Substrates based on cellulose nanofibrils for printed electronics and optics

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Manufacturing of CNF films in semi-pilot scale

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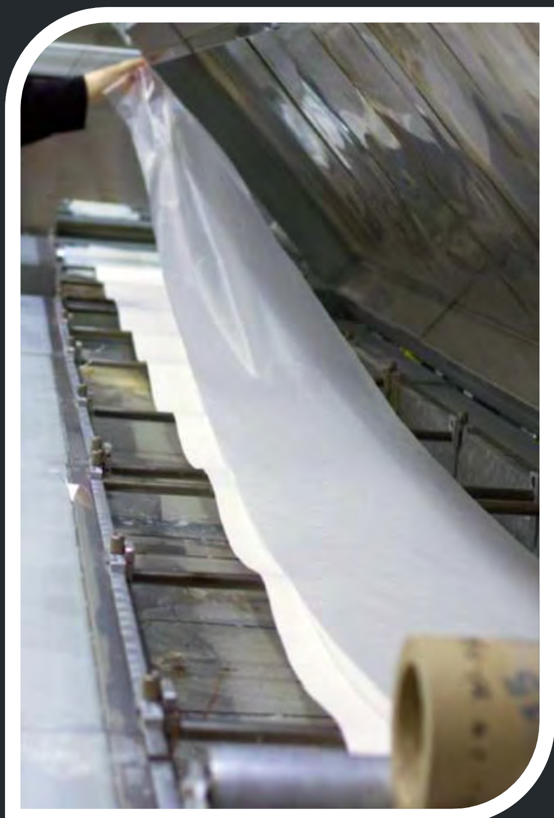

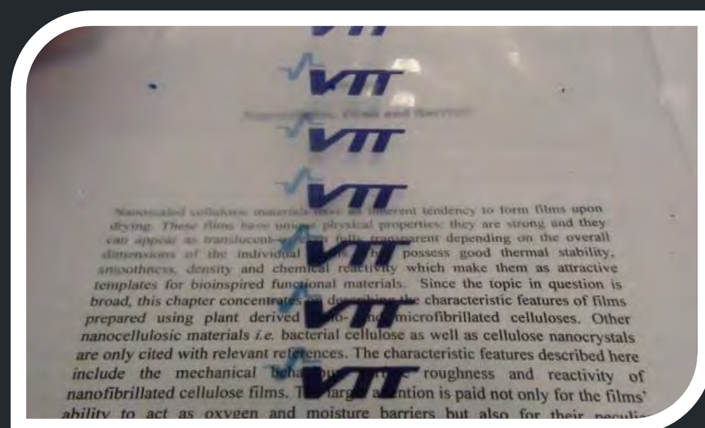

- Self-standing, flexible films
- CNF coated evenly on plastic film
- Controlled spreading and adhesion
- No shrinkage (adhered to plastic while dried)
- Translucent and smooth base surface replicated to CNF film (surface roughness of ~300 nm (1mm×1mm scale)
- Tunable thickness

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

Mäkelä et al. Microelectron. Eng., 2016, http://dx.doi.org/10.1016/j.mee.2016.05.023

Manufacturing pigment-CNF substrates in semi-pilot scale at consistency of 7% by film casting method

- Wet pressing is essential to form flexible, strong enough and smooth substrates
- The samples made with the film casting method are significantly smoother than the ones made earlier with the vacuum filtration method
- Formed calendered sheets are smooth and flexible

Drying of Pigment-Cellulose Nanofibril Substrates" Oleg Timofeev, Katariina Torvinen, Jenni Sievänen, Timo Kaljunen, Jarmo Kouko and Jukka A. Ketoja, ***Materials 2014, 7, 6893-6907; doi:10.3390/ma7106893***

Novel process for Supercapacitor production
--- proof of concept Co-operation with Tampere University of Technology

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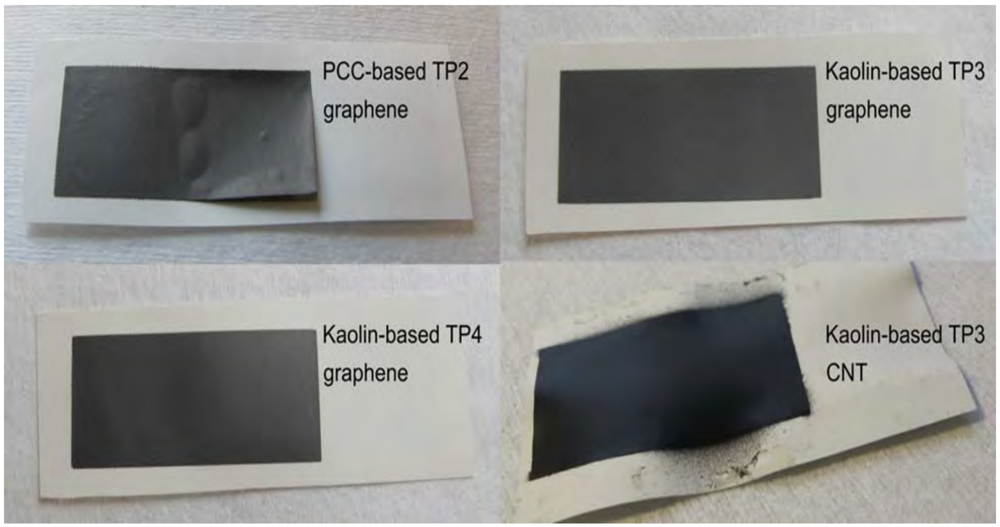

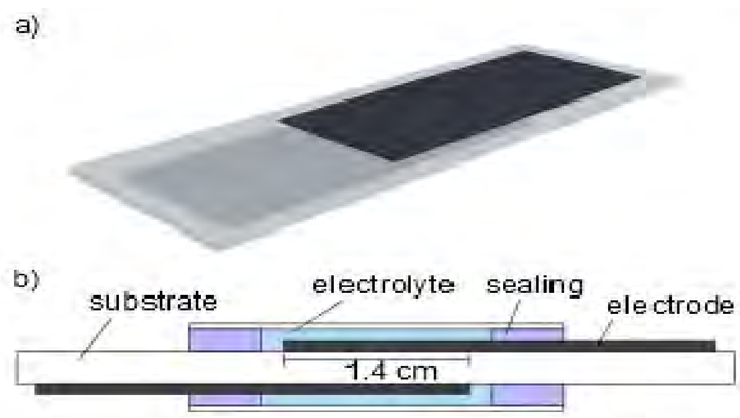

- Composite used as both separator and substrate
  - Pigment & NFC composite which is made using film casting / wet laid process
- Electrodes coated or printed into both sides of separator-substrate
  - Carbon nanotubes (CNT) ink by spray coating
  - Commercial graphene ink by screen printing
- Aqueous / nonaqueous electrolyte

"Pigment-Cellulose Nanofibril Composite and Its Application as a Separator-Substrate in Printed Supercapacitors" Katariina Torvinen, Suvi Lehtimäki, Janne T. Keränen, Jari Vartiainen, Jenni Sievänen, Erkki Hellén, Donald Lupo, Sampo Tuukkanen" Electron. Mater. Lett., Vol. 11, No. 6 (2015), pp. 1040-1047; DOI: 10.1007/s13391-015-5195-6

Novel process for Supercapacitor production
--- proof of concept Co-operation with Tampere University of Technology

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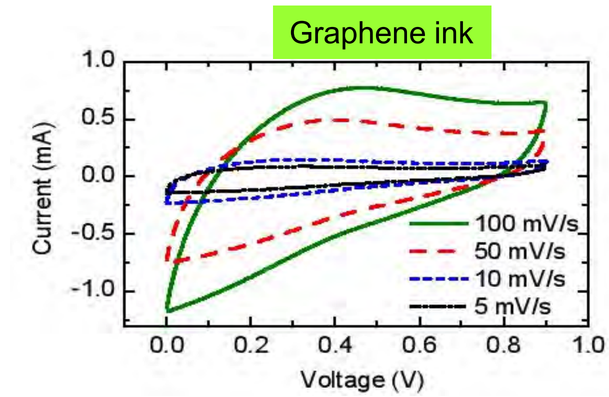
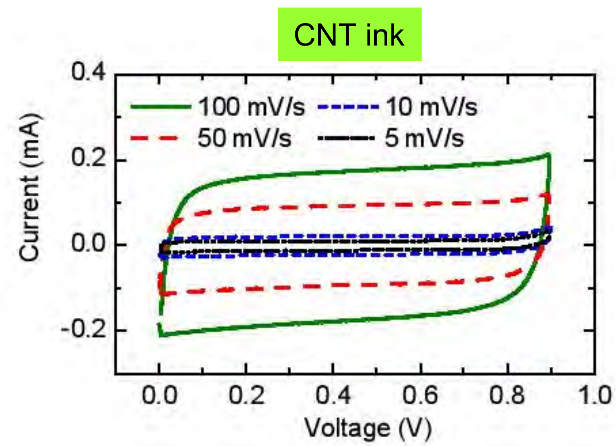
- Supecapacitor structure achieved by printing the active layers on both sides of separator-substrate
- The graphene and CNT inks used as high surface area active layer materials and simultaneously served as current collectors for supercapacitor
- The sheet resistance of the printed layers, measured with the 4-probe method, was 10 Ω/□.
- The specific capacitances were for Kaolin-CNF 4.9 and for PCC- CNF 4.2 F/g, respectively, when accounting only for the active material mass on the electrode overlap area

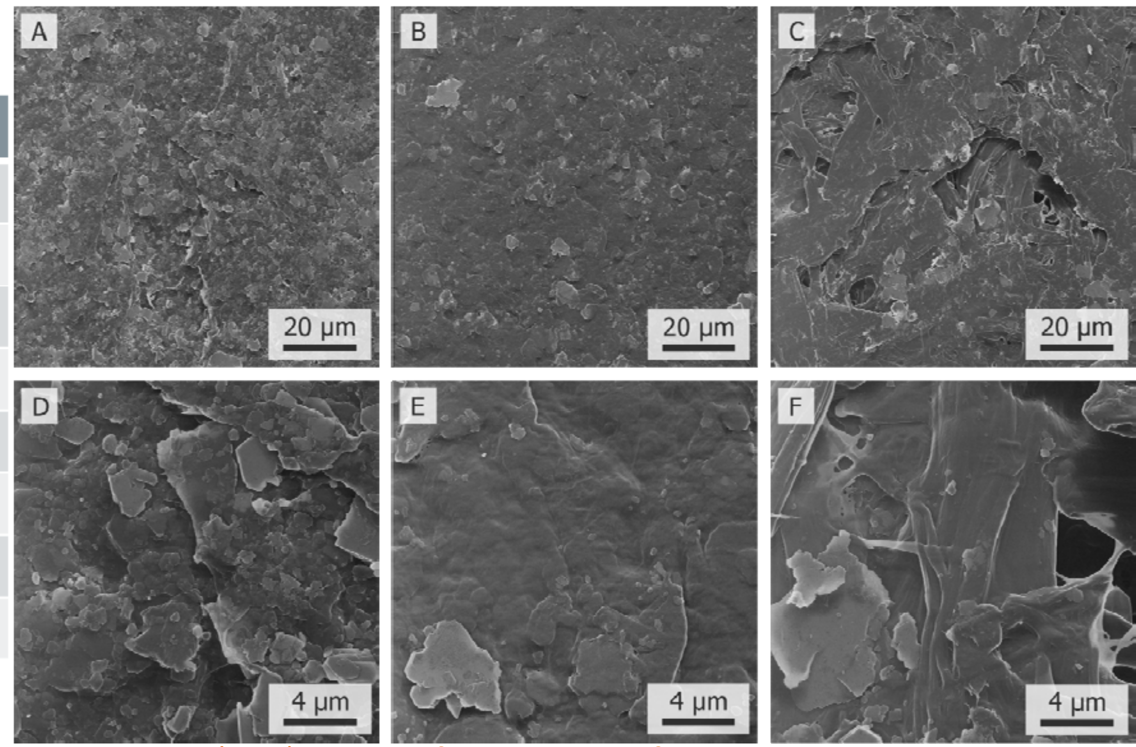
*	Fig 1
Measurement currents (C/ESR)	10 µA / 100 µA
Capacitance from PVI	17-20 mF
ESR (by fitting)	400 Ω





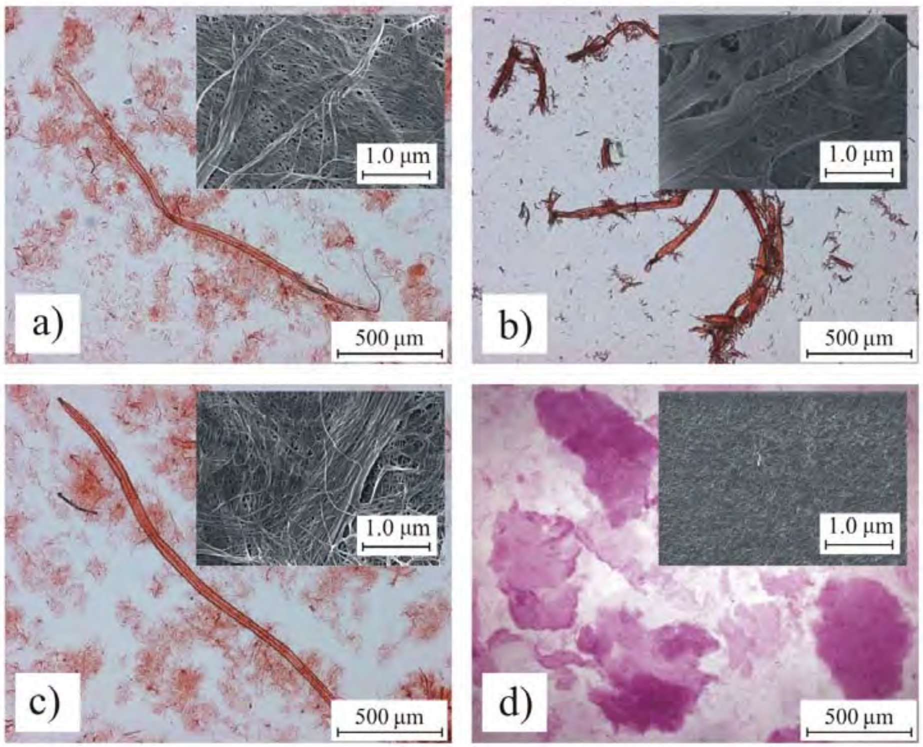
Case: Ion-modulated transistor
Proof of concept Co-operation with Åbo Akademi

Composite	CNF	Pigment	Sorbitol [%]	CNF / pigment wt-%
2	Native	Kaolin Capim SP	0	20/80
3	E-CNF	Kaolin Capim SP	15	42.5/42.5
4	E-CNF	Kaolin Capim SP	0	20/80
5	Native	Kaolin Capim SP	15	42.5/42.5
6	L-CNF	Kaolin Capim SP	15	42.5/42.5
7	L-CNF	Kaolin Capim SP	0	20/80
8	T-CNF	Kaolin Capim SP	0	20/80
10	L-CNF	Barrisurf	0	20/80



Helium Ion Microscope (HIM) images of composite surface morphology. The top side of the composites was imaged, using 100 µm (A-C) and 20 µm (D-F) fields of view. In A) and D) TCNF_20, in B) and E) LCNF_20C, and in C) and F) ECMF_20 are shown.

Characterization of nanomaterials

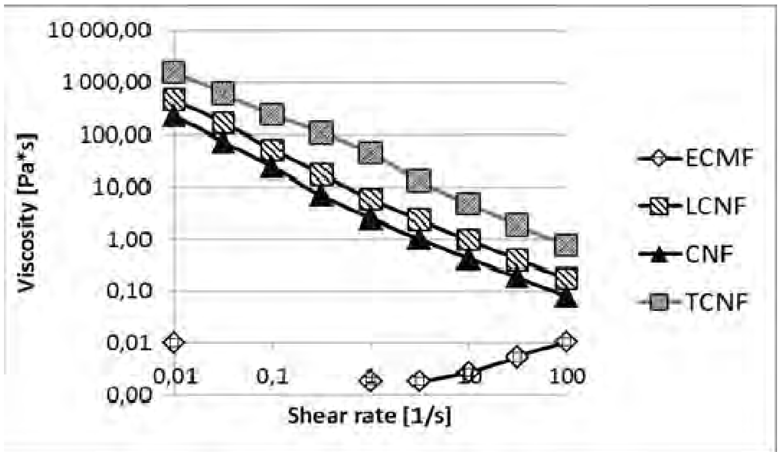


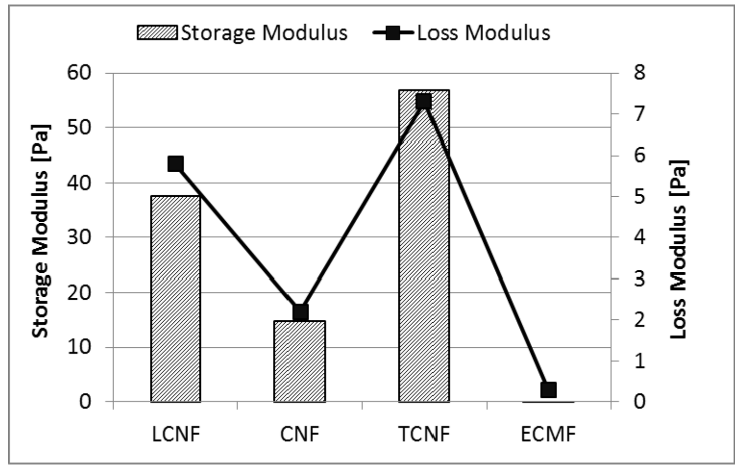
Microscopy and SEM images of different grades of cellulose nanofibrils a) CNF b) ECMF c) LCNF d) TCNF.

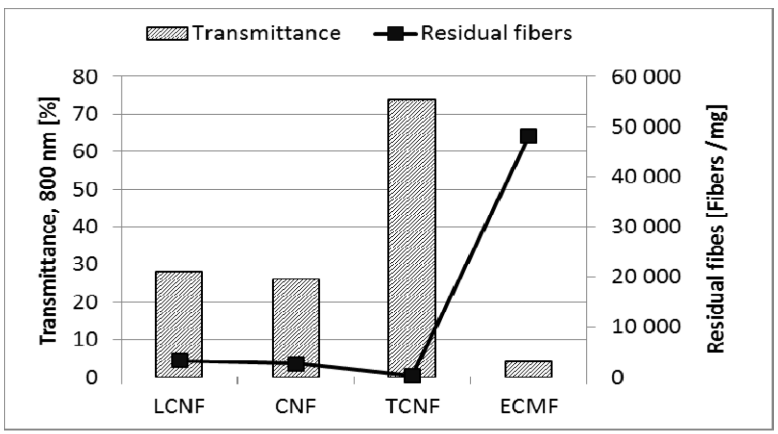
Character	Unit	LCNF	CNF	TCNF	ECMF
Pulp		Unbleached kraft	Bleached kraft	Tempo SW pulp	Bleached kraft
Charge	mmol/g	0.07	0.02	1	0.02
Fibrillation Method		Grinding	Grinding	Microfluidizatio n	Enzymatic
DP	SCAN	2087	1430	286	833
Transmittance, 800 nm	%	28	26	74	4
pH	pH	8.8	6.3	7.5	5.3
Consistency	%	1.75	1.76	1.16	18.56
Conductivity	µS/cm	403	116	794	51
Residual fibers	Fibers/m g	3272	2699	341	48105
Storage Modulus	Pa	37.5	14.8	56.8	0.02
Loss Modulus	Pa	5.8	2.2	7.3	0.3
Shear viscosity, 10 1/s	Pa·s	0.98	0.43	4.39	0.002
ÅAGWR, 30 sec.	g/g	297	233	446	229
SEC	kWh/kg	15.7	16	12	0.6

Torvinen K. *, Pettersson, Lahtinen P., Arstila K., Kumar V., Österbacka R., Toivakka M. and Saarinen J. Nanoporous kaolin – cellulose nanofibril composites for printed electronics. 2017, In : Flexible and Printed Electronics. 2, 2, 11 p., 024004.*

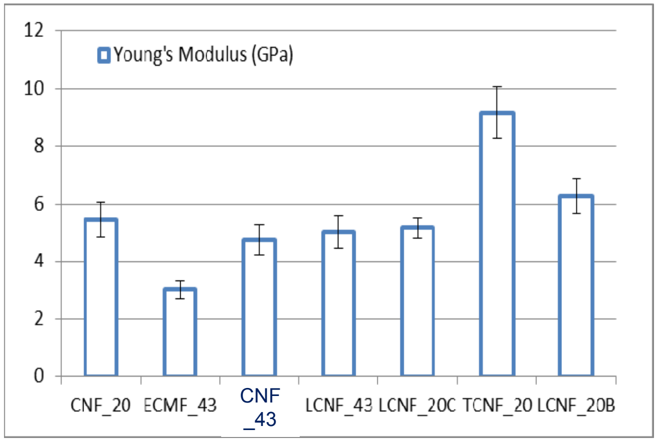
Characteristics of nanomaterials

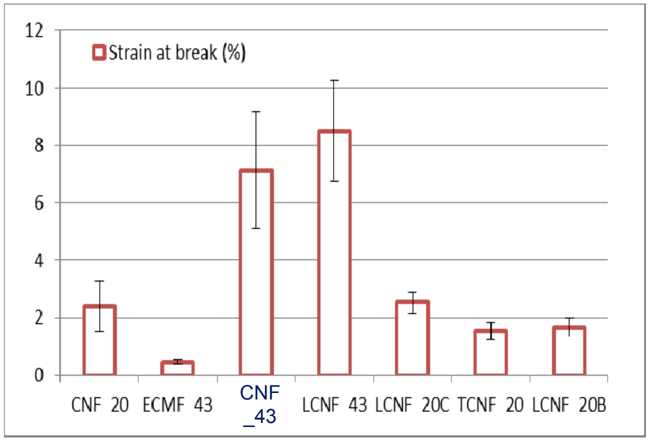


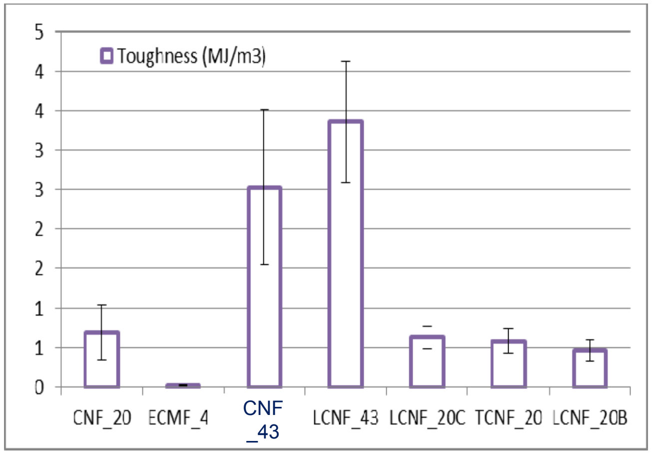


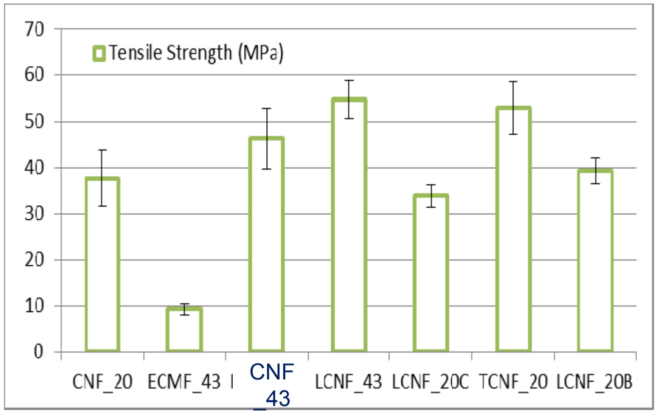


Properties of composite films









Trial point	Grammage [g/m²]	Thickness [µm]	Density [kg/m³]	Formation Spec	Roughness Ra [µm]	Stain length [mm]
CNF_20	88.2 ± 2.2	58 ± 3	1522 ± 50	0.74	0.37 ± 0.02	138
ECMF_43	100.0 ± 7.7	75 ± 5	1332 ± 78	0.78	2.23 ± 0.55	54
ECMF_20	108.7 ± 2.5	76 ± 3	1427 ± 21	0.76	1.96 ± 0.27	-
CNF_43	112.6 ± 2.7	71 ± 1	1597 ± 28	-	0.54 ± 0.07	144
LCNF_43	102.1 ± 1.6	66 ± 1	1551 ± 19	-	0.67 ± 0.06	170
LCNF_20C	114.3 ± 2.5	76 ± 2	1512 ± 43	0.66	0.39 ± 0.04	159
TCNF_20	116.5 ± 1.5	76 ± 4	1531 ± 90	0.43	0.41 ± 0.06	138
LCNF_20B	111.6 ± 9.5	86 ± 7	1306 ± 101	0.59	0.74 ± 0.19	121

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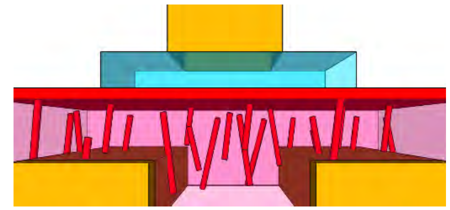
Transistor characteristics

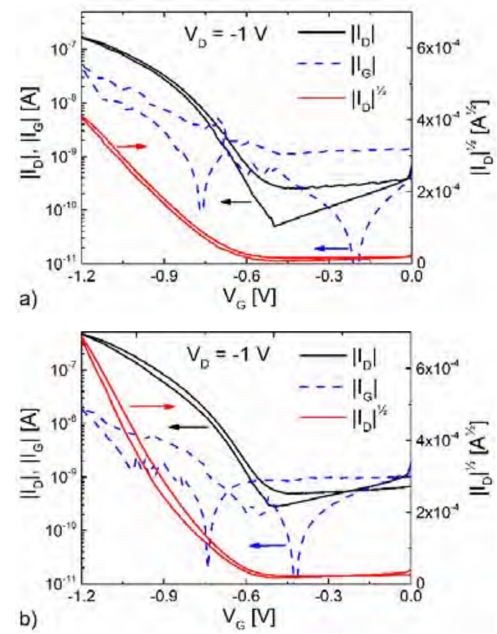
Collaboration with Åbo Akademi

Trial point	ON-current [E-07 A]	OFF-current [E-10 A]	ON/OFF-ratio	Leakage [E-08 A]	Leakage/ON-current
CNF_20	1.4	9.1	150	14	1.01
ECMF_43	-	-	-	-	-
CNF_43	3.0	2.1	1460	4.0	0.13
LCNF_43	2.8	2.1	1370	3.3	0.12
LCNF_20 C	0.3	10	30	0.4	0.13
TCNF_20	1.7	0.5	3460	5.0	0.29
LCNF_20 B	3.9	2.5	1570	3.0	0.08
ÅA	4.7	2.9	1650	2.0	0.04

FOMs, calculated using the transfer curves of the same transistor model, fabricated on different substrates. Trial point ECMF_43 did not show transistor characteristics and therefore corresponding FOMs could not be calculated. A multilayer paper from Åbo Akademi was used as a reference. All units are in amperes, except for the ratios that are unitless.

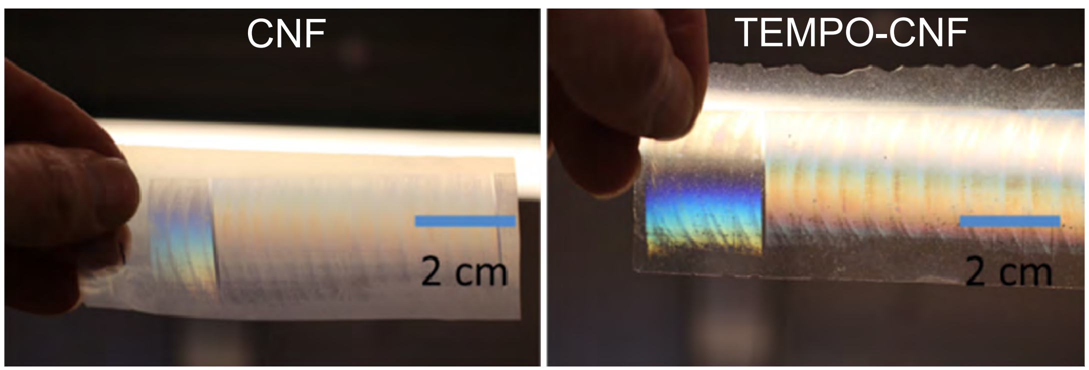


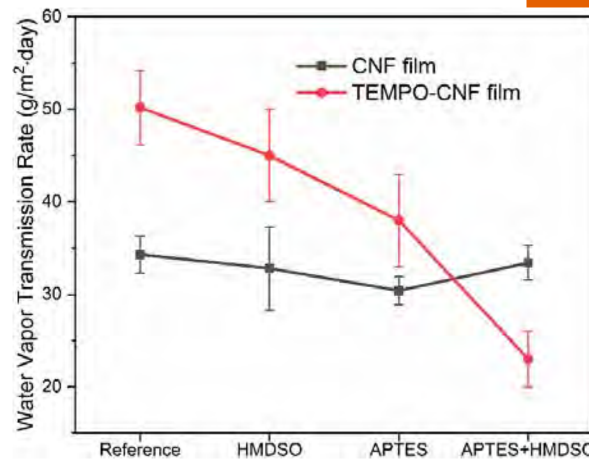
A schematic view of the device structure. The transistor electrodes have been drawn in orange, the solid electrolyte in blue, the semiconductor in red and the polymer insulator in pink.

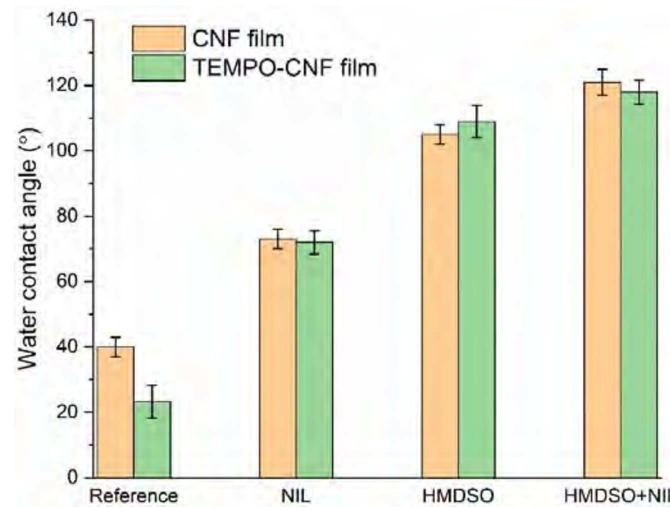


Tailoring nanoarchitecture towards versatile nanocellulose films

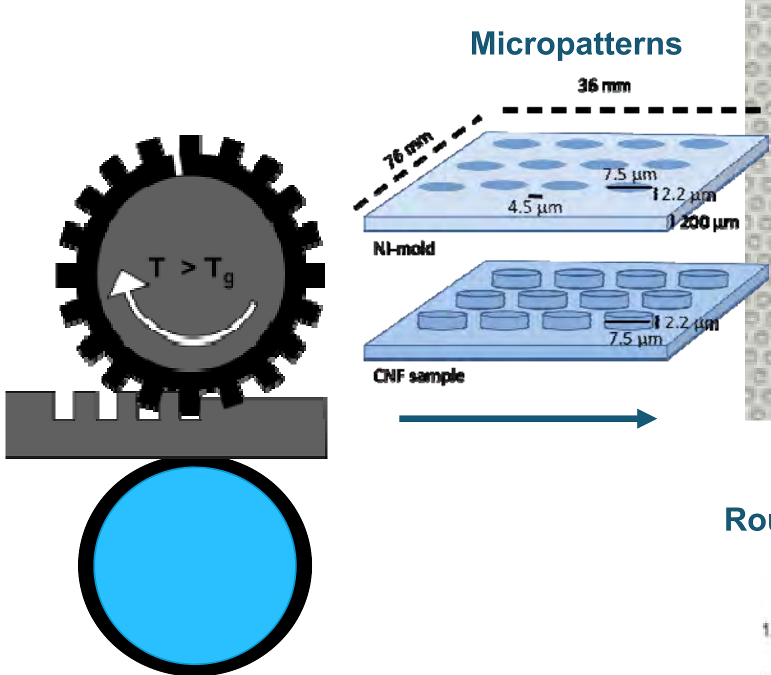
- Optical properties
- Hydrophobic/hydrophilic balance
- Oxygen and water vapor transmission rates
- **Simultaneously!**
- Large-scale R2R processes

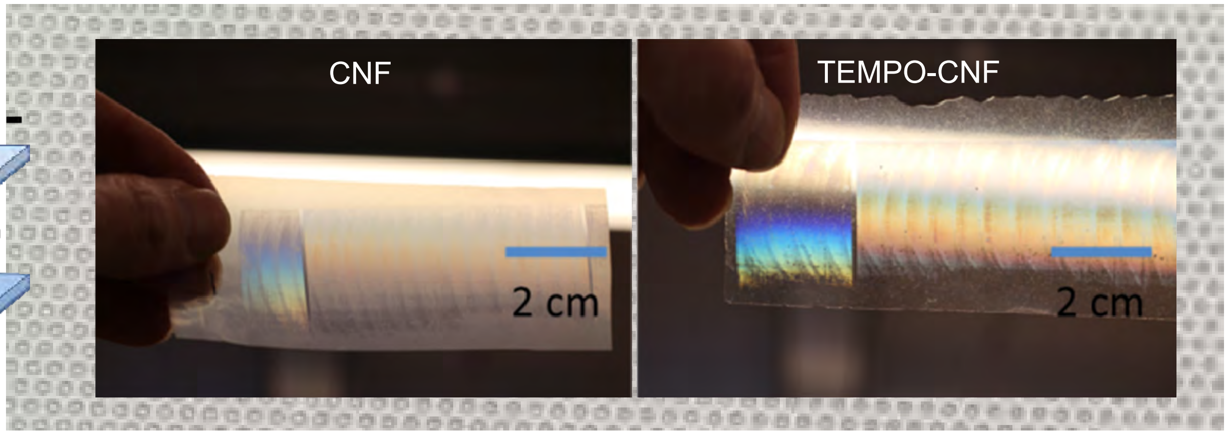


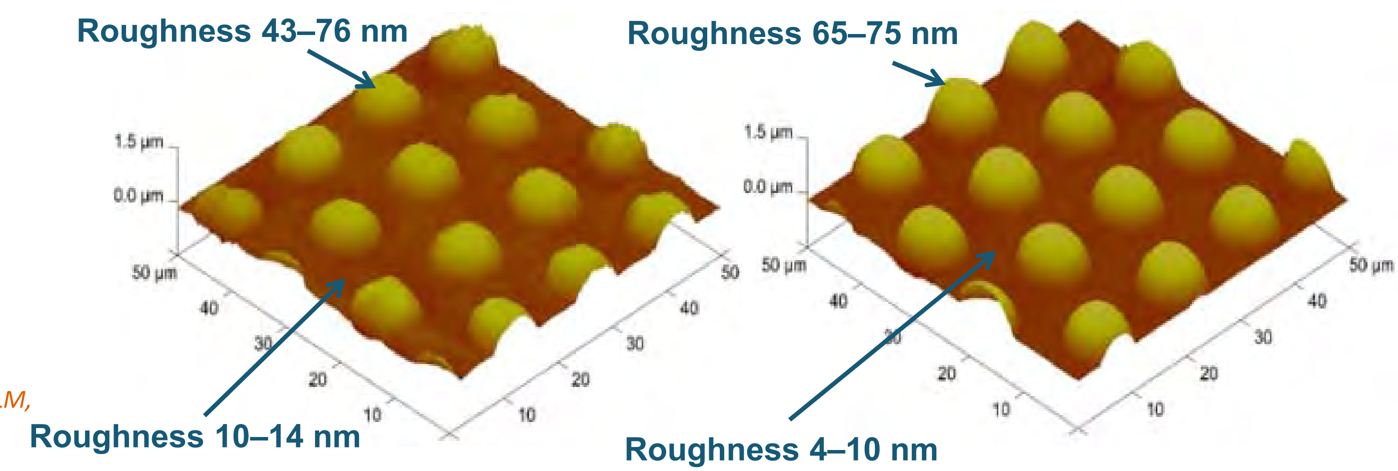




Nanoimprint lithography (NIL): surface patterning of CNF films







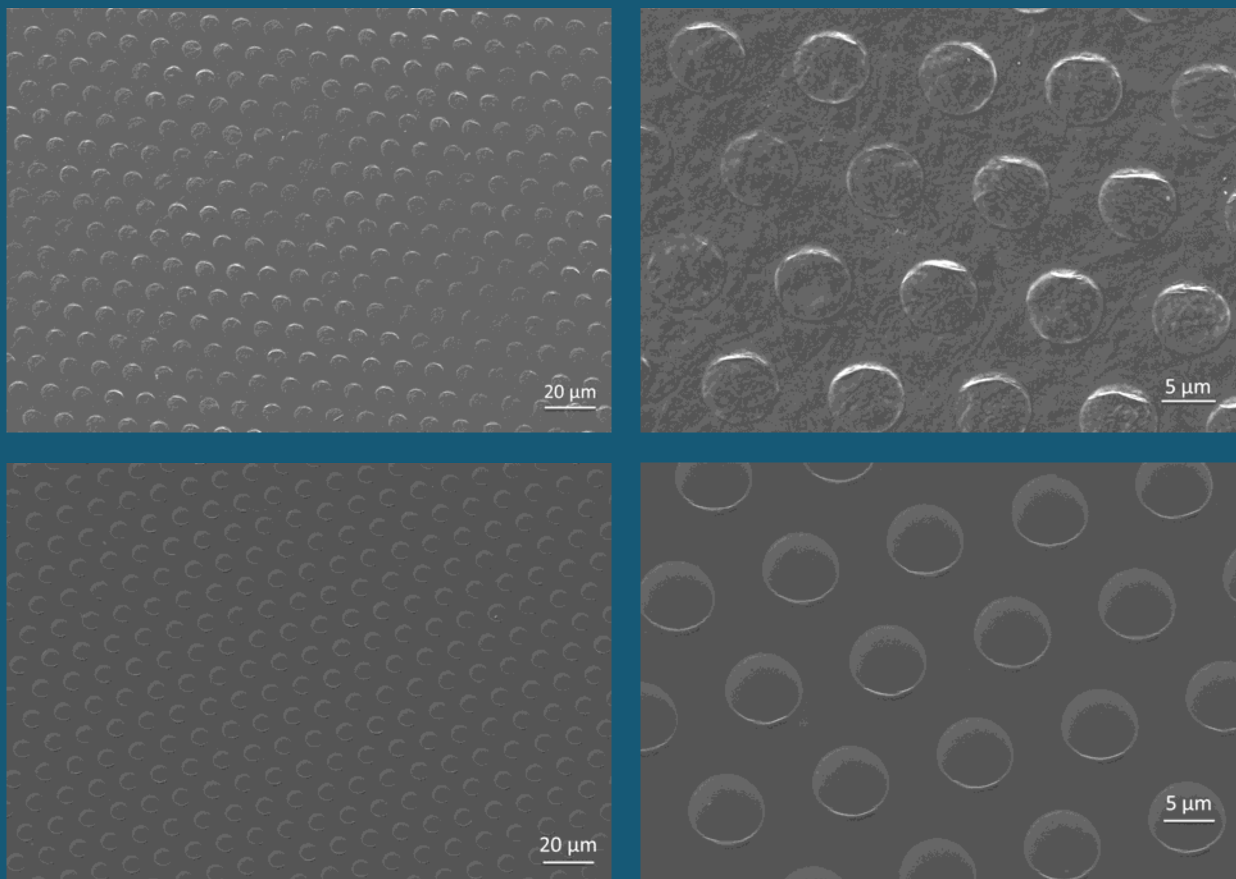
Printing speed 0.1-0.2 m/min
Pressure 2 MPa – 8 MPa
Variable: temperature 20°C -150° C

T. Mäkelä, MANUFACTURING PATTERNED CELLULOSE-BASED FILM, patent application FI20197019

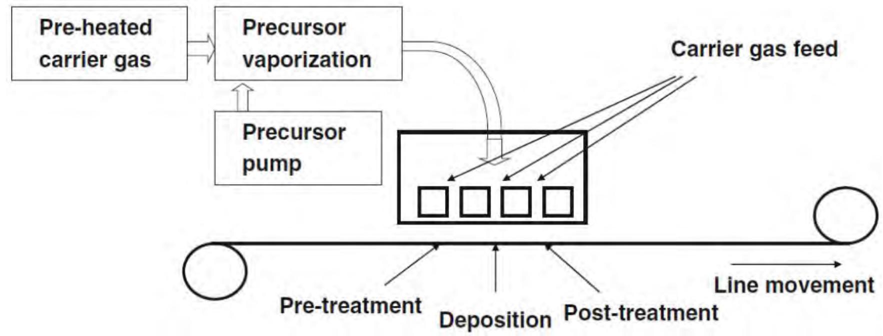
Pillars on modified CNF films by NIL patterning

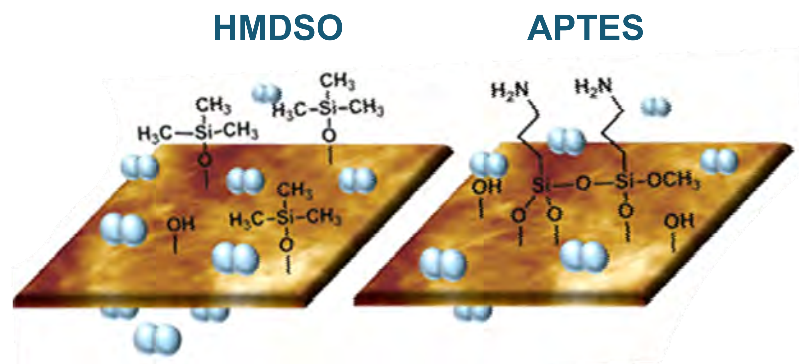
CNF

TEMPO-CNF

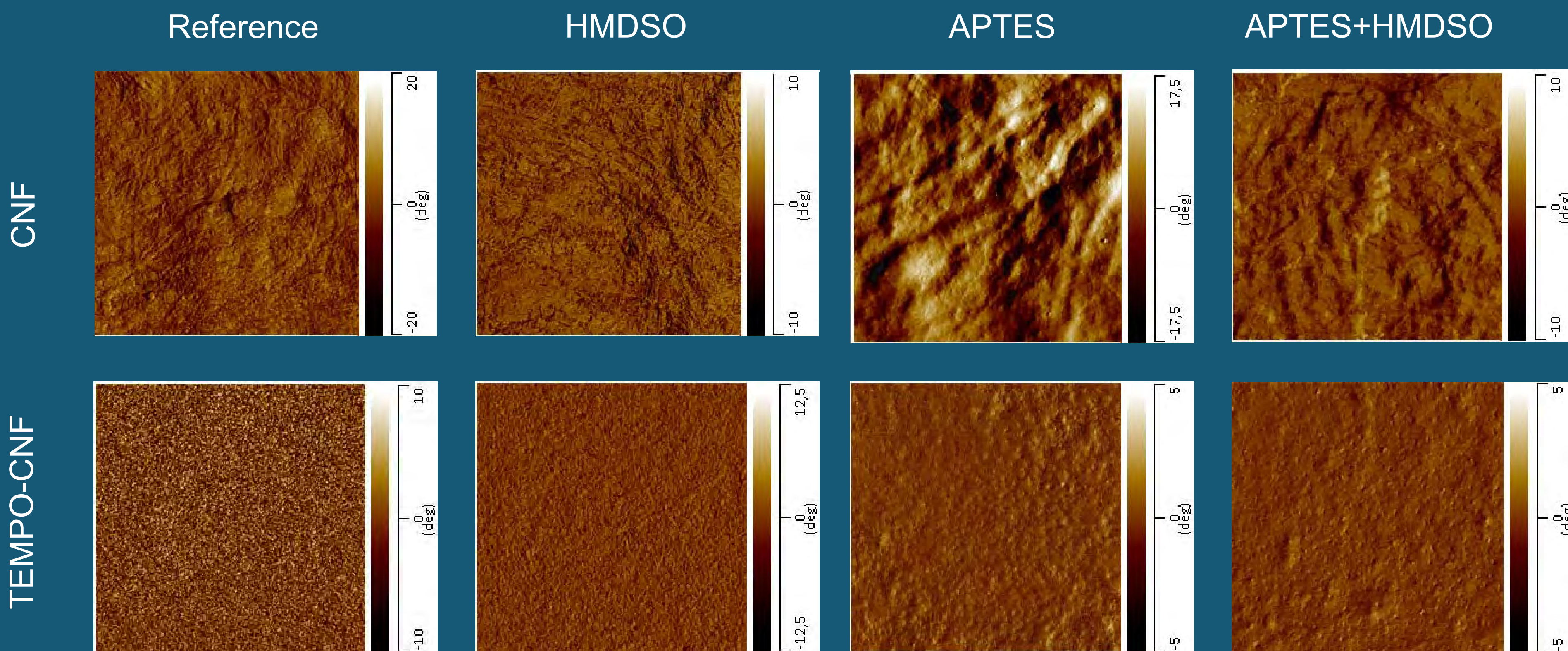


Gas phase reactions - molecular level chemical modification towards controlled hydrophobicity and barrier performance

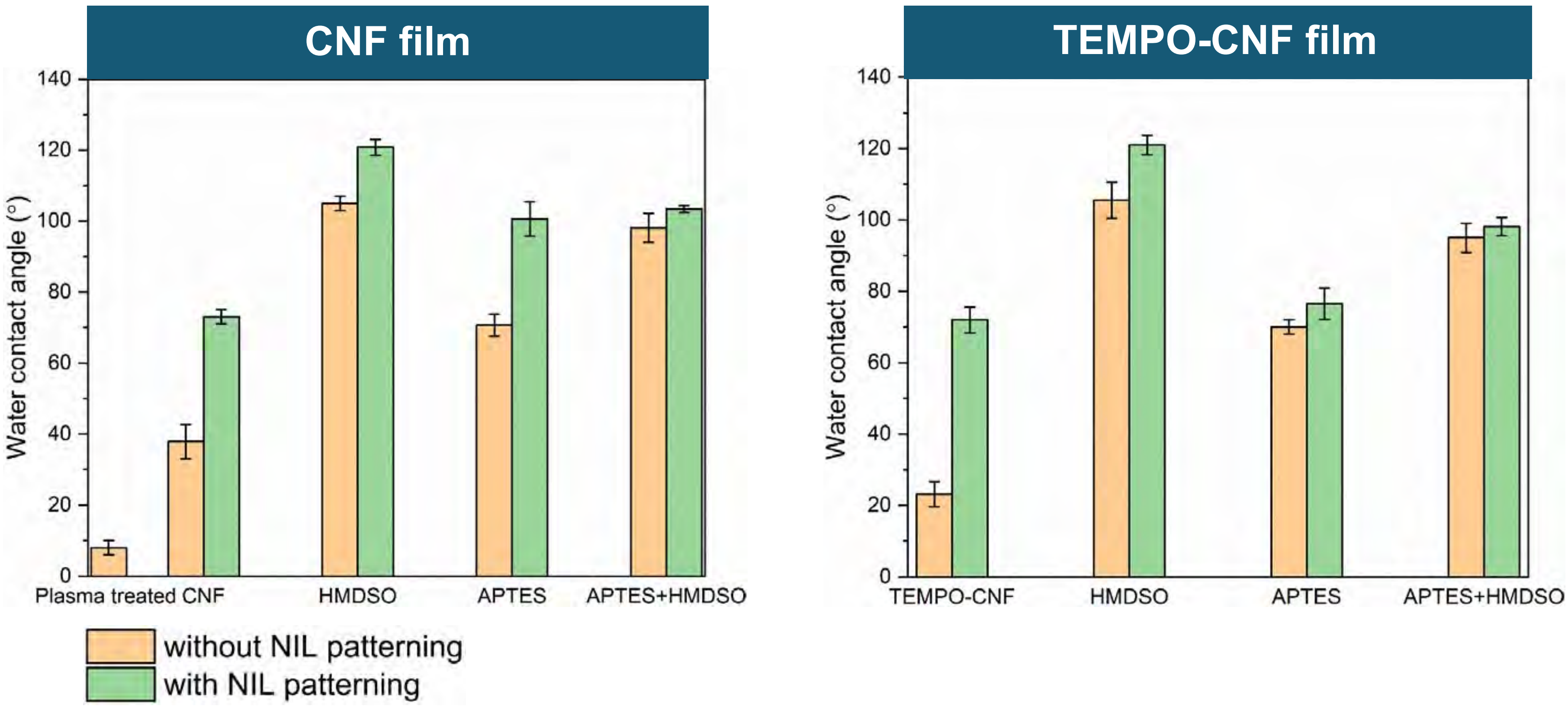




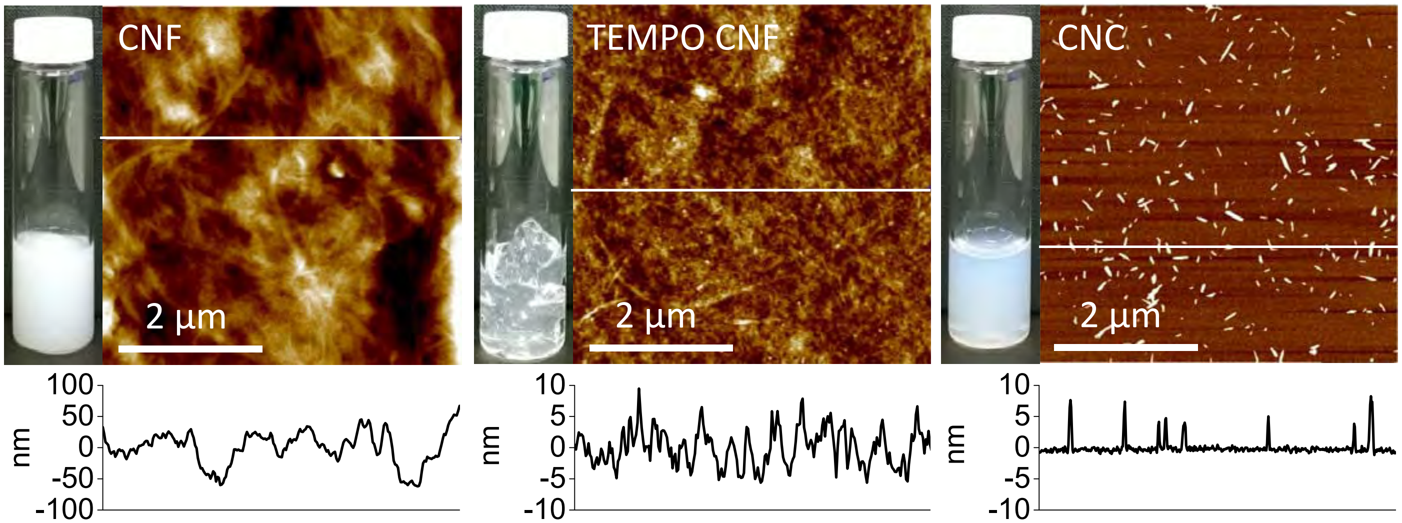
AFM investigation of CNF films



WCA of surface modified CNF films



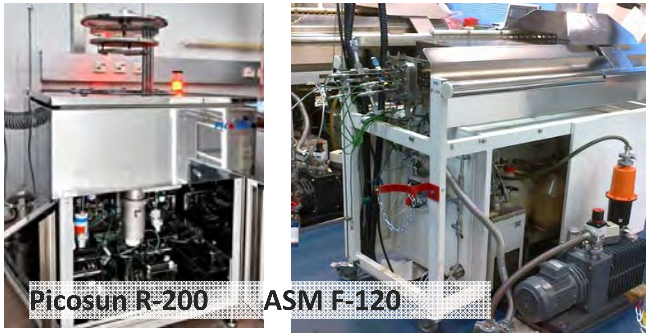
Cellulosic materials for thin film construction



Charge: (-) (- - -) (- -)

Inorganic Thin Films by ALD

- ZnO is one of the best thermoelectric oxide materials
- Aluminum doping improves the thermoelectric power
- Typical ZnO:Al resistivity ~10^{-2} Ωcm on glass



- ZnO and ZnO:Al were deposited by ALD on nanocellulosic layers at 150 ^{o}C
  - Thin films grow layer-by-layer based on self-limiting gas phase chemical surface reactions
- Deposited film thickness 15-20 nm

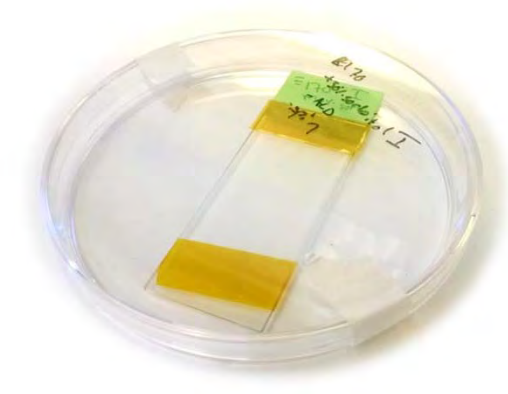
Tynell, T. et al. Thermoelectric characteristics of (Zn,Al)/O hydroquinone superlattices. *J. Mater. Chem. A.* **2013**, 1, 13619.

Multilayer hybrid structures on self-standing flexible CNF film

- Self-standing films from
  - TEMPO oxidized CNF
  - Unmodified, mechanically disintegrated CNF

- Multilayers deposited on CNF films by
  1. ALD deposition
  2. Spin-coating of TEMPO CNF/CNF/CNC
  3. ALD deposition

- ALD layer: 100 cycles (~16 nm) of ZnO/ZnO doped with Al

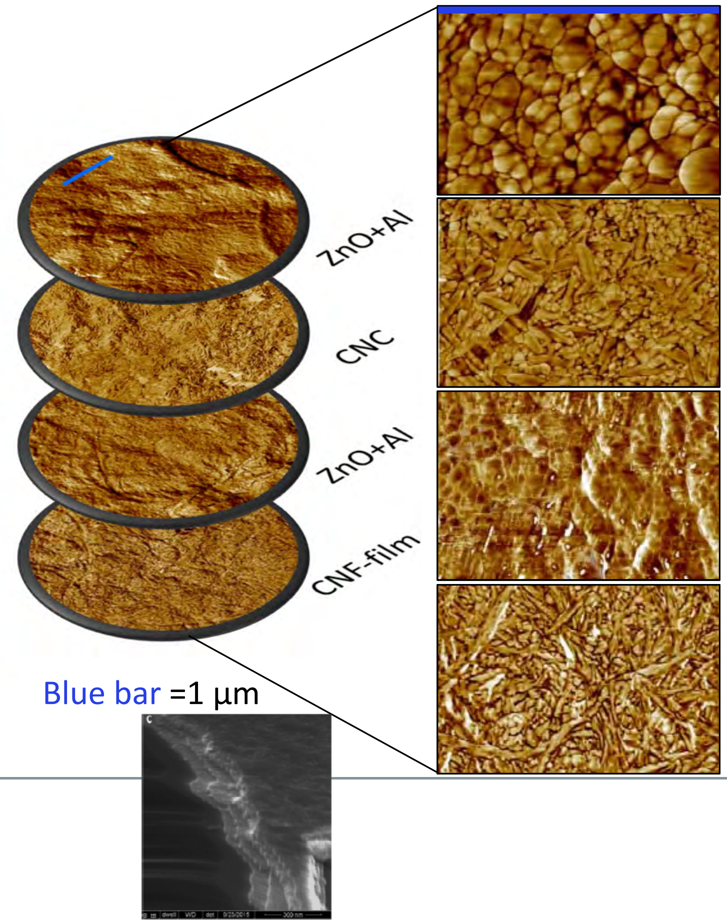


Thermoelectric properties

$$ZT \equiv \frac{S^2 T}{\rho \kappa}$$

Sample	Resistivity (kΩ)	Seebeck (μV/K)
ZnO	2-3	120
CNF - freestanding film	2000	n/a
ZnO – TEMPO – ZnO	10-20	237
ZnO – CA – ZnO	~100	109
ZnO – CNF – ZnO	1000-2000	n/a
ZnO+Al – CNF – ZnO+Al	10-20	150-160
ZnO+Al – CNC – ZnO+Al	75-95	135

References | Solid substrate | Freestanding film



Outcomes

- Inorganic-CNF composites have potential as substrates in printed electronics applications and moreover in energy storage applications as a separate-substrates
- Structural properties (porosity, smoothness) can be adjusted by selection of raw materials depending on target applications needs
- Ion-modulated transistor performance achieved for kaolin-CNF composite films
- Surface patterning by roll-to-roll nanoimprinting enabled optical features and improved the hydrophobicity of CNF and TEMPO-CNF films
- Surface modification with by roll-to-roll plasma deposition improved the hydrophobicity and barrier performance of CNF and TEMPO-CNF films.
  - Surface modifications can be done simultaneously and on the large - scale R2R processes
- Cellulosic materials are suitable for thin film construction
- Inorganic Thin films by ALD deposition on CNF films
- Multilayer hybrid structures provided thermoelectric properties on self-standing flexible CNF films

Thank you

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