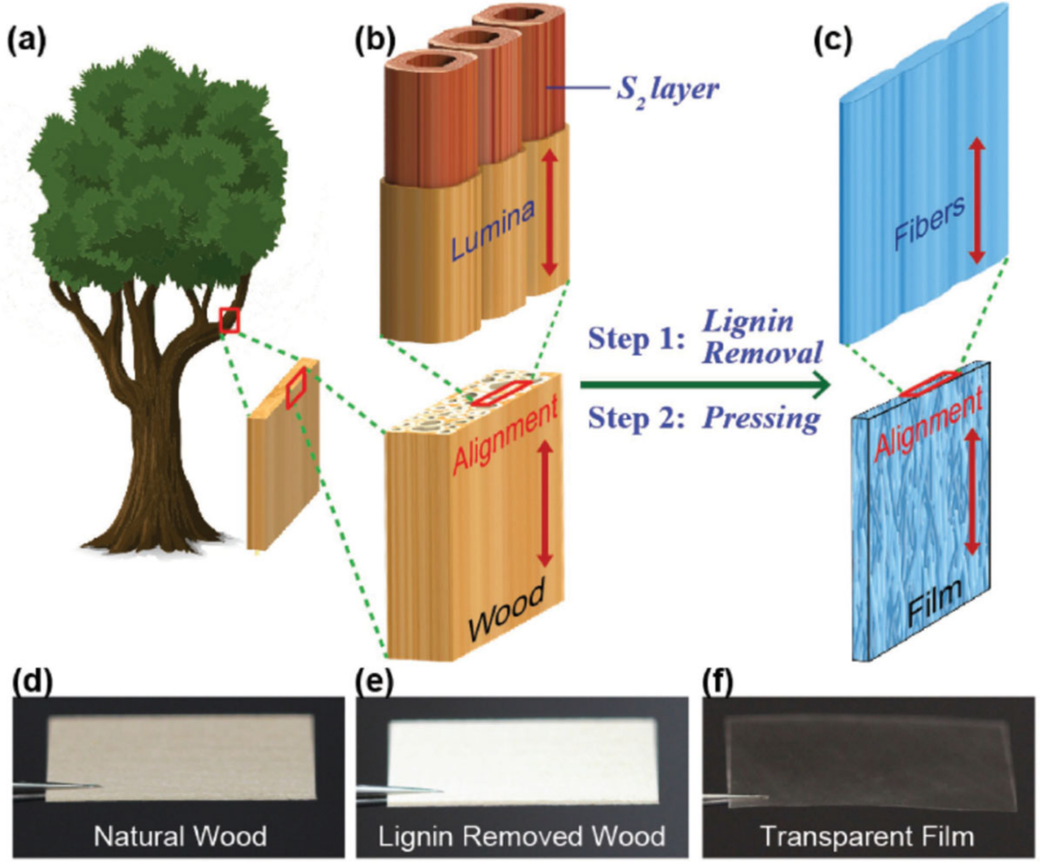
Comparison of bending transistor supports



characteristics	nanopaper	traditional paper	plastic
surface roughness (nm)	5	5000–10000	5
porosity (%)	20–40	50	0
pore size (nm)	10–50	3000	0
optical transparency at 550 nm (%)	90	20	90
max loading stress (MPa)	200–400	6	50
coefficient of thermal expansion (CTE) (ppm K^{-1})	12–28.5	28–40	20–100
printability	good	excellent	poor
Young modulus (GPa)	7.4–14	0.5	2–2.7
bending radius (mm)	1	1	5
renewable	high	high	low

Huang et al. *ACS Nano* **2013**, *7*, 2106.

Nanopaper from aligned CNFs

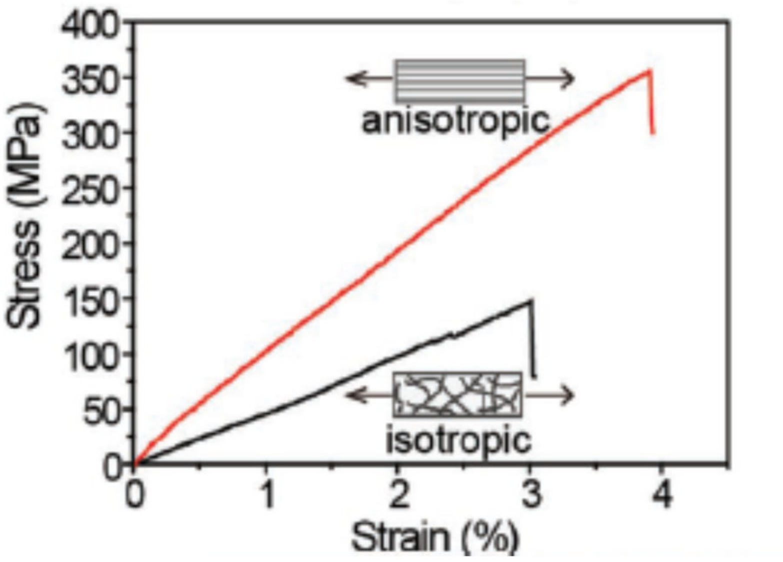


Wood structure of aligned fibres *and* aligned microfibrils (secondary wall) is preserved upon delignification, resulting in nanopaper of aligned CNFs

Zhu et al. *Adv. Mater.* **2017**, *29*, 1606284.

Aligned CNF vs. isotropic CNFs

Tensile strength



Isotropic nanopaper sample here may be deliberately downplayed (inferior strength)

- Aligned CNFs lead to a stronger “nanopaper” (350 MPa tensile strength)
- Modern nanopapers usually have tensile strengths at ~200-300 MPa

Zhu et al. *Adv. Mater.* **2017**, *29*, 1606284.

Cellulose nanocomposites

Nanocomposites – why?

- Nanoparticles are small

→ High surface area

- Stress transfer between reinforcing material and continuous matrix occurs via the interface

→ Much higher stress transfer from reinforcing nanoparticles than from bigger reinforcing particles

Cellulose nanocomposites

- Cellulose nanocomposites usually consist of cellulose nanofibres or cellulose nanocrystals embedded in a continuous polymer matrix

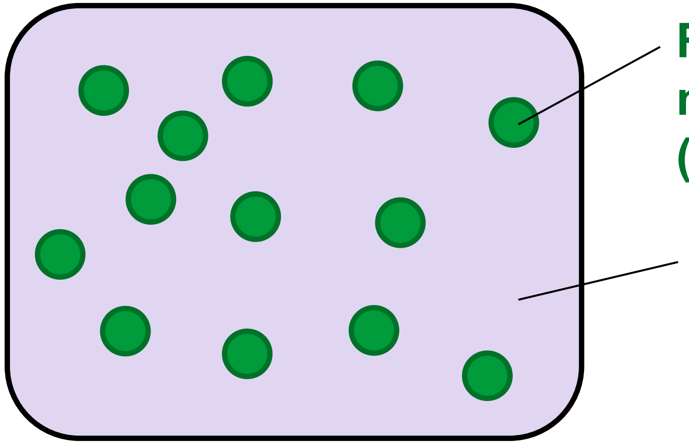
- The challenge is often to retain the nanometer dimensions of the cellulosic objects (i.e., prevent their aggregation)

- One of the big trends is to end up with materials that would be equal to plastics (or to surpass the properties of plastics)

- Another trend is to prepare stimuli-responsive composites for niche applications

Nanocomposites from nanocellulose

Schematic cross section
of a nanocomposite



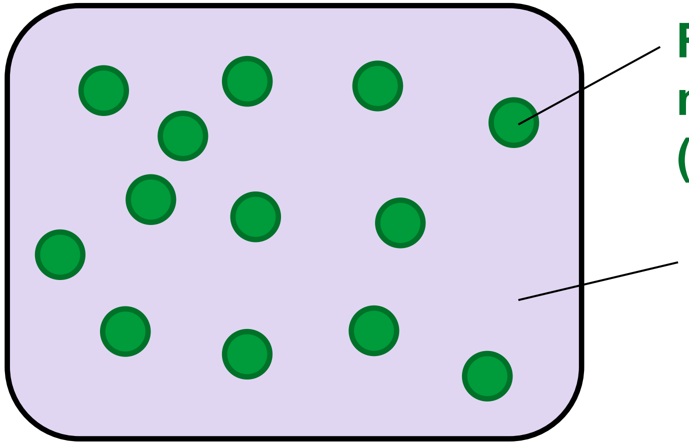
Reinforcing phase: Nanofibril or nanocrystal cross section (cellulose)

Continuous polymer matrix
(preferrably from a biodegradable polymer)

OFTEN REFERRED TO SCENARIO: Poly(lactic acid) as a continuous matrix and nanofibrillar cellulose as the reinforcing phase. *Both* are bio-based and biodegradable.

Nanocomposites from nanocellulose

Schematic cross section
of a nanocomposite



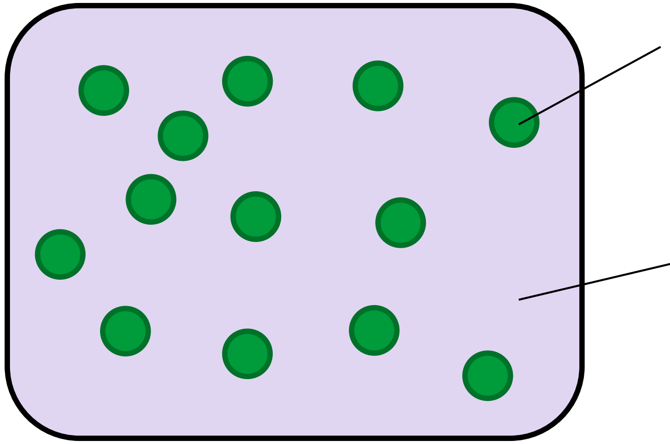
Reinforcing phase: Nanofibril or nanocrystal cross section (cellulose)

Continuous polymer matrix
(preferrably from a biodegradable polymer)

WHY CELLULOSE?
Poly(lactic acid) is brittle and weak on its own. Cellulose with strong mechanical properties would boost its strength.

Nanocomposites from nanocellulose

Schematic cross section
of a nanocomposite

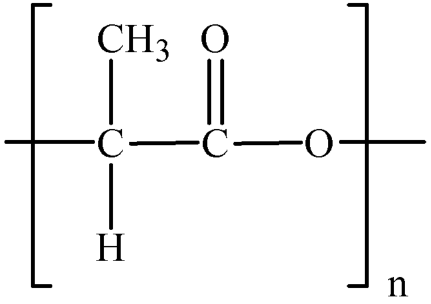


Reinforcing phase: Nanofibril or nanocrystal cross section (cellulose)

Continuous polymer matrix
(preferrably from a biodegradable polymer)

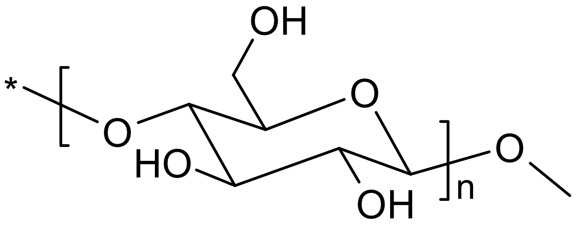
WHY NANOCOMPOSITES?
Nanocellulose has a very large surface area, that is, a lot of contact points with the continuous poly(lactic acid) matrix, plus it is very strong.

Nanocomposites from nanocellulose


$$\left[\,-\mathrm{CH(CH_3)}-\mathrm{C(=O)}-\mathrm{O}-\,\right]_n$$

Poly(lactic acid)

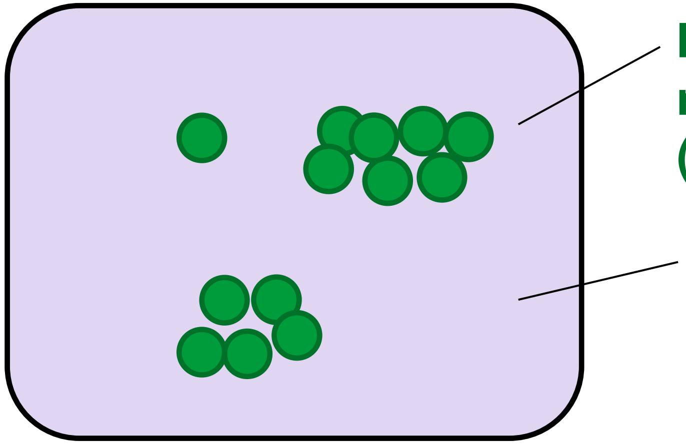
Dissolves in hydrophobic solvents



Cellulose

Dissolves in very few solvents

Nanocomposites from nanocellulose



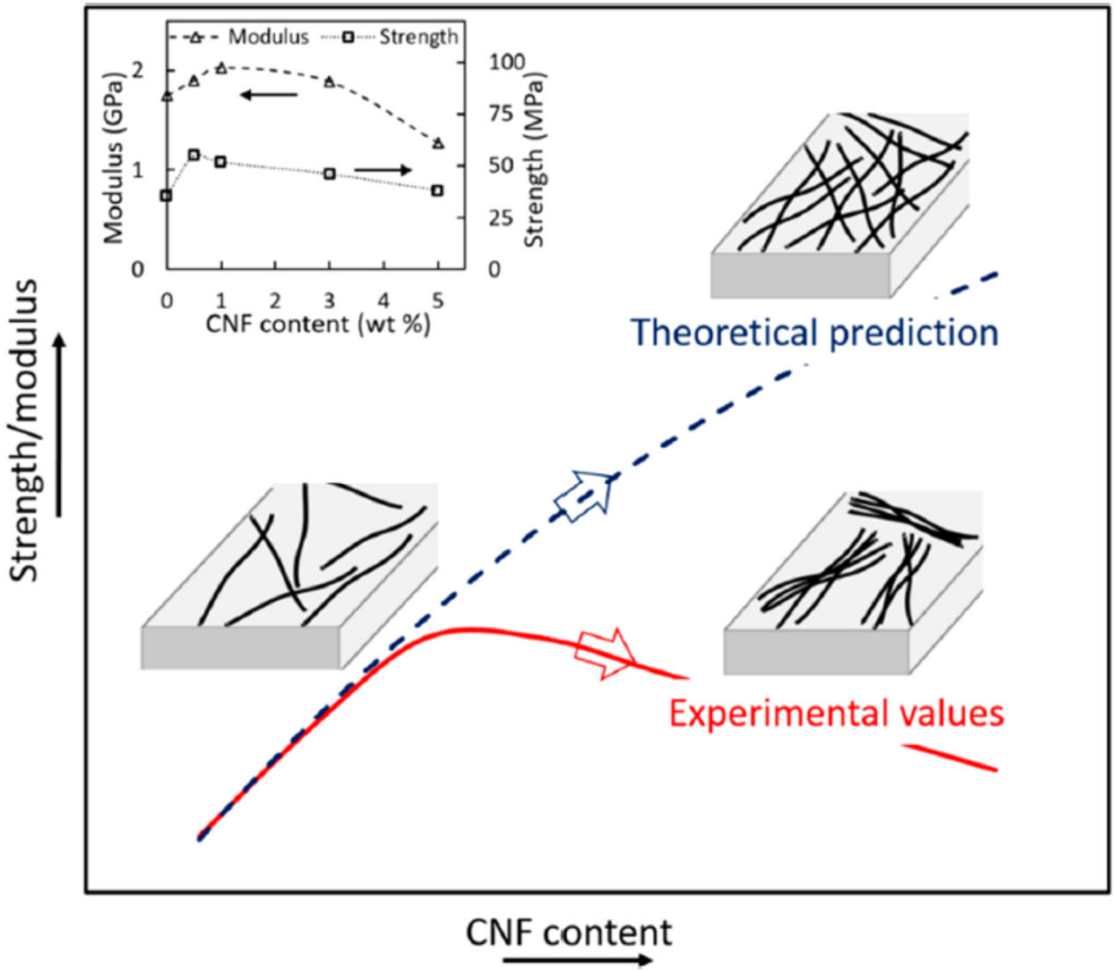
Schematic cross section
of a nanocomposite

Reinforcing phase: Nanofibril or nanocrystal cross section (cellulose)

Continuous polymer matrix
(preferrably from a biodegradable polymer)

WHAT IS THE PROBLEM?
Cellulose aggregates easily with itself. It is incompatible with nearly anything else than the lignin/hemicellulose matrix in the plant cell wall.
→ Loss in surface area → No nanocomposite anymore

Aggregation of nanocellulose

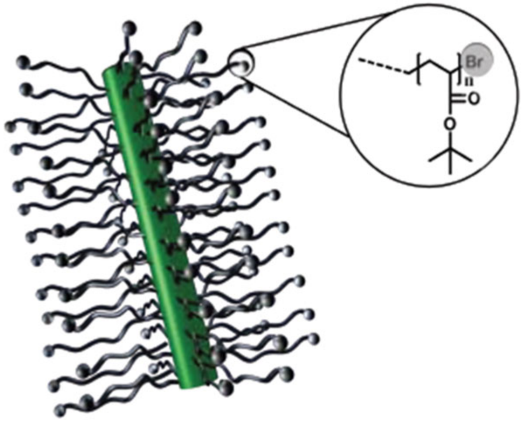


Because of aggregation, nanocellulose reinforcement often works well only with low nanocellulose contents.

Biomacromolecules **2018**, *19*, 2341.

Nanocellulose modification for nanocomposites

How does one solve the problem?
One approach: modify the surface of nanocellulose



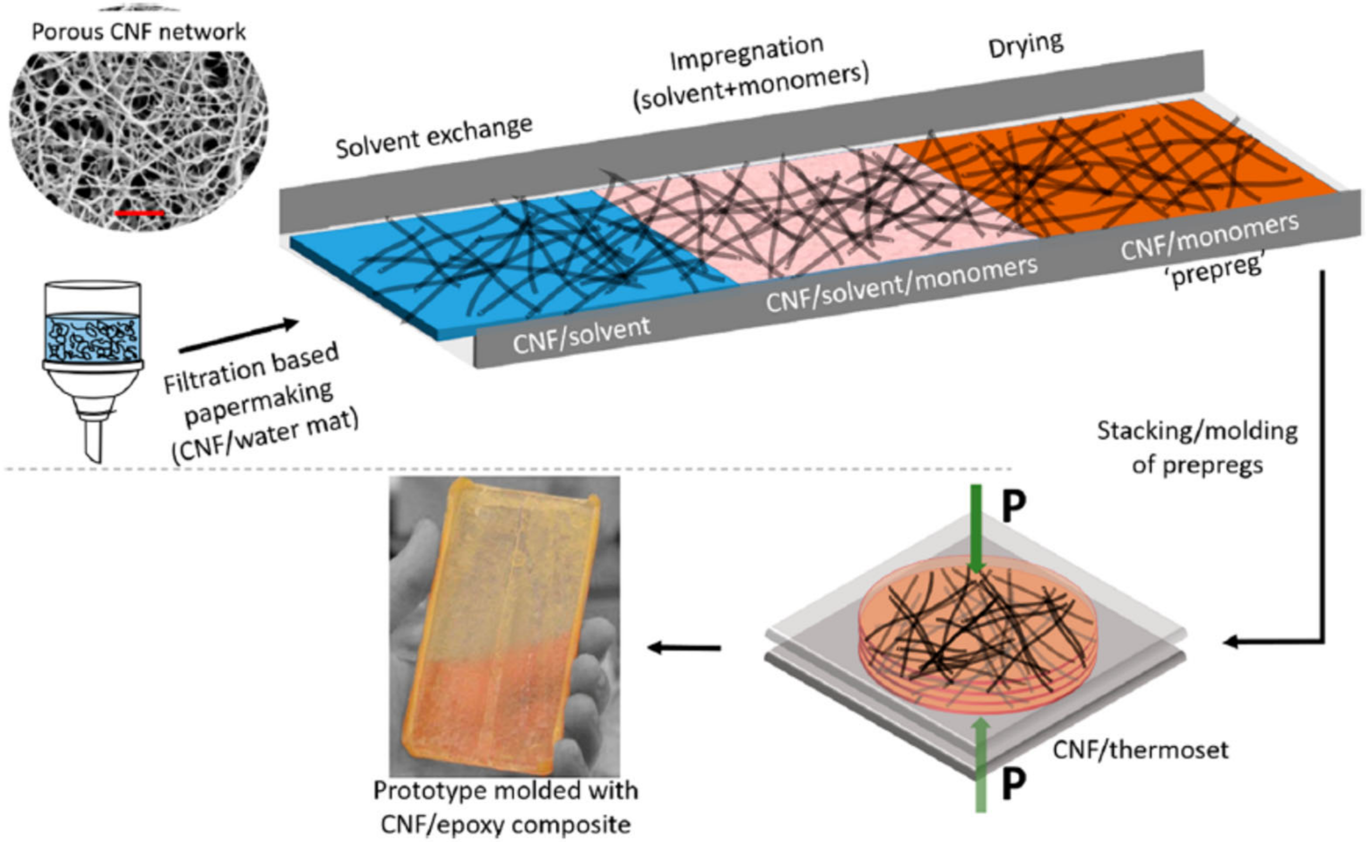
Surface modifiation:

- Surface of nanocellulose is more compatible with the surrounding polymer matrix in nanocomposites
- Crystalline core of cellulose stays intact

→ Strength properties of nanocellulose stay intact

At the moment, the methods to do this are expensive and not scalable.

Another solution: preparing nanocellulose network before composite preparation

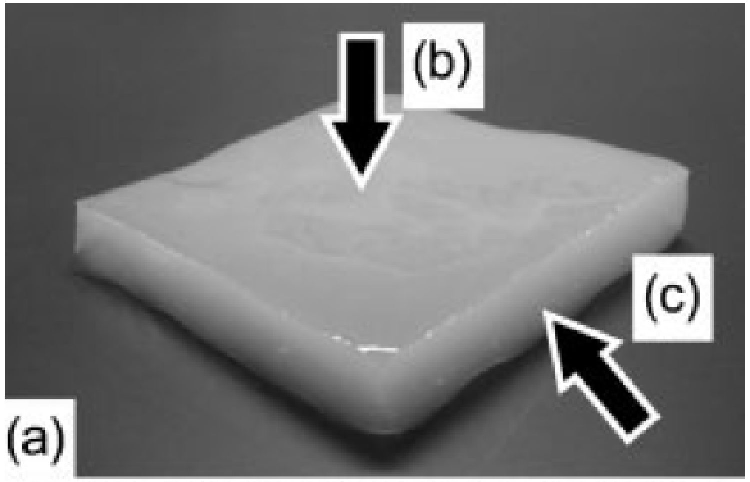


Enables
higher
nanocellulose
contents

Biomacromolecules **2018**, *19*, 2341.

Composites with nanofibrillar cellulose

Acrylic resin / bacterial cellulose

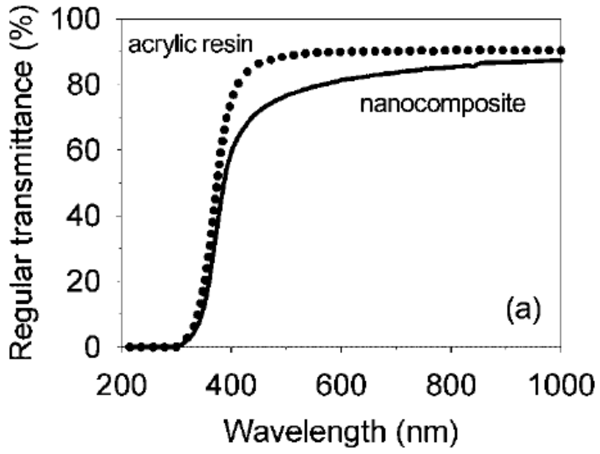


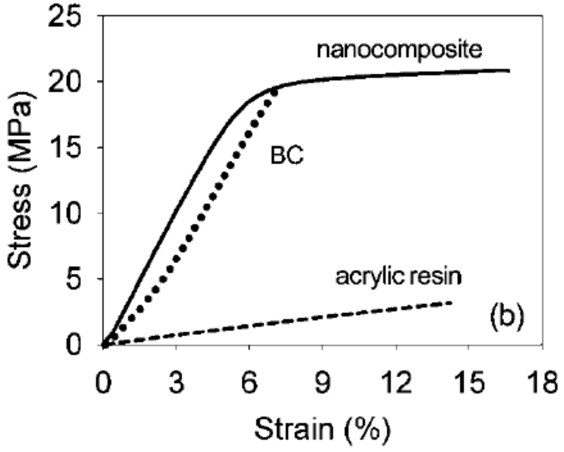
Bacterial cellulose pellicle

Water in a bacterial cellulose pellicle is replaced gradually with ethanol and impregnated with acrylic resin which is subsequently cured.

Nogi and Yano *Adv. Mater.* **2008**, *20*, 1849.

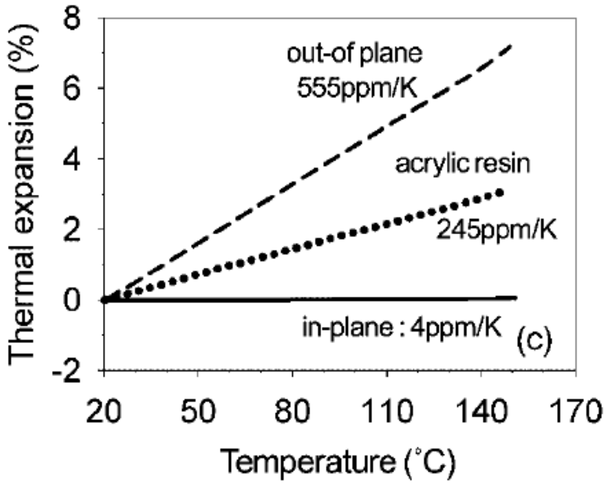
Acrylic resin / bacterial cellulose





Light transmittance of the resin is retained while the mechanical properties are enhanced.

Thermal expansion is very low.



Nogi and Yano *Adv. Mater.* **2008**, *20*, 1849.

Acrylic resin / bacterial cellulose

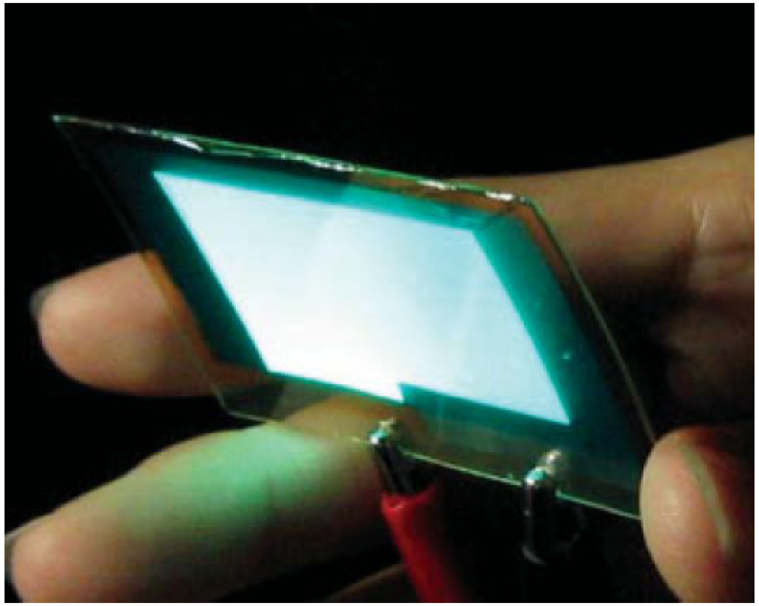


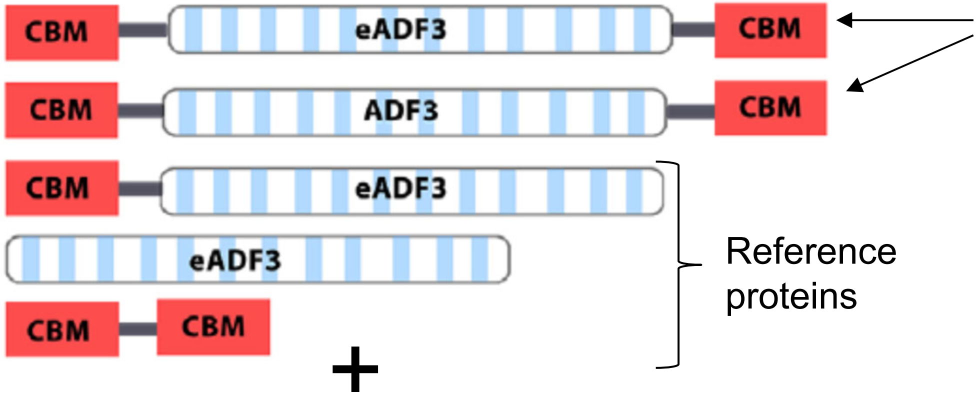
Figure 1. Luminescence of an organic light-emitting diode deposited onto a transparent BC nanocomposite. The luminescence area is 40 × 25 mm^2. This work was carried out in collaboration with Mitsubishi Chemical Corporation and Pioneer Corporation.

Potential usage for foldable flat panel displays in the electronics device industry.

Most plastics have too large a thermal expansion for electronics devices.

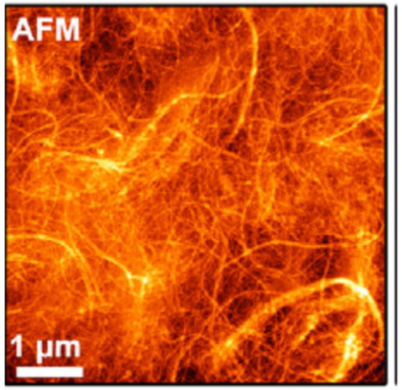
Nogi and Yano *Adv. Mater.* **2008**, *20*, 1849.

CNF with silk proteins



Reference proteins

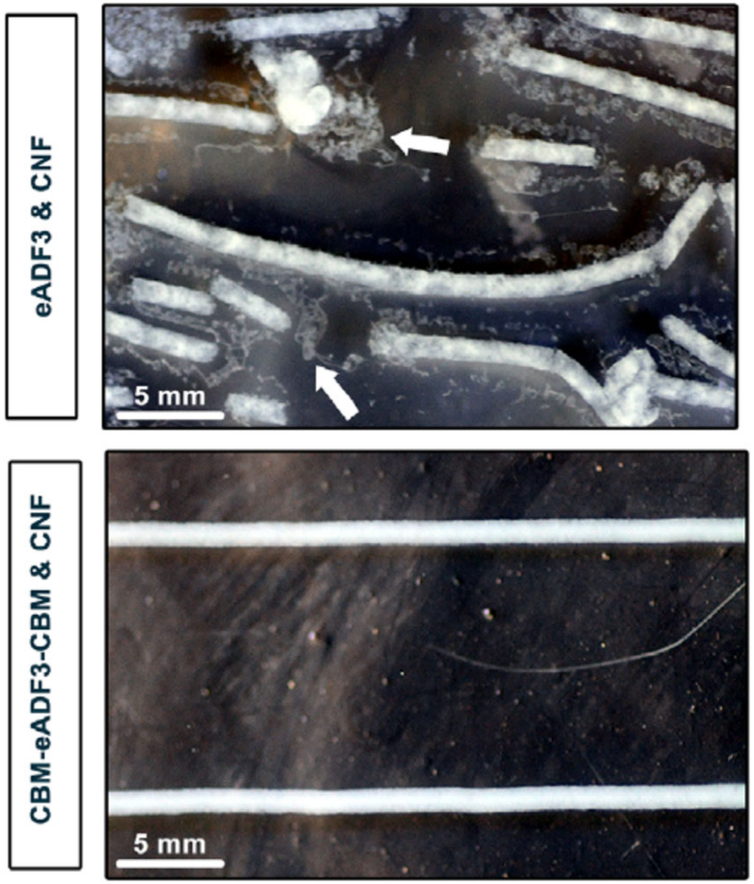
Engineered triblock proteins
CBM – Cellulose Binding Module (isolated from cellulase enzymes)
ADF3 – Spidroin protein from spider silk



Wood-based CNF

Sci. Adv. **2019**, *5*, eaaw2541.

CNF with silk proteins: fibre extrusion



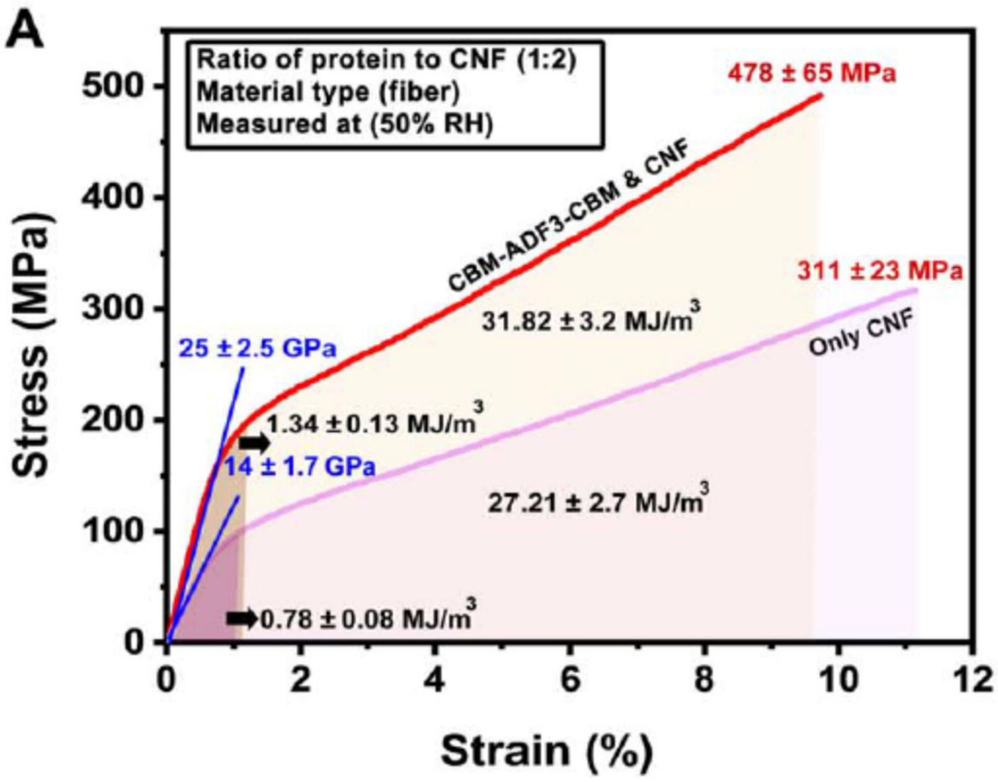
Ratio CBM-eADF3-CBM:CNF 1:2

Proteins without CBM block
→ Poor adhesion between CNF and protein
→ Fragmented fibres

Proteins with CBM block
→ Good adhesion between CNF and protein
→ Fibres with good integrity

Sci. Adv. **2019**, *5*, eaaw2541.

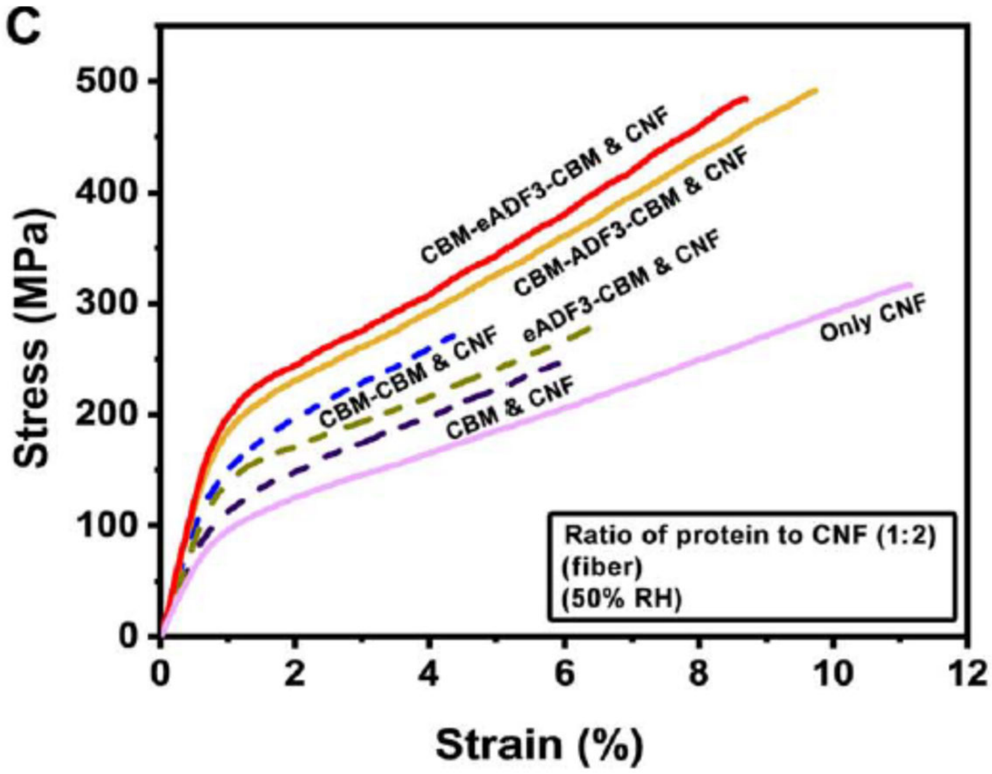
CNF with silk proteins



Composite fibres have a far higher tensile strength than pure CNF fibres

Sci. Adv. **2019**, *5*, eaaw2541.

CNF with silk proteins



Triblock proteins with cellulose binding domains (CBM) are necessary for high strength

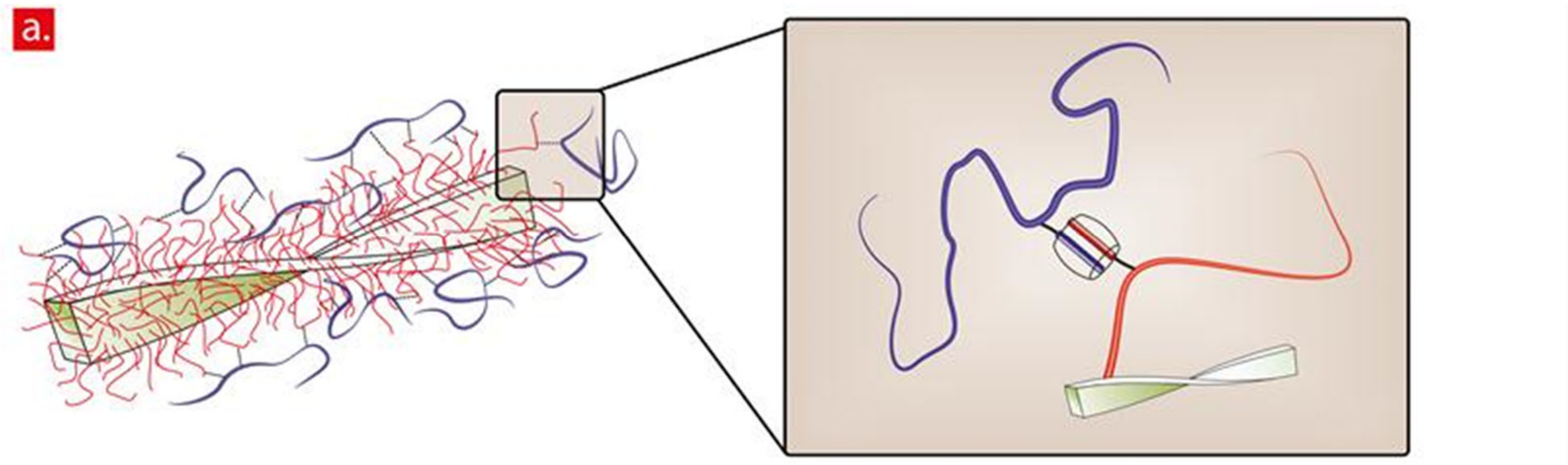
Sci. Adv. **2019**, *5*, eaaw2541.

Composites with cellulose nanocrystals

Self-healing hydrogels with CNCs

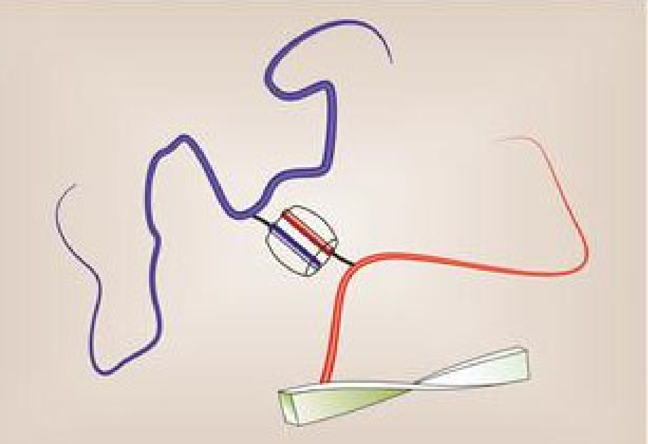
Basic idea:

(i) Graft polymers on CNCs
(ii) Blend grafted CNCs within a continuous polymer network
(iii) Use strong cross linking agents that enable strength and self-healing



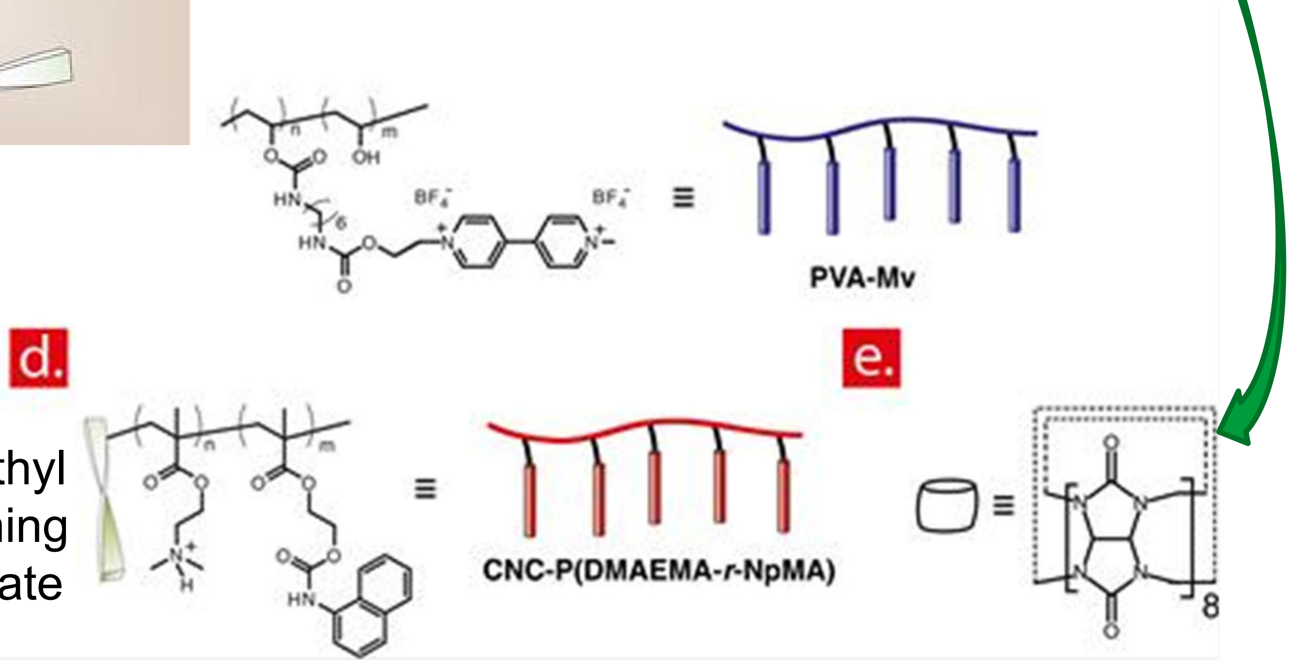
McKee et al. *Adv. Funct. Mater.* **2014**, *24*, 2706.

Self-healing hydrogels with CNCs



Cucurbit[8]uril: ”handcuff” binder with both viologens and naphthyls as guests

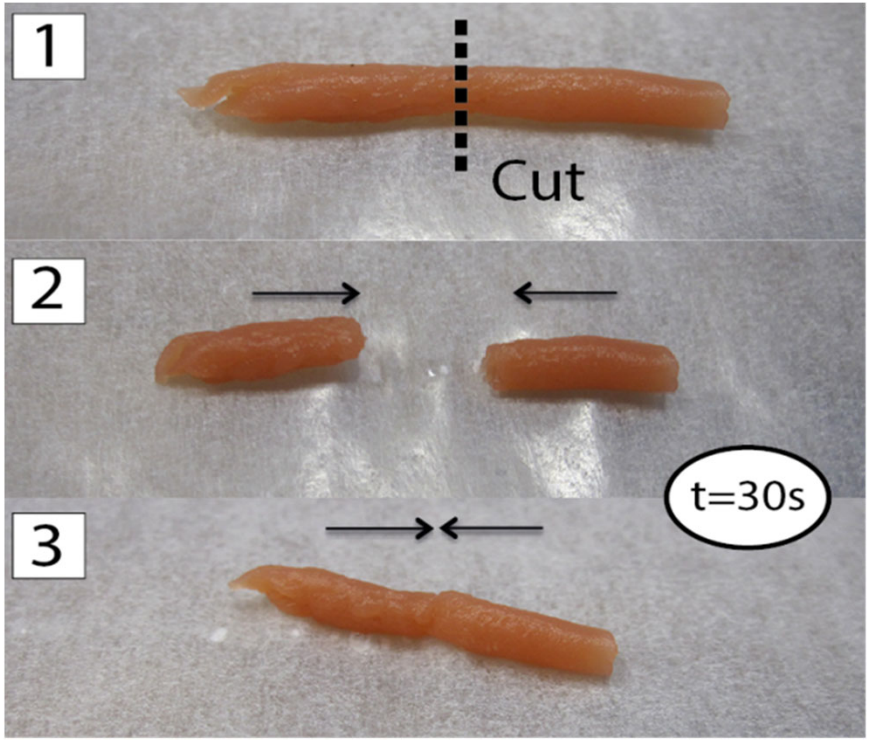
Poly(vinyl alcohol) (PVA)
containing methyl viologen (MV)



Poly(dimethylaminoethyl methacrylate) containing naphthyl methyl acrylate

McKee et al. *Adv. Funct. Mater.* **2014**, *24*, 2706.

Self-healing hydrogels with CNCs

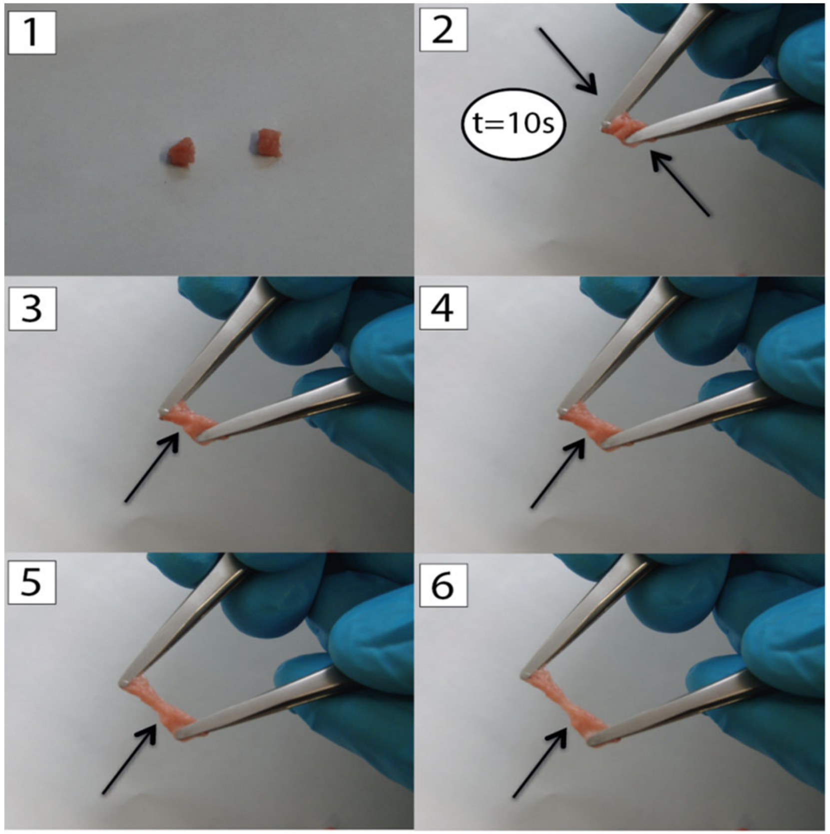


Self-healing immediately after cutting:

Supramolecular binding with cucurbit[8]uril is fast and strong.

McKee et al. *Adv. Funct. Mater.* **2014**, *24*, 2706.

Self-healing hydrogels with CNCs



Self-healing after 4 months storage:

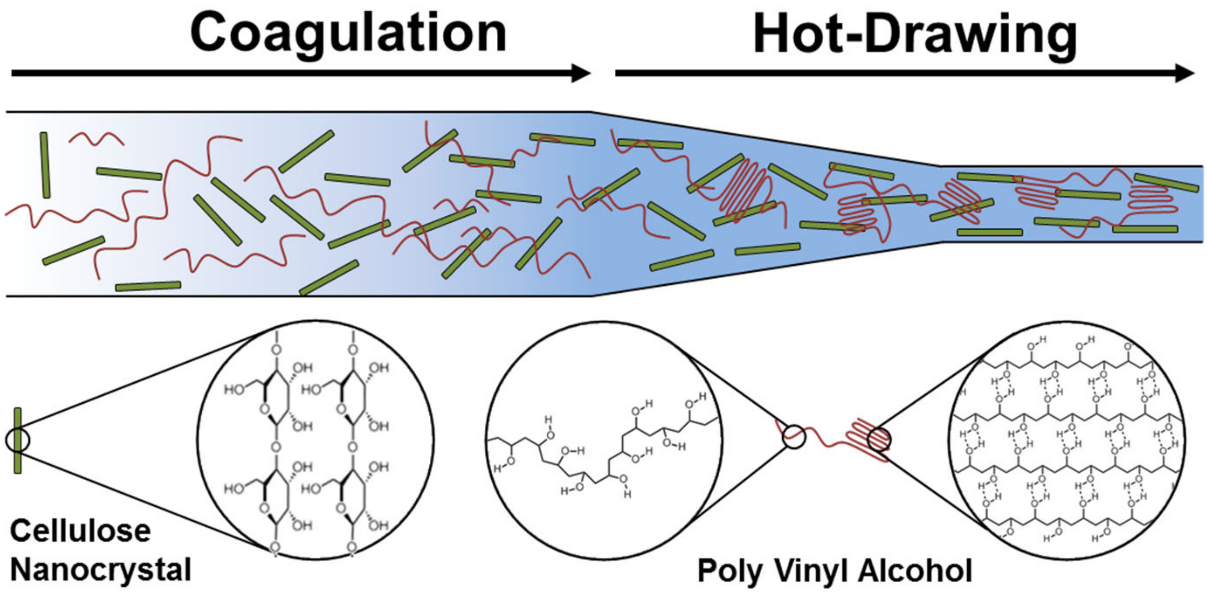
The mechanism with cucurbit[8]uril still works and it is still very fast.

McKee et al. *Adv. Funct. Mater.* **2014**, *24*, 2706.

CNC composite fibres with polyvinyl alcohol

- PVA with loads of hydroxyl groups is a compatible matrix with CNCs

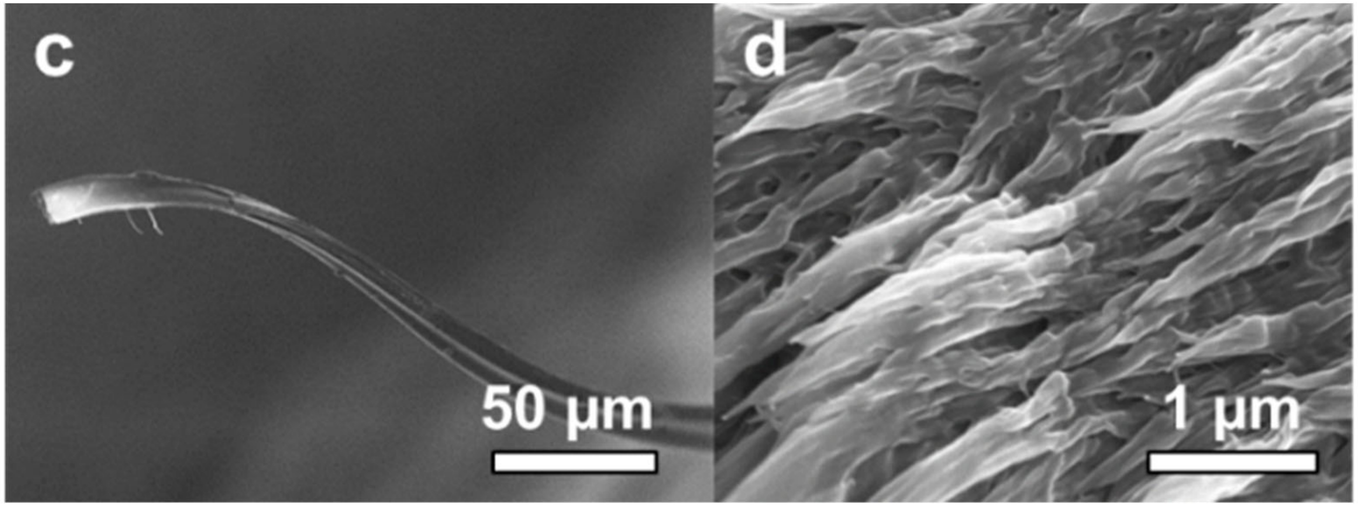
→ No compatibilizing modifications on CNCs required



Lee et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31500.

CNC composite fibres with polyvinyl alcohol

- Result: CNC/PVA composite fibers with tens of µm diameter



- CNC concentration upon fibre spinning is fairly high

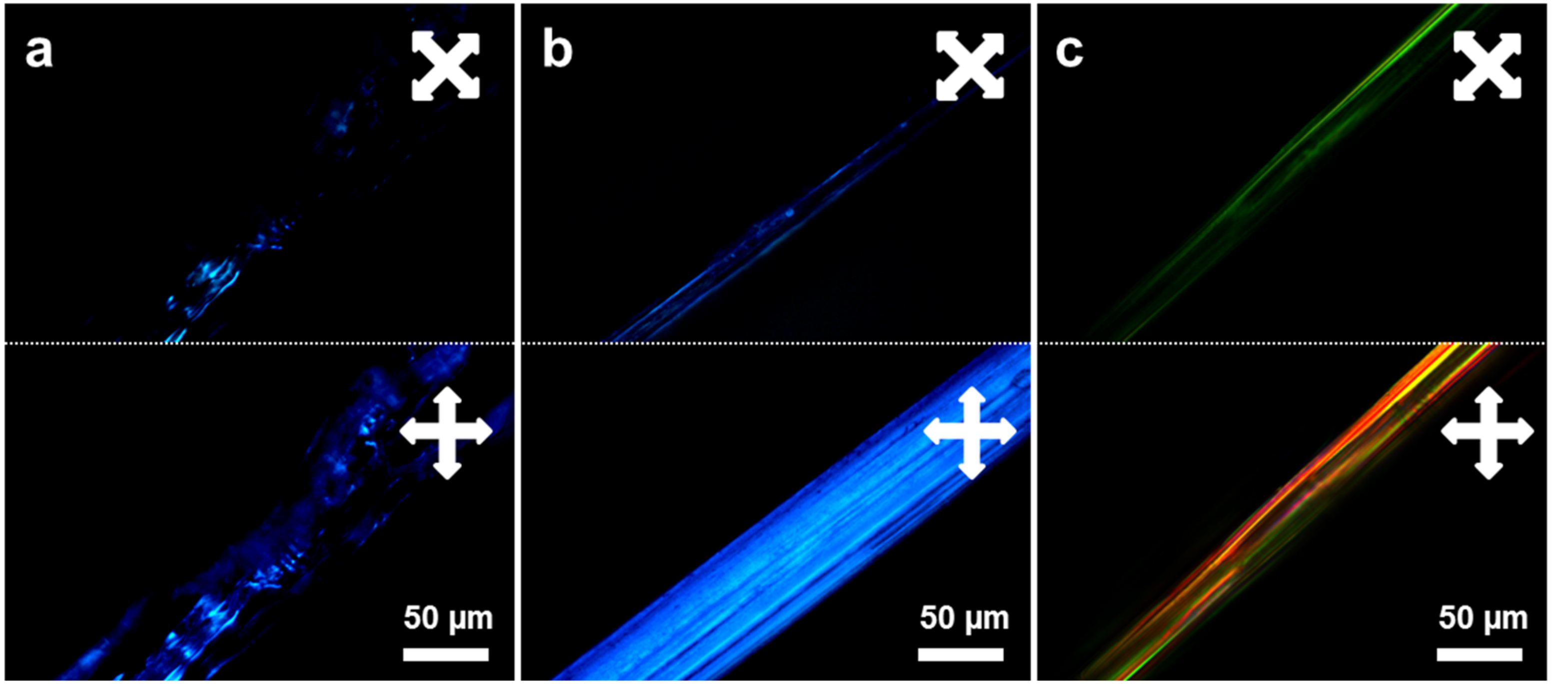
→ Above the concentration for liquid crystal formation

→ Liquid crystal phase induces alignment of CNCs in resulting fibres

Lee et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31500.

CNC composite fibres with polyvinyl alcohol

- Hot drawing further induces alignment and order in PVA/CNC fibres

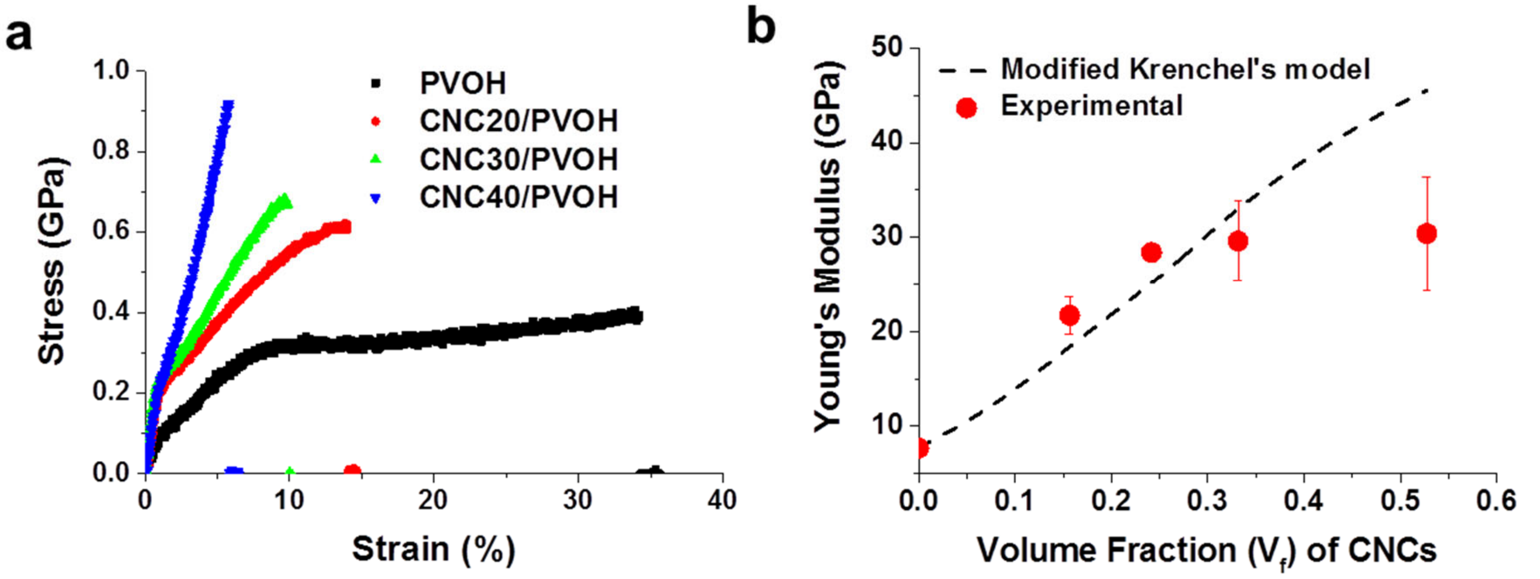


Undrawn PVA	Hot drawn PVA	Hot drawn PVA/CNC (60/40 ratio)

Lee et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31500.

CNC composite fibres with polyvinyl alcohol

- Very high mechanical properties for the resulting PVA/CNC fibres: tensile strenght of close to 1 MPa with 40% CNC loading



Lee et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31500.

Aalto University
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Applications of nanocellulose hydrogels

Nanocellulose hydrogels

- Particularly CNFs form gels at low concentrations in water
- Gel formation can be an advantage, utilized in specific applications
- Most biomedical applications utilise the gel formation properties of CNF

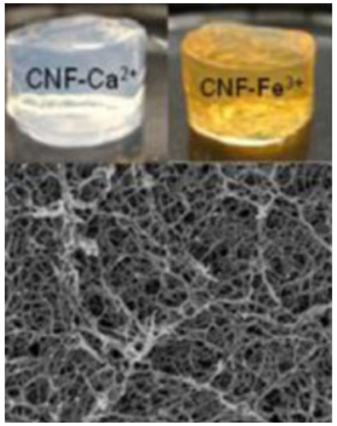
CNF hydrogels as scaffolds for tissue engineering

- Tissue engineering scaffolds provide 3D foundation to direct cellular attachment, proliferation, and differentiation – ultimately tissue formation

- Requirements: biocompatibility, non-toxicity, biodegradability, sufficient (tunable) porosity and mechanical properties

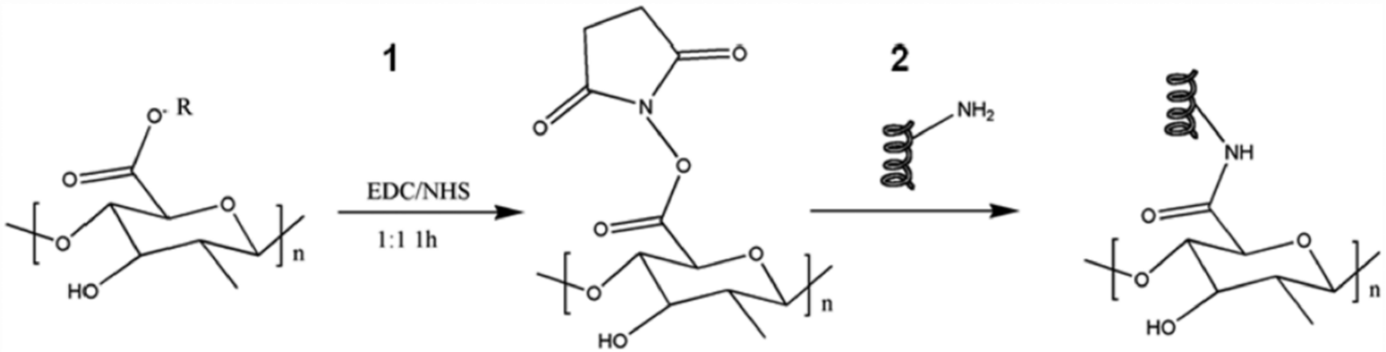
CNF hydrogels as tissue scaffolds:
- Cellulose lacks the adhesive sites necessary for cell signalling and migration
- Tuning the porosity and mechanical properties is not always straightforward

CNF hydrogels as tissue growth scaffold



Cross-linking TEMPO-oxidized CNFs
by multivalent metal ions
→ Stronger gels

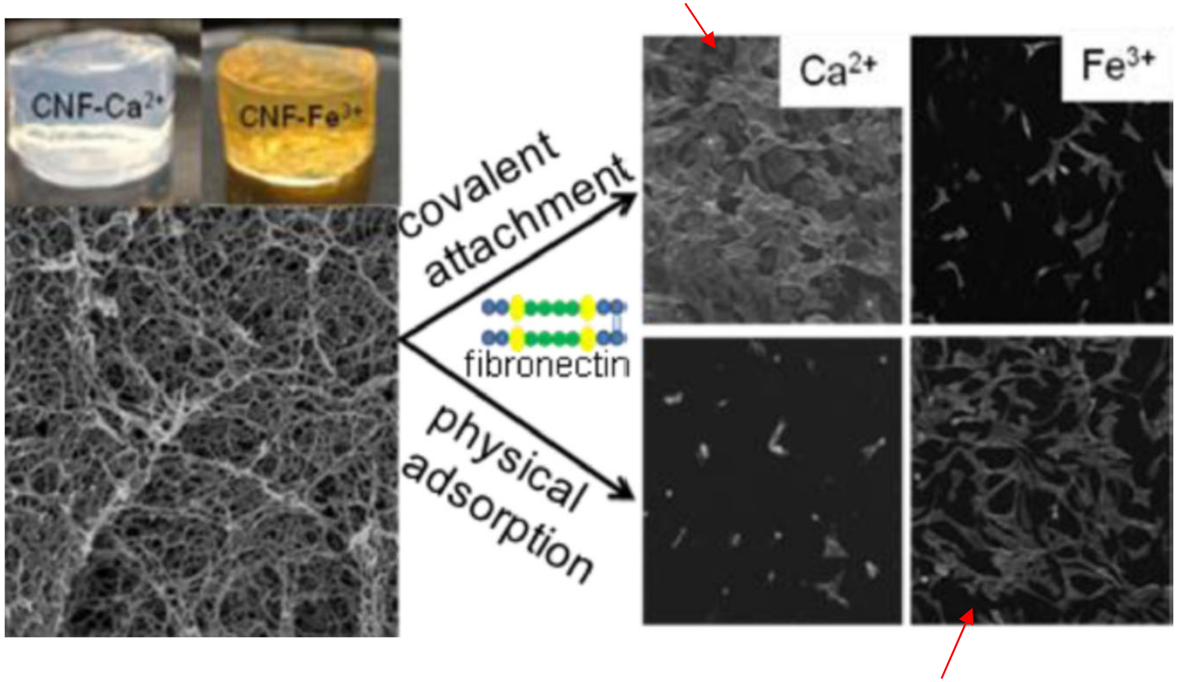
Physical adsorption or covalent attachment of
fibronectin protein
→ Supports biorecognition



ACS Appl. Mater. Interfaces **2014**, *6*, 18502.

CNF hydrogels as tissue growth scaffold: fibroblast cell growth

Good cell proliferation:
Ca cross linking + covalent fibronectin attachment



Good cell proliferation:
Fe cross linking + physical fibronectin attachment

ACS Appl. Mater. Interfaces **2014**, *6*, 18502.

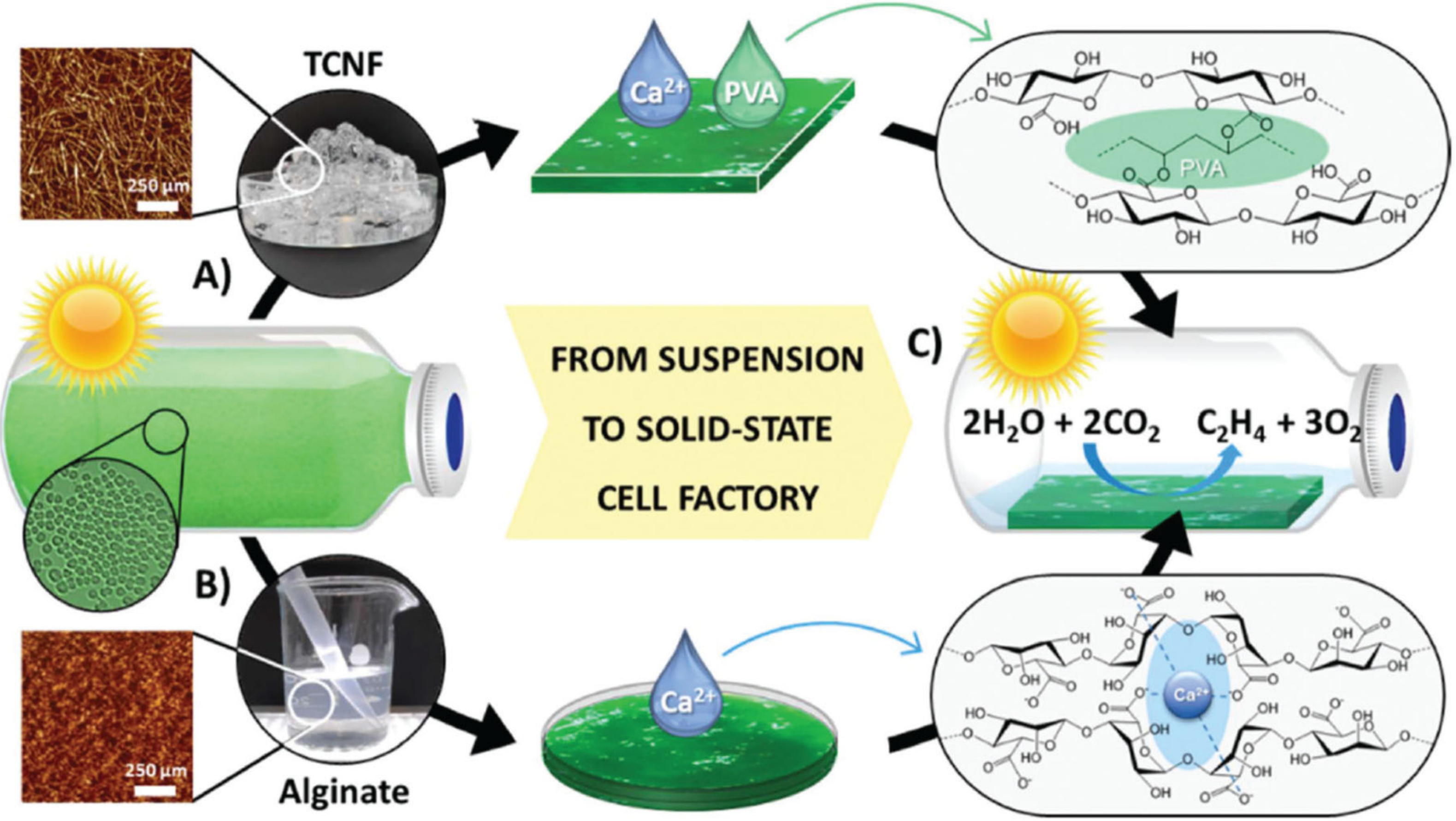
Solid-state cell factories

- Photosynthetic cell factories are platforms where microbial cells of cyanobacteria or green algae are used as biocatalysts to produce biofuels or platform chemicals

- They generally consist of pools of water where the cells are located (suspension culture)

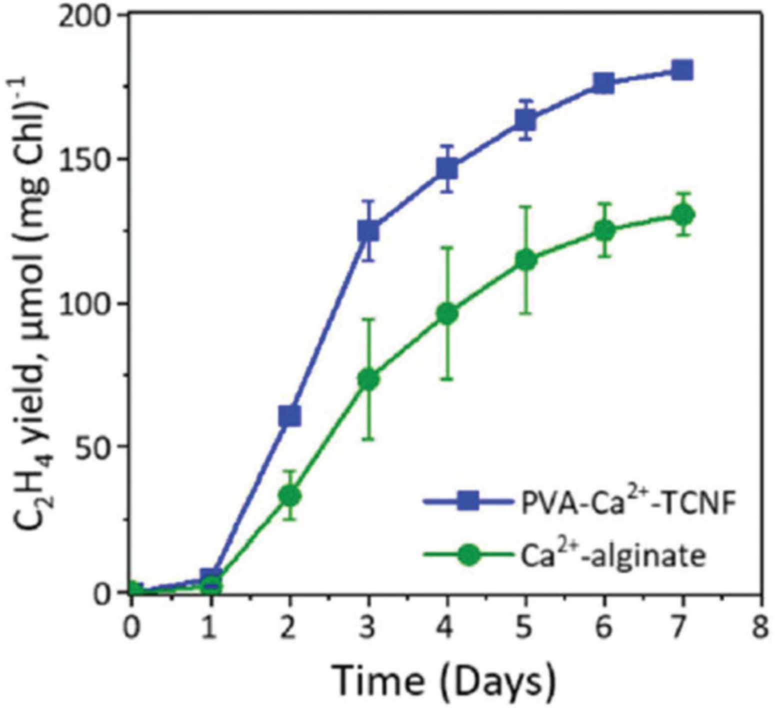
- Application for nanocellulose hydrogels: “solid state” cell factories where the photosynthetic cells are trapped in a nanocellulose gel matrix
  - Enables better control over the chemicals production and collection
  - Harmful proliferation of cells (instead of chemical production) can be better controlled
  - Enables better control over light-to-production efficiency

Solid state cell factories



Green Chem. **2021**, *23*, 3715.

Solid state cell factories



Production of ethylene by photosynthetic cells:

- Higher conversion by cross linked CNF matrix than by alginate matrix

(Note: alginate is currently the only other option for “solid state” cell factories)

Green Chem. **2021**, *23*, 3715.

Conclusions

- Materials incorporating nanocellulosics is a highly visible research area

- Some applications require just film formation (e.g., gas barriers, transistor supports), some require complex chemistry and recognition mechanisms (e.g., self-healing composites, tissue growth scaffolds)

Examples of versatility in research:

  - Transparent films
  - Plastic surrogates
  - Supports for electronics
  - Tissue growth scaffolds
  - Solid state cell factories

Conclusions

Nanocellulose:

- High potential: high strength, bio-based origin, biodegradability, non-toxicity
- Difficulties: compatibility with composite matrix, realisation of potential, susceptibility to water
- Native properties of cellulose in the plant cell wall are underutilised