International Conference on Nanotechnology for Renewable Materials

Nanocellulose-Based Membranes for Nutrient Capture

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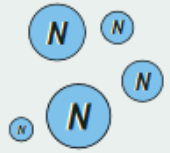
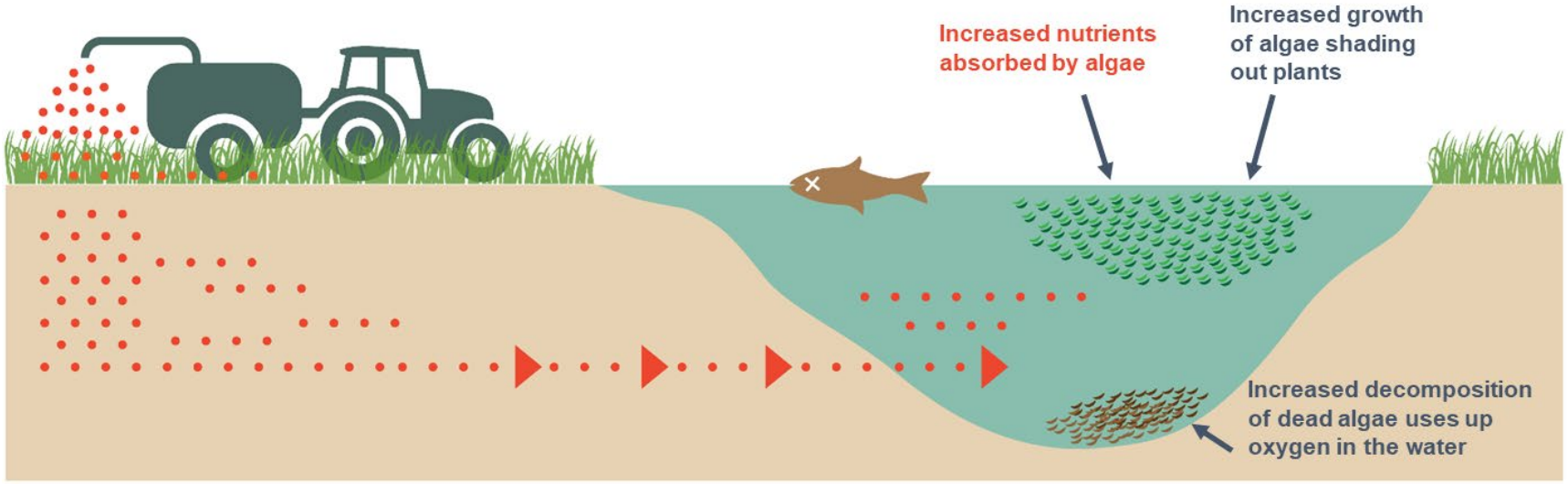
Nutrient pollution

Nitrogen is a vital nutrient that helps plants and crops grow, but high concentrations are harmful to people and nature.

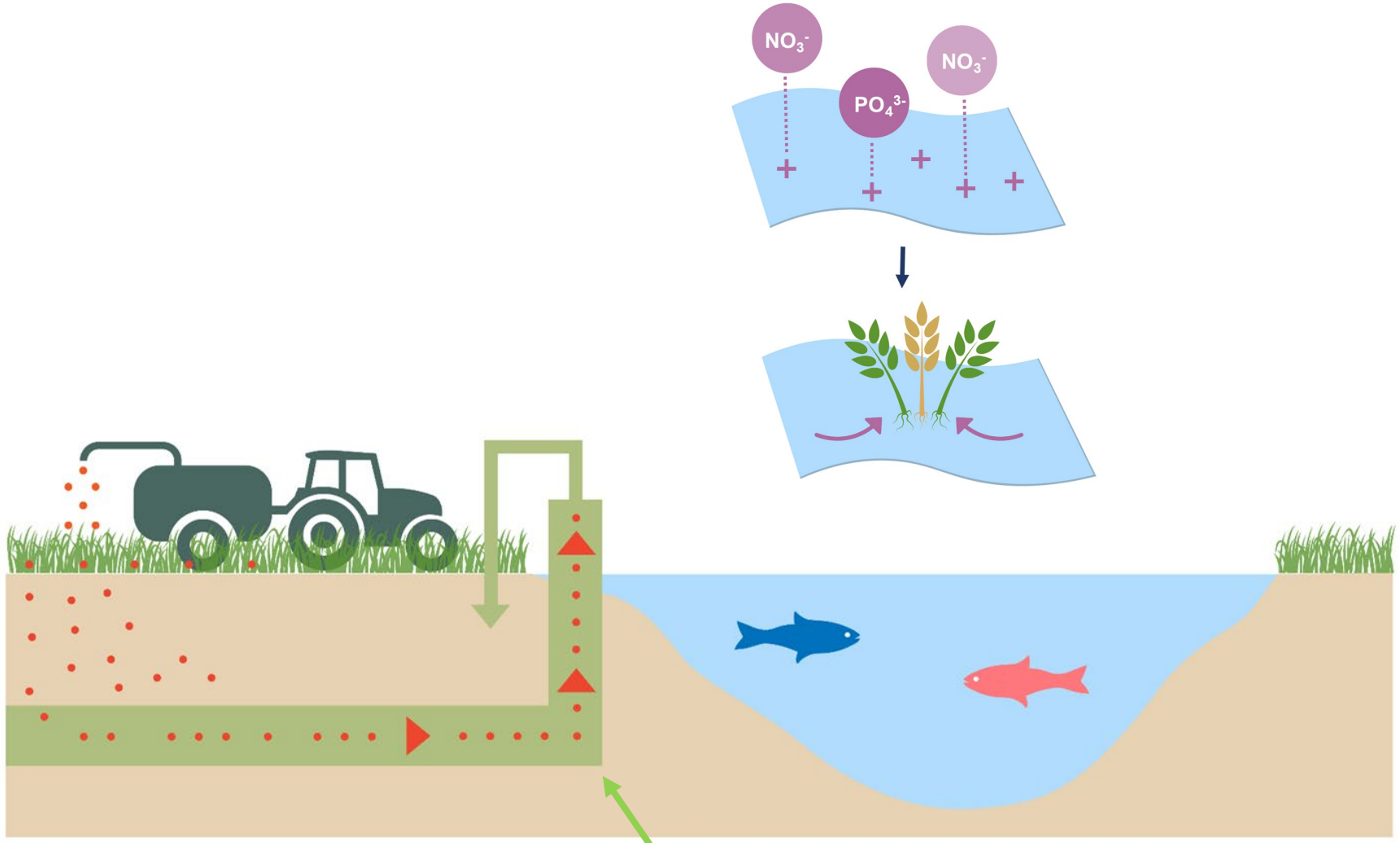
Pure, clean water is vital to human health and to natural ecosystems.



Excess nitrogen from agricultural sources is one of the main causes of water pollution in Europe.



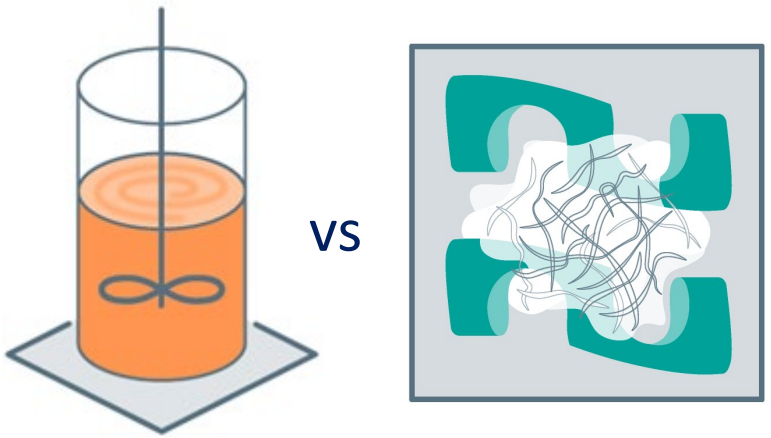
Solution: capture and reuse nutrients

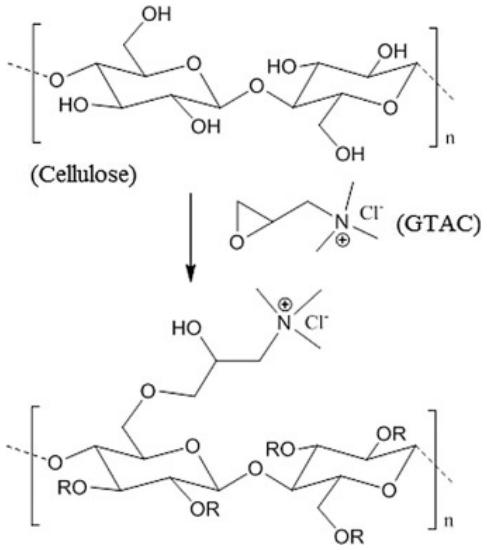


Functionalization of nanocellulose-based membranes

Approach I: cationization of pulp prior to fibrillation (bulk modification)

- Cationization occurs via substituting hydroxyl groups with GTAC (glycidyltrimethylammonium chloride, quaternary ammonium cation):
  - Low consistency (~5 wt.%) modification, molar ratio of GTAC/AGU is 2.1
  - High consistency (~50 wt.%) modification, molar ratio of GTAC/AGU is 1





Reaction pathway of GTAC substitution in cellulose.

Approach II: Surface cationization of assembled CNF film

- Surface cationization of already assembled nanocellulose membranes; e.g., via atmospheric plasma enhanced chemical vapor deposition

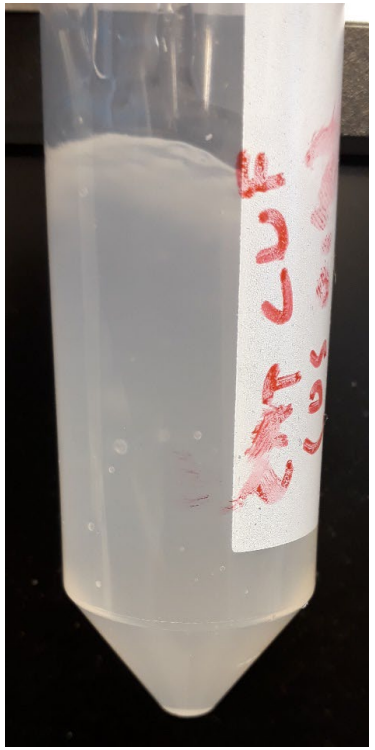


Fig 1. Visual appearance of cationic CNF made at VTT (DS 0.2).

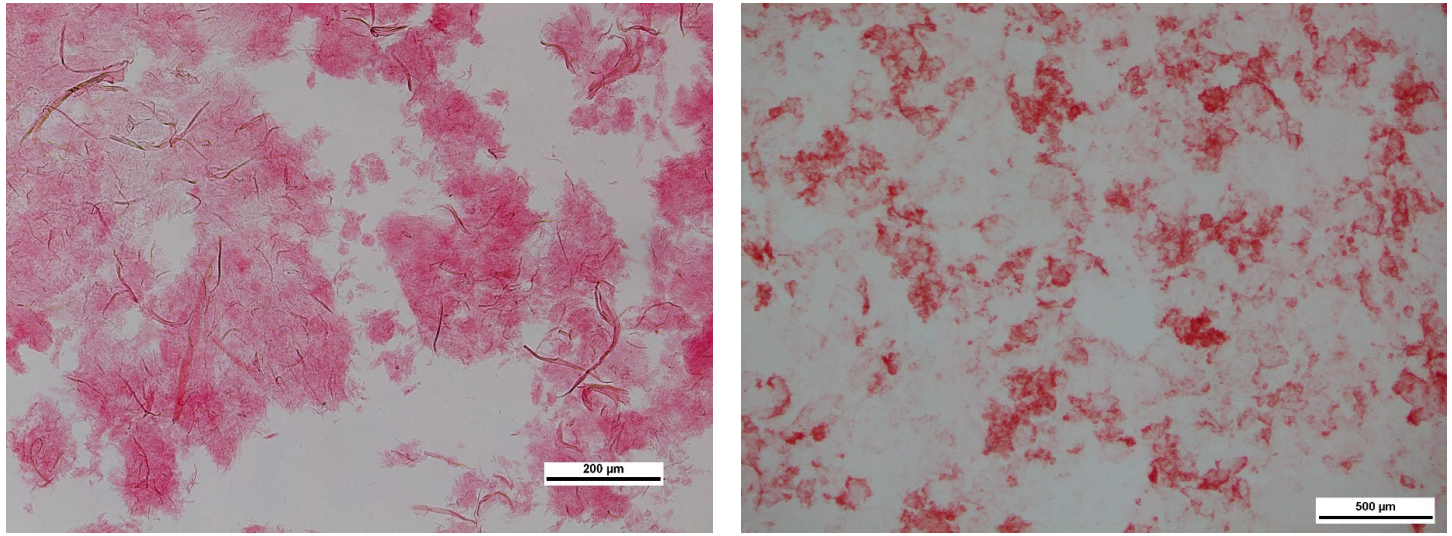


Fig 2. Optical microscopy images of cationic CNF with DS of 0.05 (left) and 0.2 (right), dyed with Congo Red.

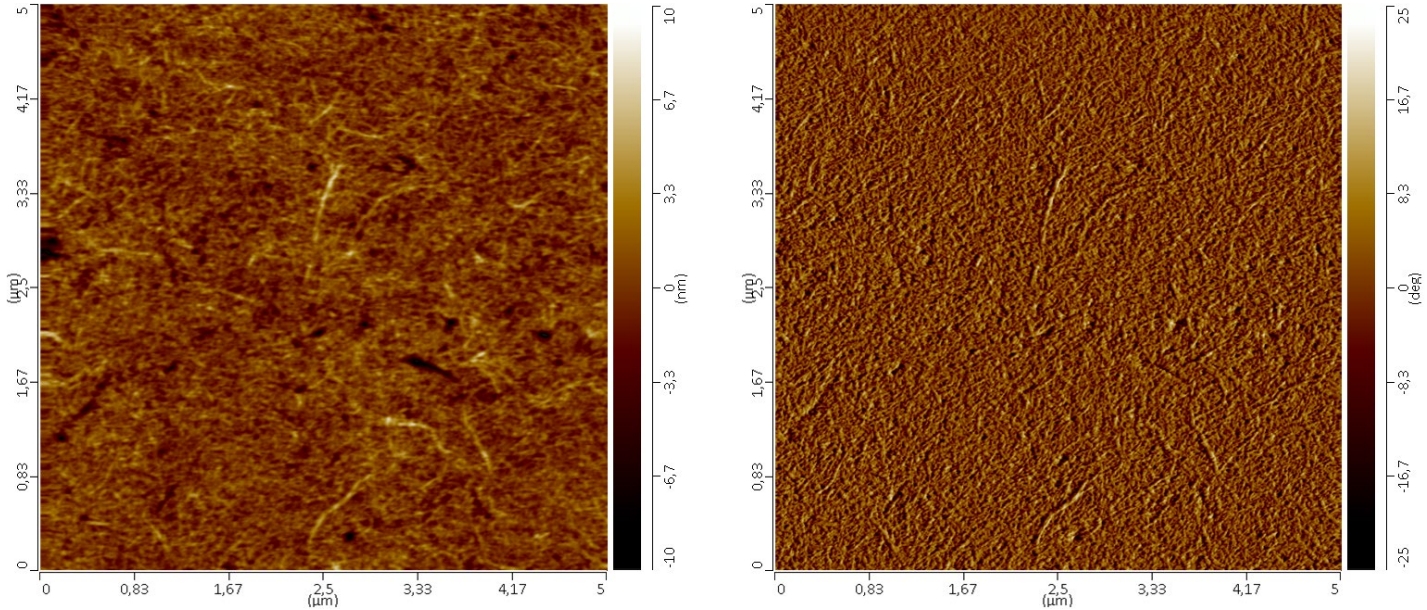
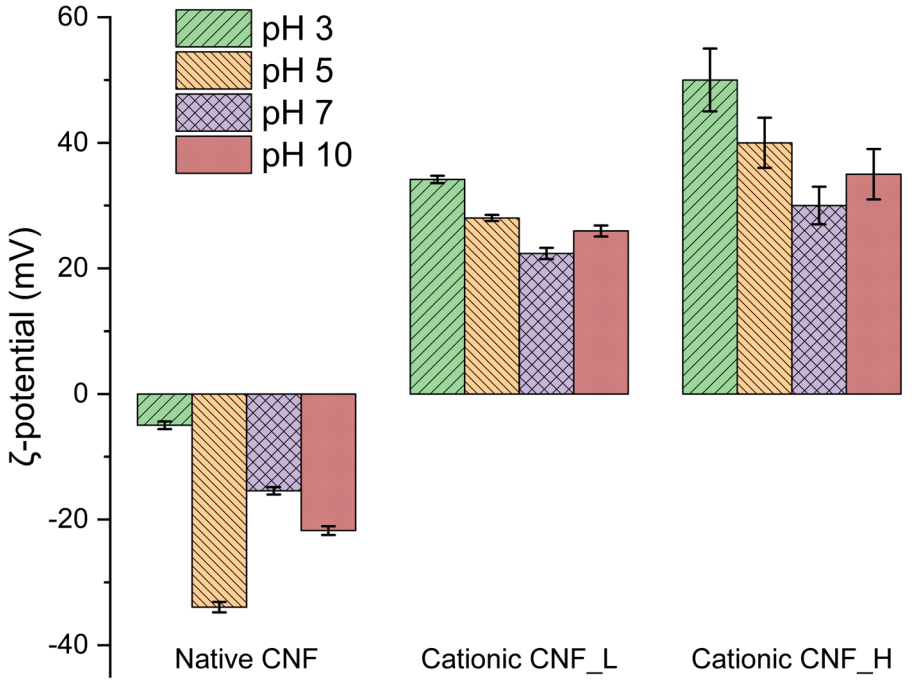
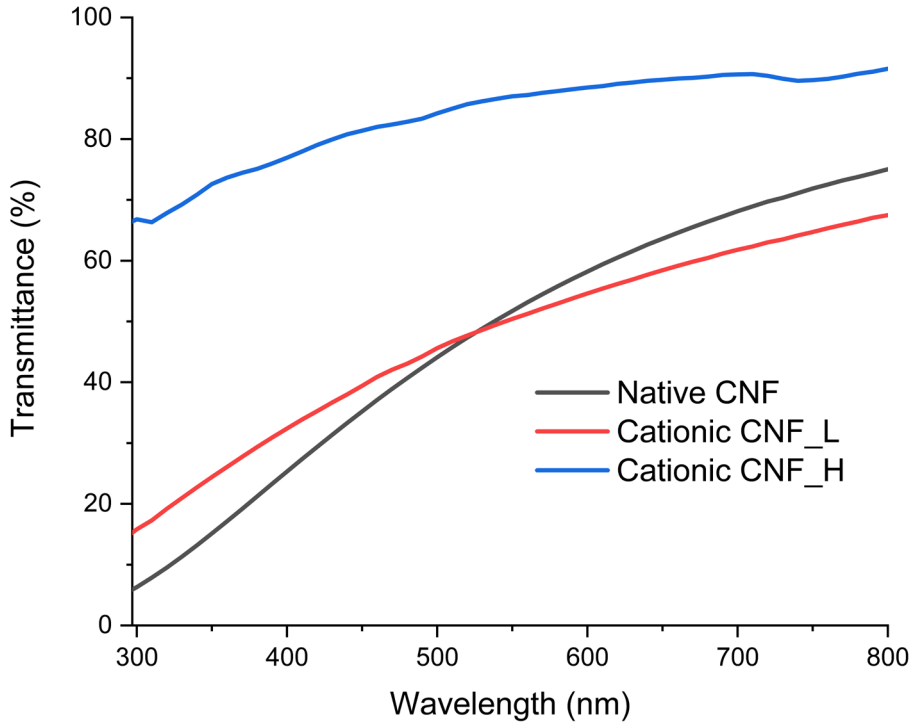


Fig 3. Atomic Force Microscopy (AFM) topography (left) and phase contrast (right) images of cationic CNF with DS of 0.2.

Properties of cationic CNFs



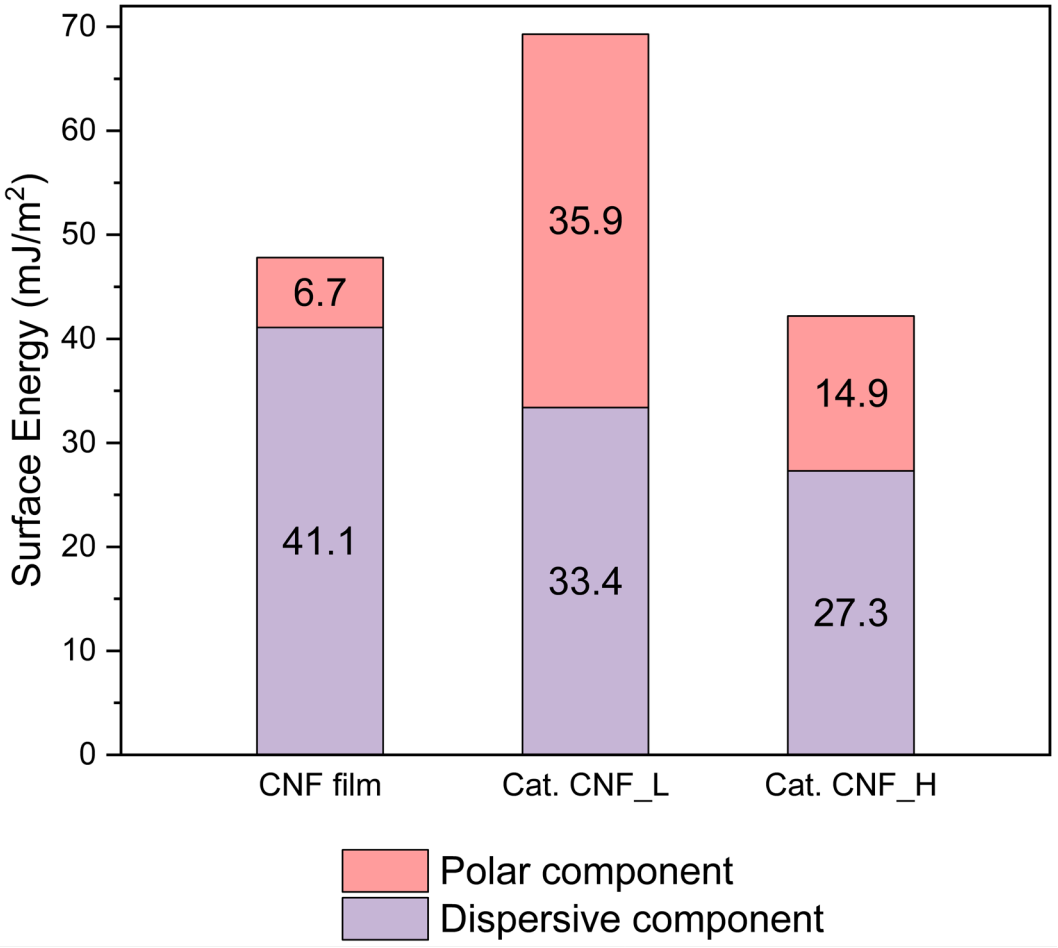


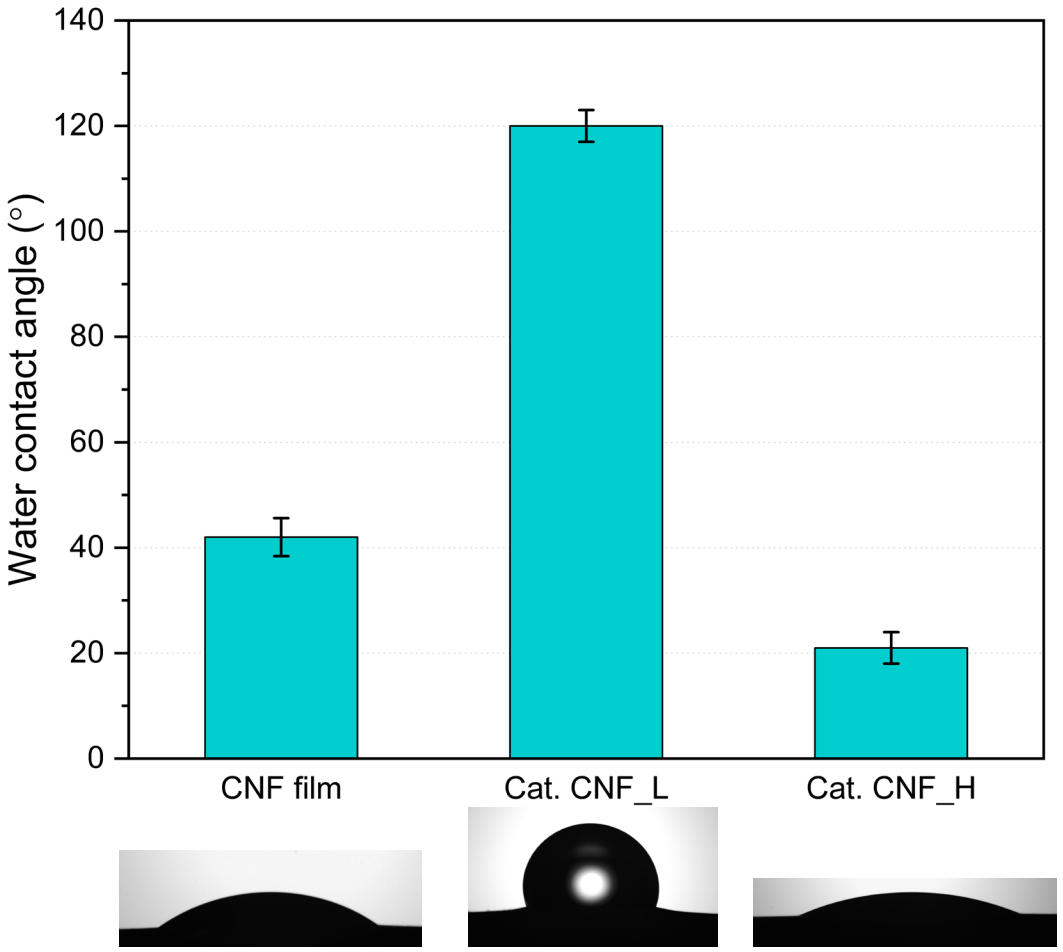
Manufacturing of nanocellulose films in semi-pilot scale

- Nanocellulose coated evenly on substrate film
- Controlled spreading and adhesion
- No shrinkage (adhered to substrate while dried)
- Tunable thickness

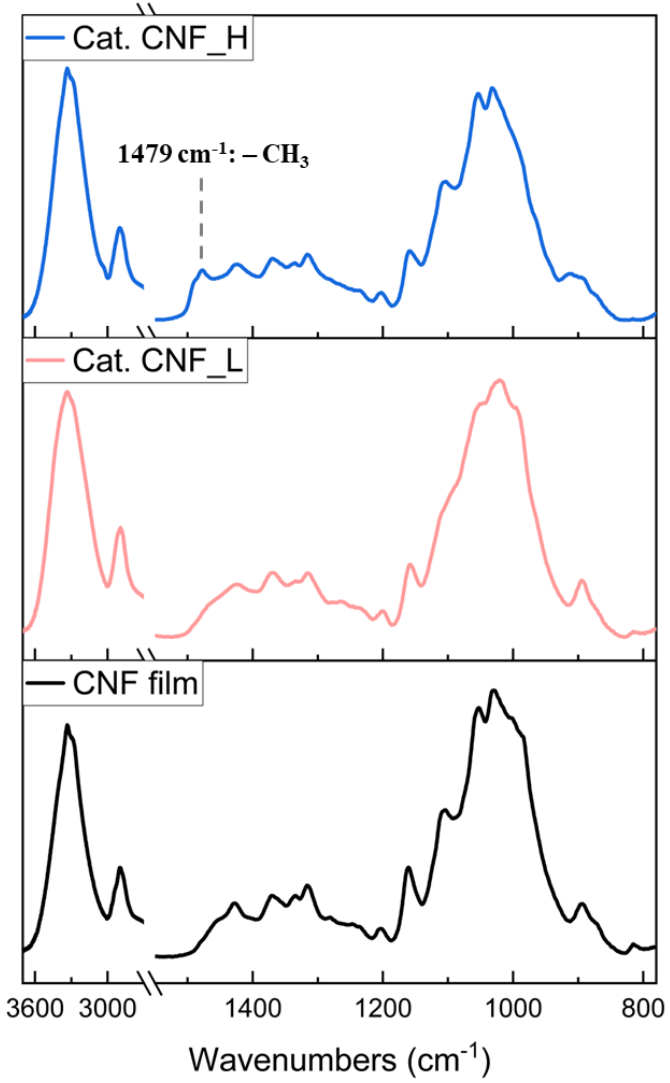
Tammelin et al. PCT Int. Appl. (2013), WO 2013060934 A2 20130502

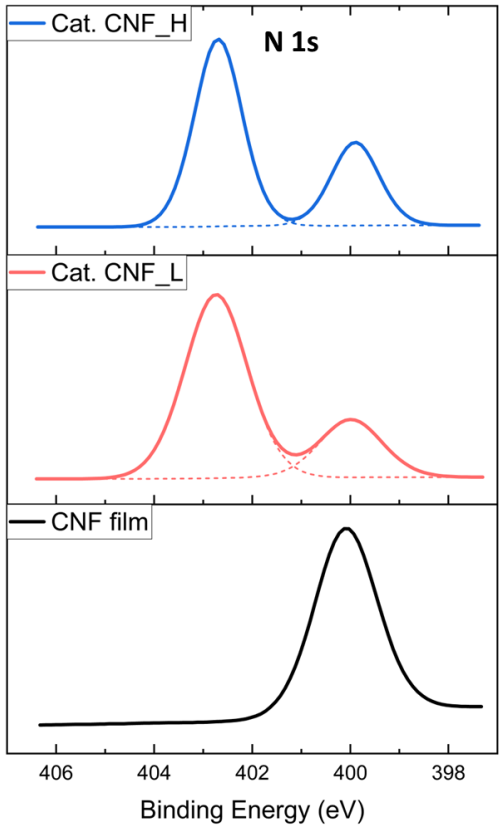
Surface energy and WCA of CNF films

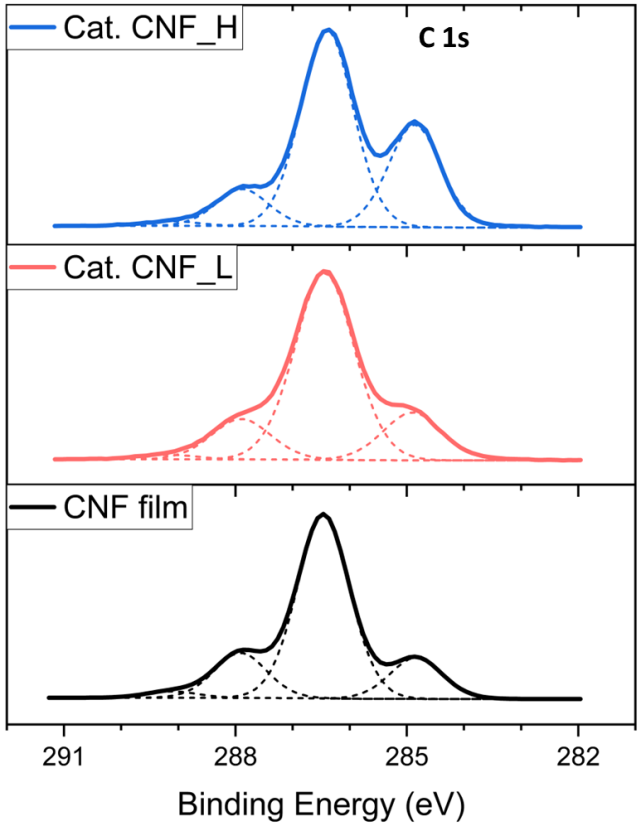




Chemical characterization of films



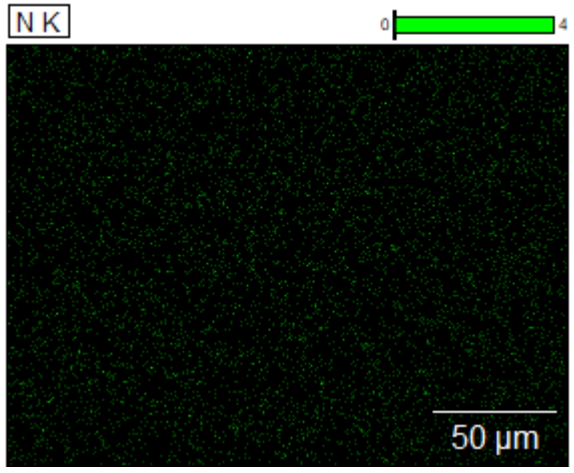




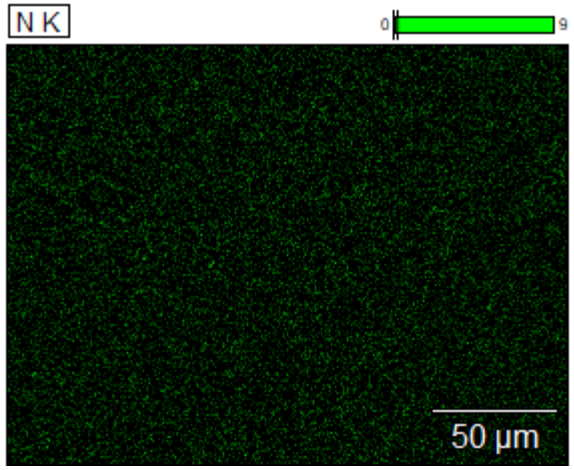
Sample	Atomic concentrations, %			High resolution C survey, %				% of total N	
	C1s	O1s	N1s	C-C	C-O or C-N	C=O	O-C=O	amide/ NH	quaternary
CNF film	59,1	40,7	0,2	14,5	67,2	16,2	2,2	100,0	0,00
Cat. CNF_L	61,0	38,1	0,6	17,0	67,8	13,8	1,3	20,7	79,3
Cat. CNF_H	67,2	28,6	2,2	27,7	59,4	11,3	1,6	29,3	70,7

Surface morphology

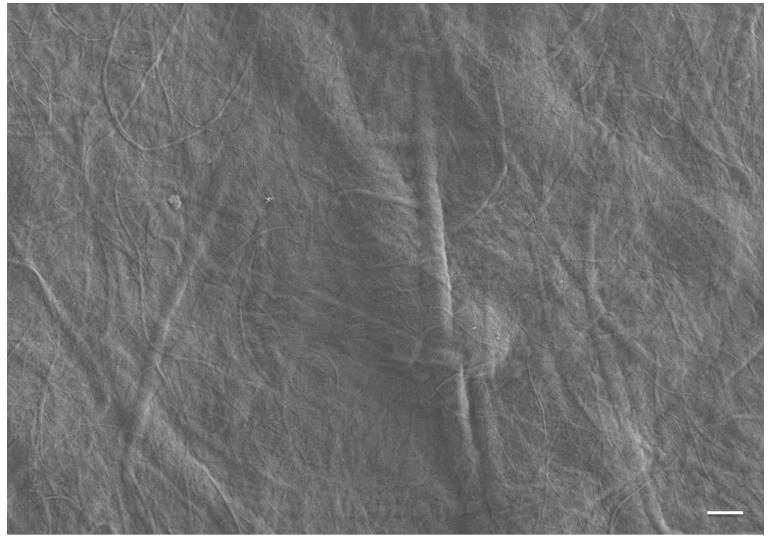
CNF film

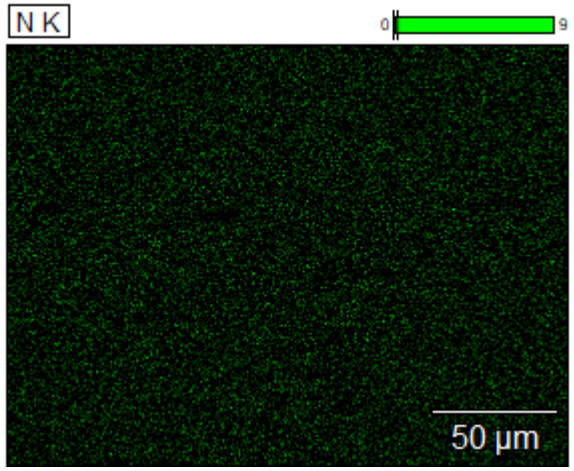


Cat. CNF_L



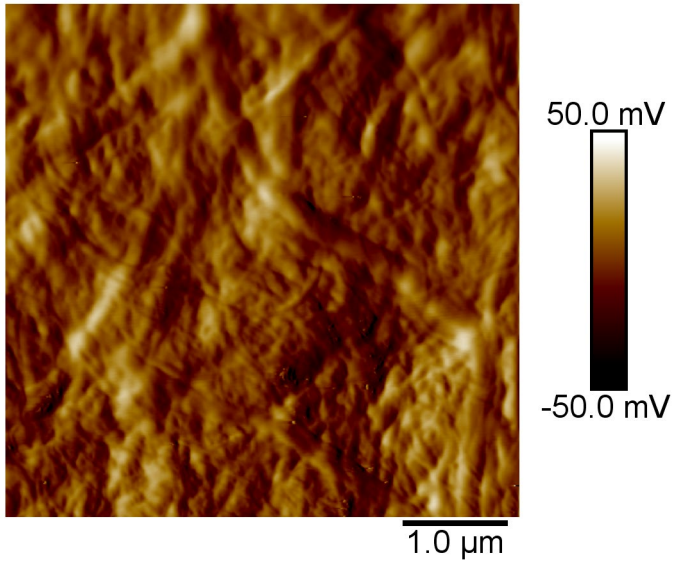
Cat. CNF_H

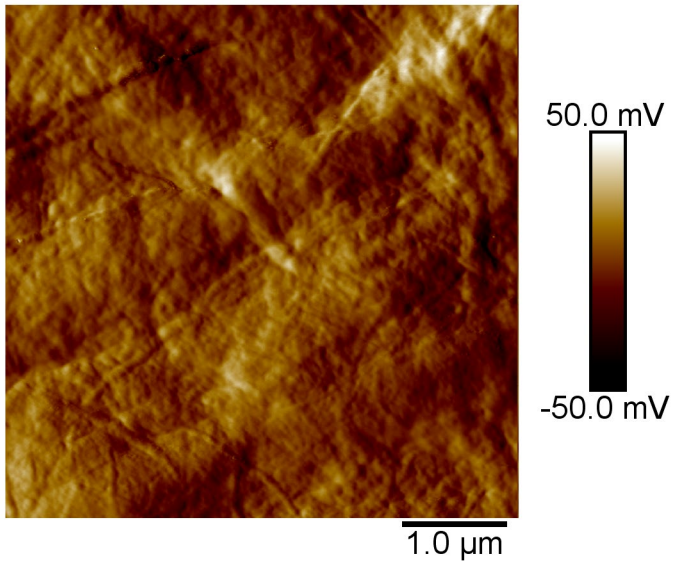


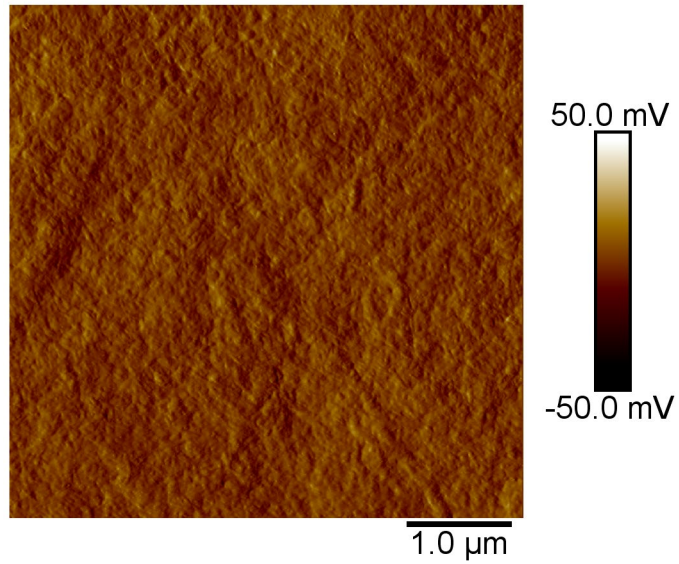


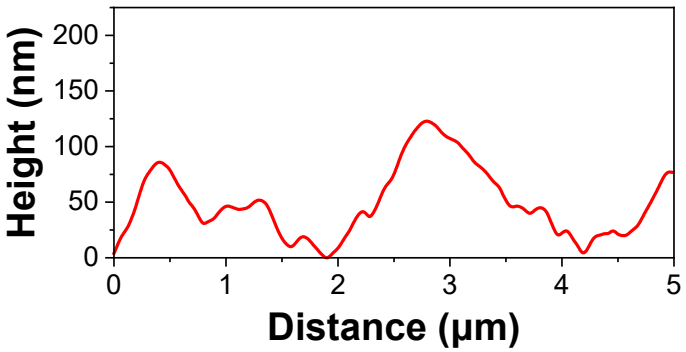
AFM investigation of CNF films

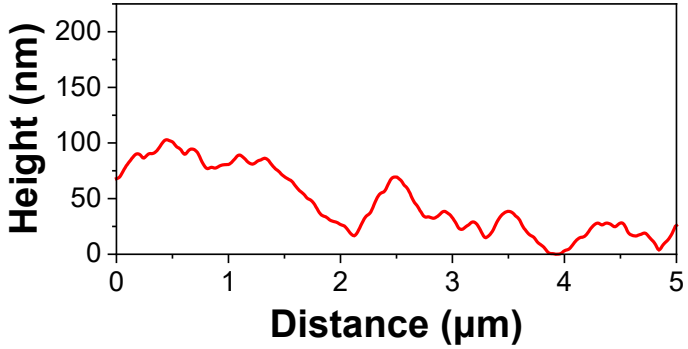
Amplitude error

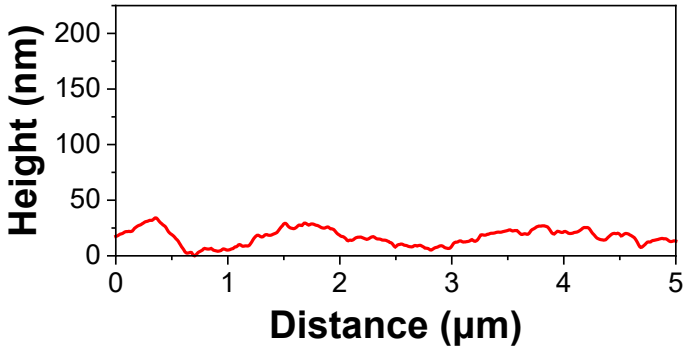






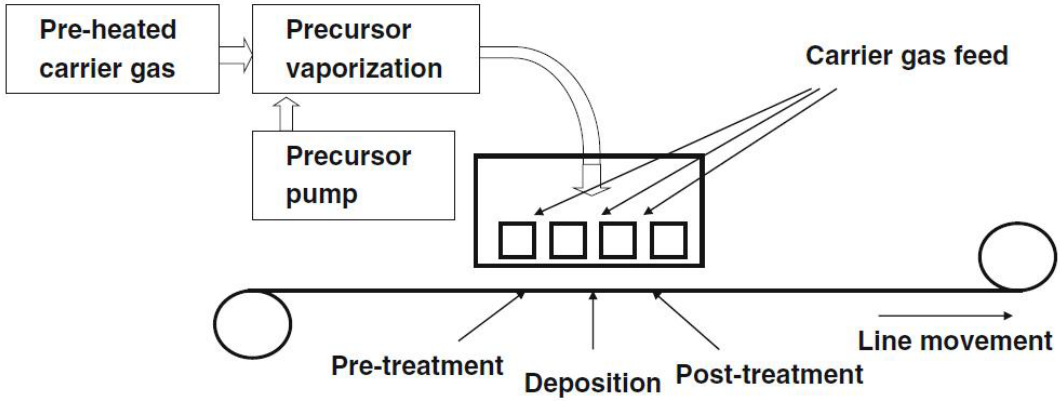






Gas phase reactions – Surface functionalization / chemical modification of nanocellulose-based films

Atmospheric plasma-enhanced chemical vapor deposition R2R pilot unit

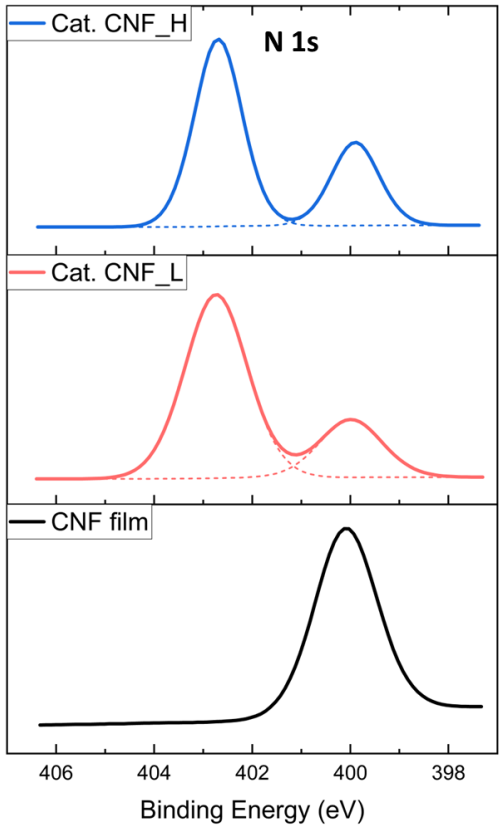


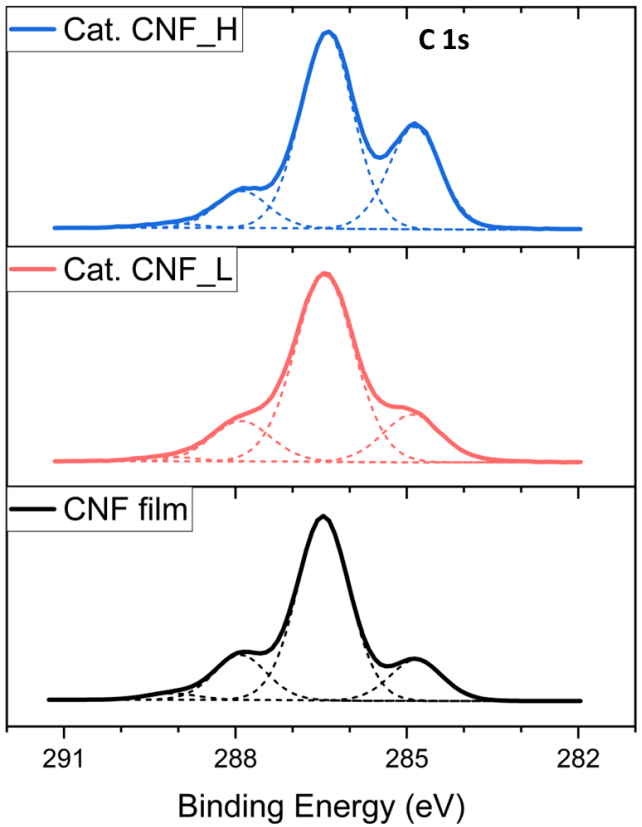
- 50 –300 nm molecular layer grafted with covalent bonds onto activated surface
- Durable modification of the chemical composition of the surface
- No loss of performance over time
- Low energy consumption
- Extremely wider ange of precursor molecules (organic, inorganic, biomolecules, nano-particles,…)

Khakalo et al. High throughput tailoring of nanocellulose films: from complex bio-based materials to defined multifunctional architectures.
ACS Appl. Bio Mater. **2020**, 3, 11, 7428–7438. https://doi.org/10.1021/acsabm.0c00576

Surface energy and WCA of Plasma treated films

Chemical characterization of plasma films





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Nutrient saturation

	Nutrient adsorption, mg/g (dry)		
	Unmodified membrane	Cationic (bulk)	Cationic (surface)
K^+	2,7	7,6	1,7
NO_3^-	1,1	8,2	0,6
PO_4^{3-}	2,0	11,3	0,5

Antimicrobial activity

Pseudomonas aeruginosa VTT E-96728			
	Viability of the cells on sample		
Samples	Log colony forming units		
1. Reference- CNF	3,4		
2. Cationic CNF (DS 0,06)	2,9		
3. 250W (CNF+Plasma)	3,1		
4.350W (CNF+Plasma)	3,3		
5.450W (CNF+Plasma)	2,9		
6.550W (CNF+Plasma)	3,1		
7. Cationic CNF (DS 0,2)	<1		
Staphylococcus aureus VTT E-70045			
	Viability of the cells on sample		
Samples	Log colony forming units		
1. Reference- CNF	3,1		
2. Cationic CNF (DS 0,06)	3,4		
3. 250W (CNF+Plasma)	3,2		
4.350W (CNF+Plasma)	3,0		
5.450W (CNF+Plasma)	2,9		
6.550W (CNF+Plasma)	2,4		
7. Cationic CNF (DS 0,2)	<1		

THANK YOU!

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