Cellulose based functional materials in electrical and electrochemical flexible devices

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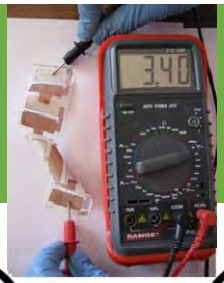
TAPPI

Outline

- Motivation
  - Paper electronics
  - Cellulose dielectrics
- Cellulose electrolyte membranes
- Cellulose/ZnO printable inks
- “Paper-like” membranes
- CNC membranes as dielectric
- Summary

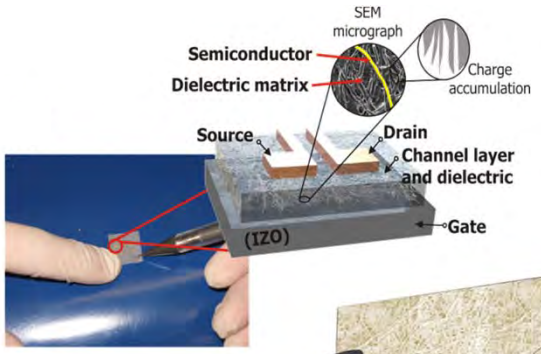
Motivation

Paper electronics

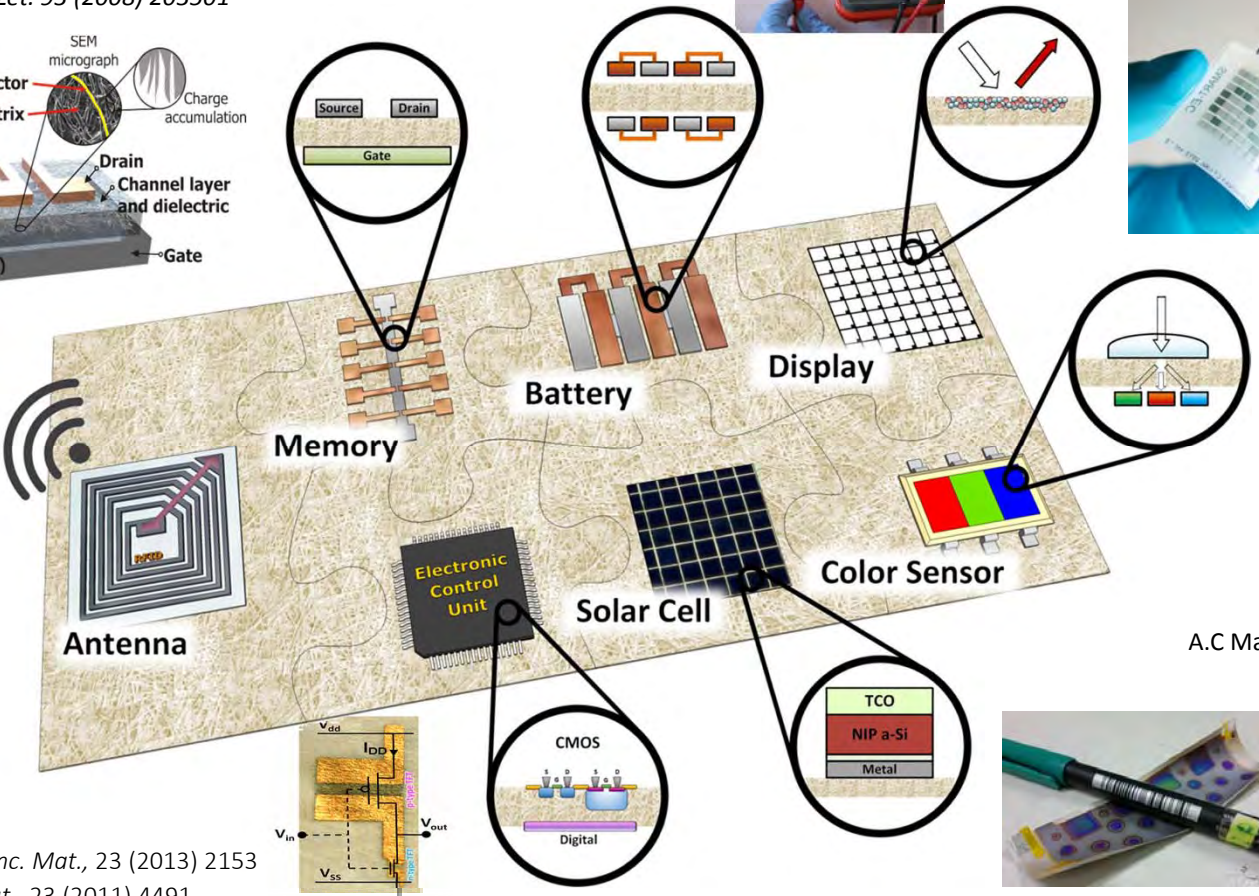


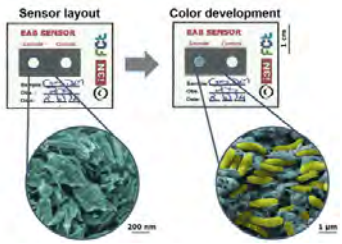
I. Ferreira, Electrochimica Acta. 56 (2011): 1099-1105

R. Martins et al, A. Phys. Let. 93 (2008) 203501



P. Wojcik et al., Nanoscale, 7 (2015) 1696
P. Wojcik, et al., J. Mat. Chem., 22 (2012) 13268





A.C Marques et al., Sci. Reports, 5 (2015) 9910

2500 µm

R. Martins et al, Adv. Func. Mat., 23 (2013) 2153
R. Martins et al, Adv. Mat., 23 (2011) 4491

A. Vicente et al, J. Mat. Chem. A, 2 (2015)
H. Aguas et al, Adv. Func. Mat., (2015)

Motivation

Cellulose electronics

Cellulose-based paper as the substrate

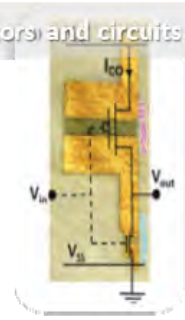
Barrero et al, 2017
(https://doi.org/10.1088/2058-8585/aa5a19)

Vicente et al, 2016
(DOI: 10.1088/2058-8585/aa5a19)

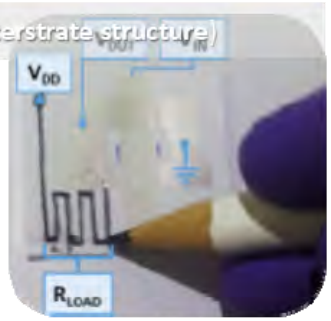
Costa et al, 2014
(DOI: 10.1088/0957-4484/25/9/094006)

Cellulose-based paper as the substrate and dielectric

Pereira et al, 2017
(DOI: 10.1088/0957-4484/25/9/094007)



Martins et al, 2011
(DOI: 10.1002/adma.201102252)



Grayet al, 2017
(DOI : 10.1002/adma.201700008)

Cellulose-based composites

Carvalho et al,
(under submission)

Barrero et al, 2017
(https://doi.org/10.1088/2058-8585/aa5a19)

Cunha et al, 2017
(DOI: 10.1002/adfm.201606793)

... And so much more in a near future

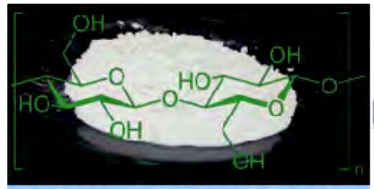
Motivation

Cellulose electronics

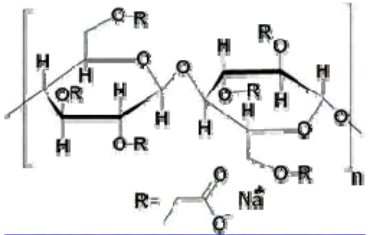
Cellulose electrolyte membranes

Cellulose electrolyte membranes

Preparation of cellulose-based hydrogel stickers



Microcrystalline cellulose (MCC)



Carboxymethyl cellulose sodium salt (CMC)

Step 1

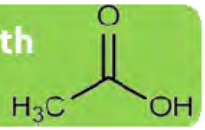
MCC dissolution in alkali salts (LiOH, NaOH):urea:H_2O

Step 2

Addition of CMC as a mechanical strengthner

Step 3

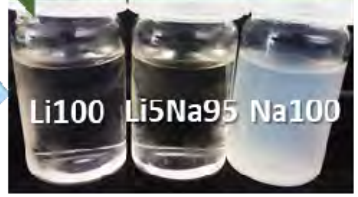
Neutralization with acetic acid



Step 4

Shear-casting and drying at ambient conditions

100 wt.% LiOH concentration 0 wt.%



0 wt.% NaOH concentration 100 wt.%

High dissolution efficiency

Poor dissolution efficiency

Low-temperature
(~-8 ºC)

Environmentally friendly
(abundant materials)

Cost savings
(saves resources, time and energy)

Cellulose electrolyte membranes

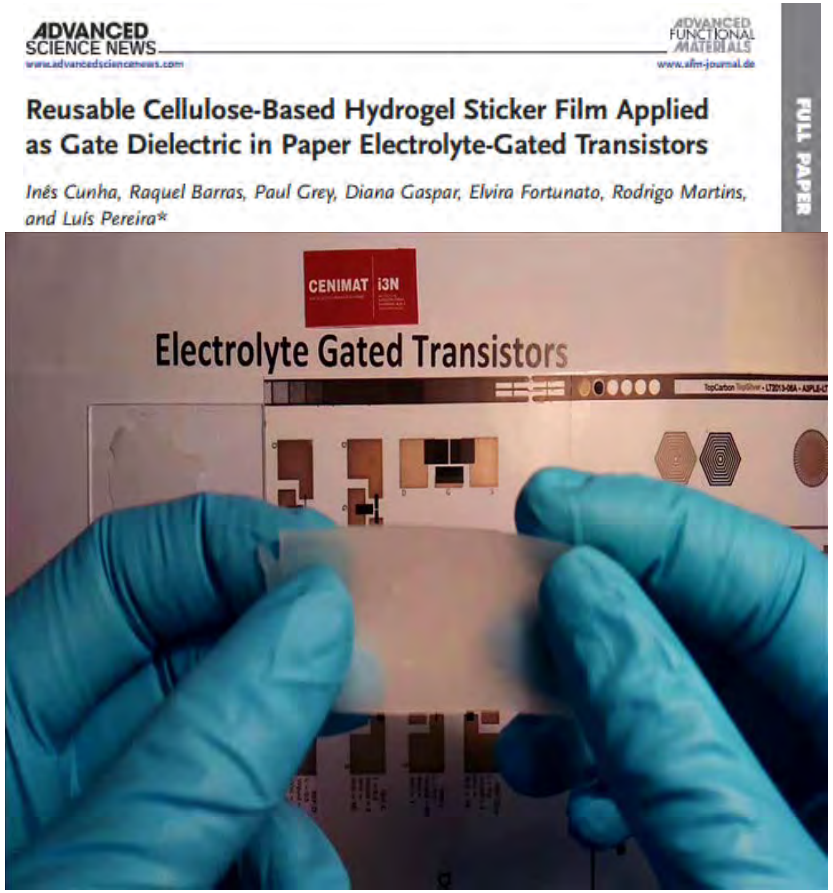
Preparation of cellulose-based hydrogel stickers

- Flexible and robust
- Light and portable
- Moldable and comformable
- Sticky and gooye
- Translucid
- (Self)healing abilities
- Reusable and recyclable

→

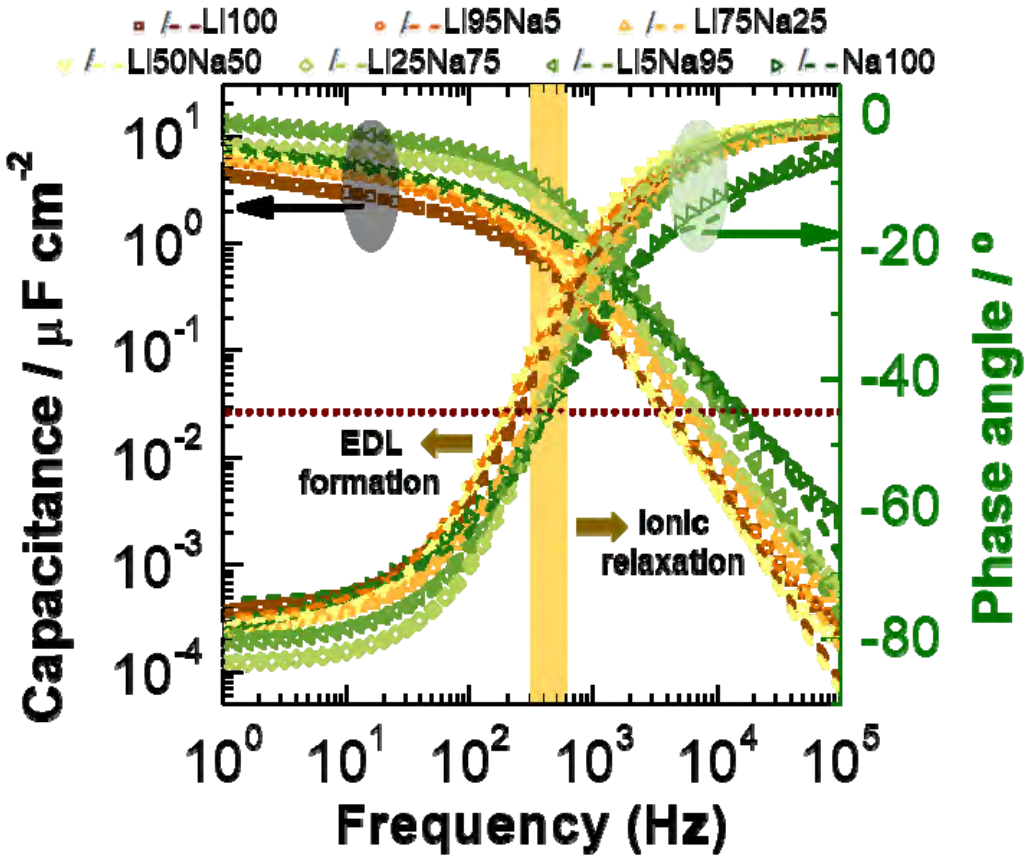
- **Mechanical damage**
- **Temperature**
- **Humidity**

Cunha et al, 2017 (DOI: 10.1002/adfm.201606755)

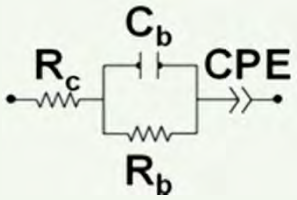


Cellulose electrolyte membranes

Impedance spectroscopy



Dasgupta's model[1]



C_{DL} – Electrical double layer (EDL) capacitance
σ_i – Ionic conductivity
R_c – Contact resistance
R_b – Bulk resistance
C_b – Bulk capacitance
CPE – Constant phase element

[1] Dasgupta et al, 2012 (DOI: 10.1002/adfm.201200951)

- C_{DL} values according to the literature
- σ_i (~10^{-3} S cm^{-1}) is far superior than usual solid polymer electrolytes at room temperature (~ 10^{-5}-10^{-4} S cm^{-1})

Cellulose electrolyte membranes

Electrolyte Gated Transistors - EGTs

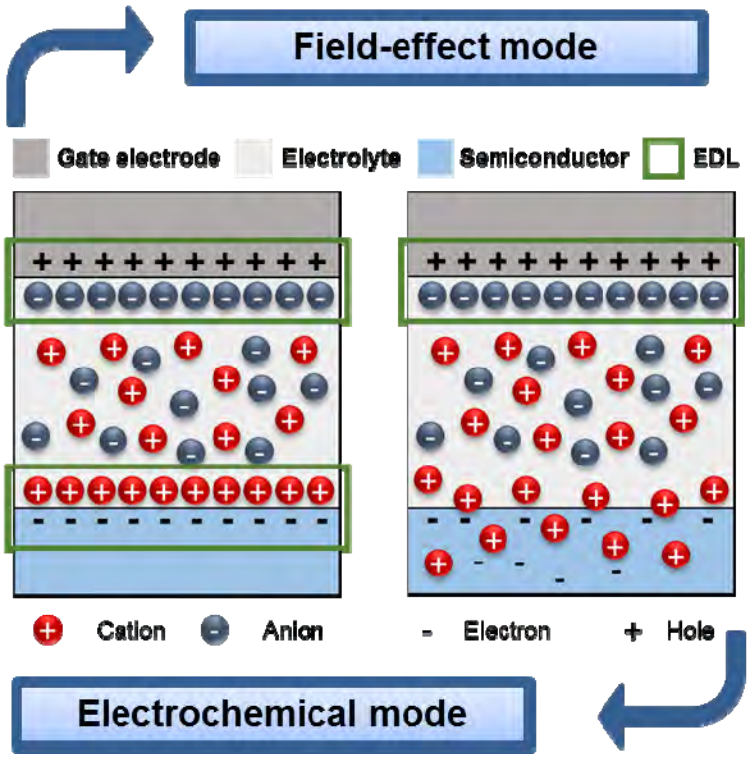
Main features

- Low operation voltages
- High Capacitance Electrolyte 1-10 μF/cm^2;
- Electrical Double Layer (EDL)
- Fully-printed
- Two operation modes

Weaknesses

- High leakage currents
- High switching delays
- Large parasitic capacitances

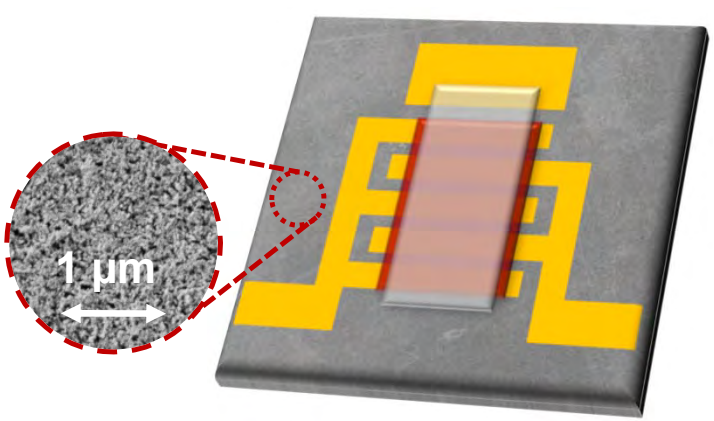
Operation modes



S.H. Kim *et al.,* Adv. Mater., **25**, no.13, (2013)

Cellulose electrolyte membranes

Implementation in EGTs

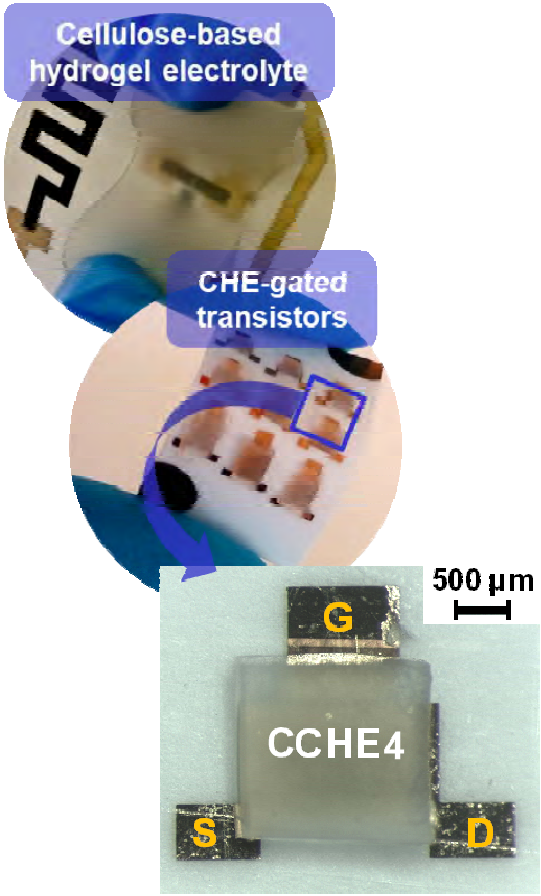


Multilayer-coated paper

Titanium /Gold electrodes

Sputtered IGZO

Laminated CHE sticker



Ti/Au electrodes

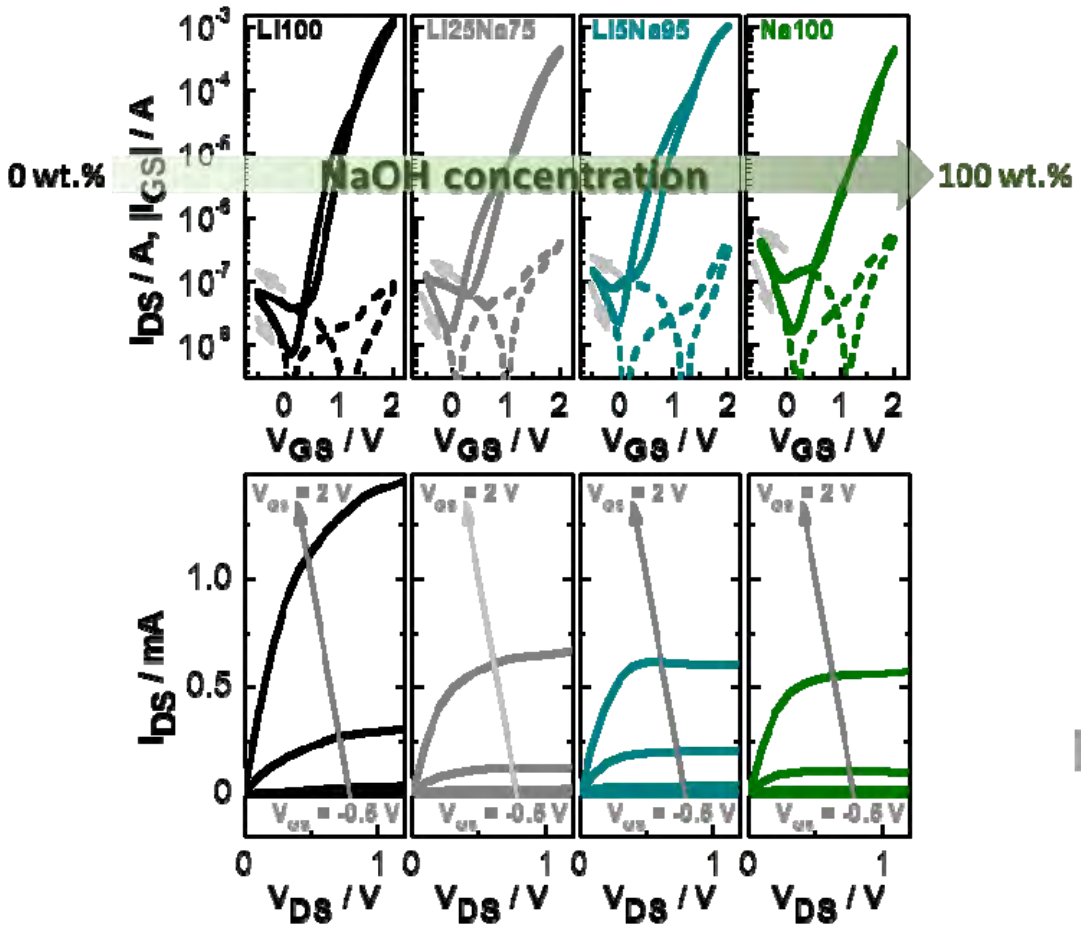
- Planar interdigital architecture
- E-beam
- Thickness: 6/ 65 nm
- W/L = 170

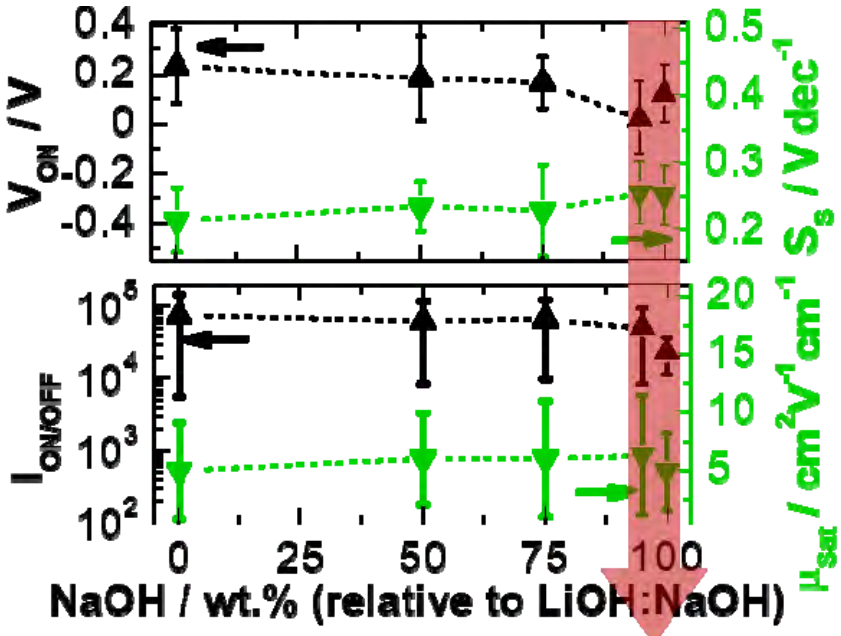
IGZO semiconductor

- RF magnetron sputtering
- In_2O_3:Ga_2O_3:ZnO - 2:1:2 mol.%
- Thickness: 35 nm
- Annealing: 150ºC @ 30 min

EGTs – LiOH/NaOH membranes

Transfer and output characteristics

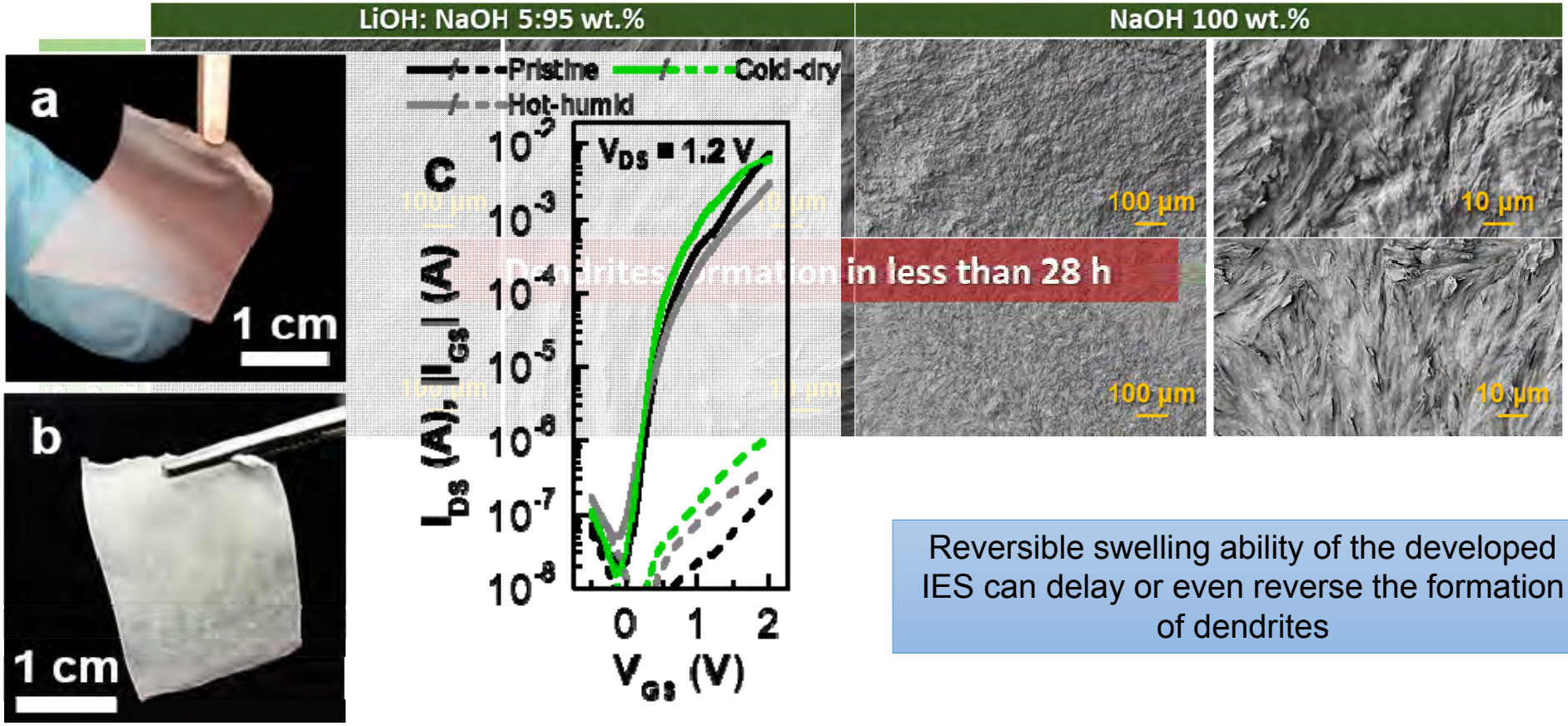




IES	V_{ON} [V]	$I_{on/off}$ (x10^4)	S_S [V dec^{-1}]	μ_{Sat} [cm^2 V^{-1} s^{-1}]
LI100	0.23 ± 0.15	7.64 ± 7.08	0.22 ± 0.05	4.98 ± 4.08
LI25Na75	0.17± 0.10	6.69 ± 5.72	0.23 ± 0.07	6.02 ± 4.97
LI5Na95	0.02 ± 0.15	4.96 ± 4.17	0.25 ± 0.05	6.25 ± 5.18
Na100	0.12 ± 0.12	2.28 ± 1.21	0.25 ± 0.04	4.79 ± 3.35

EGTs – LiOH/NaOH membranes

(Self)healing



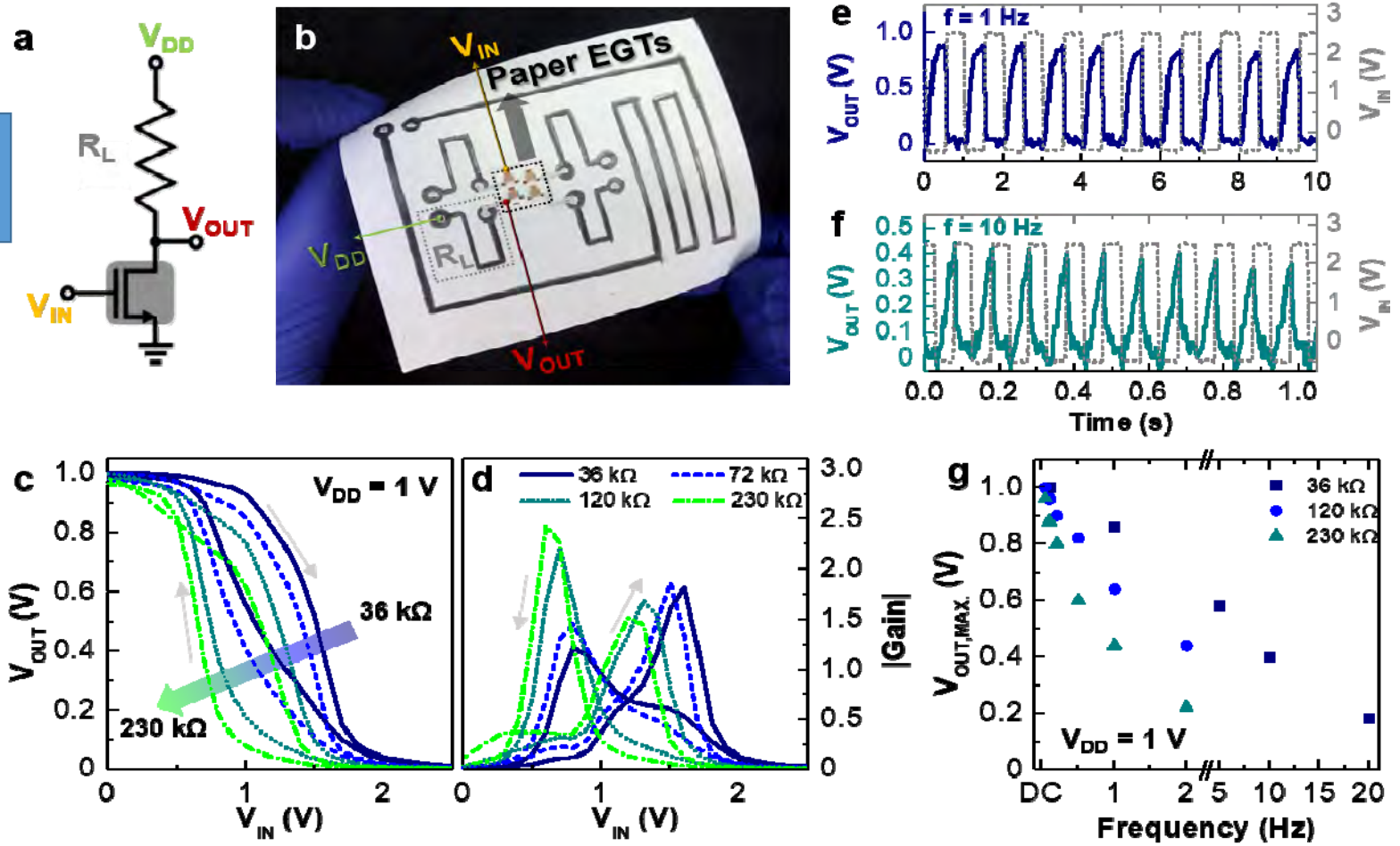
Reversible swelling ability of the developed IES can delay or even reverse the formation of dendrites

Cunha et al, submitted

EGTs – LiOH/NaOH membranes

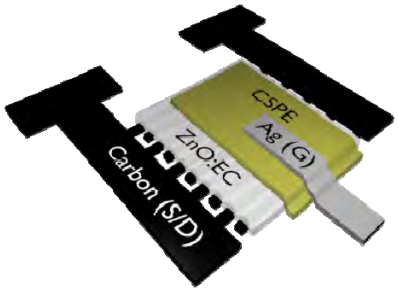
Logic circuits

NAND logic gates on paper



Cunha et al, submitted

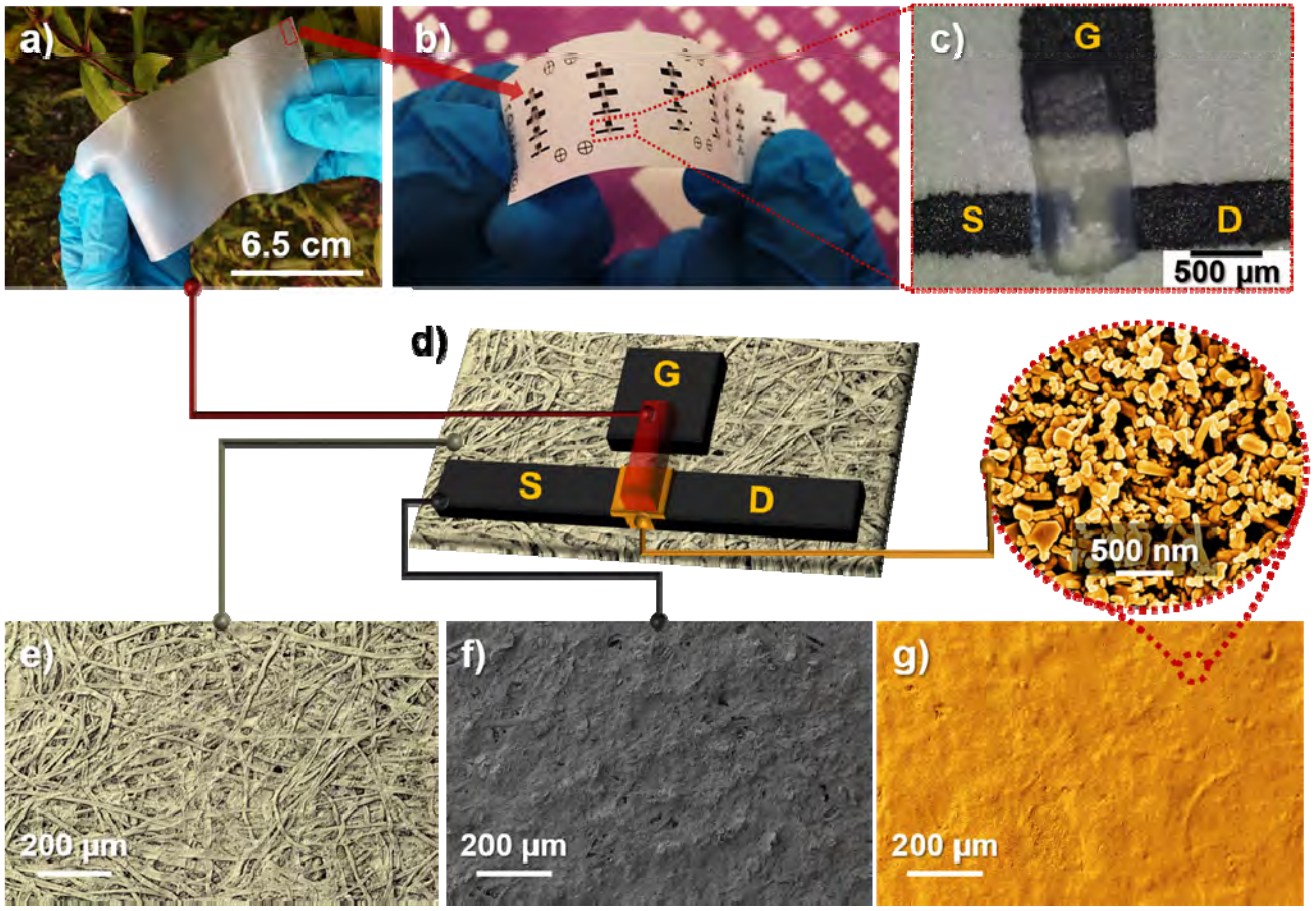
Cellulose/ZnO printable inks



Cellulose/ZnO NPs inks

ZnO ink formulation and transistors printing

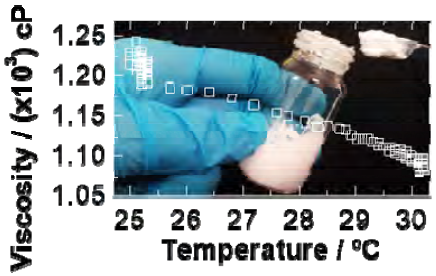
CHE electrolyte



Printed EGTs on paper

Printed ZnO ink

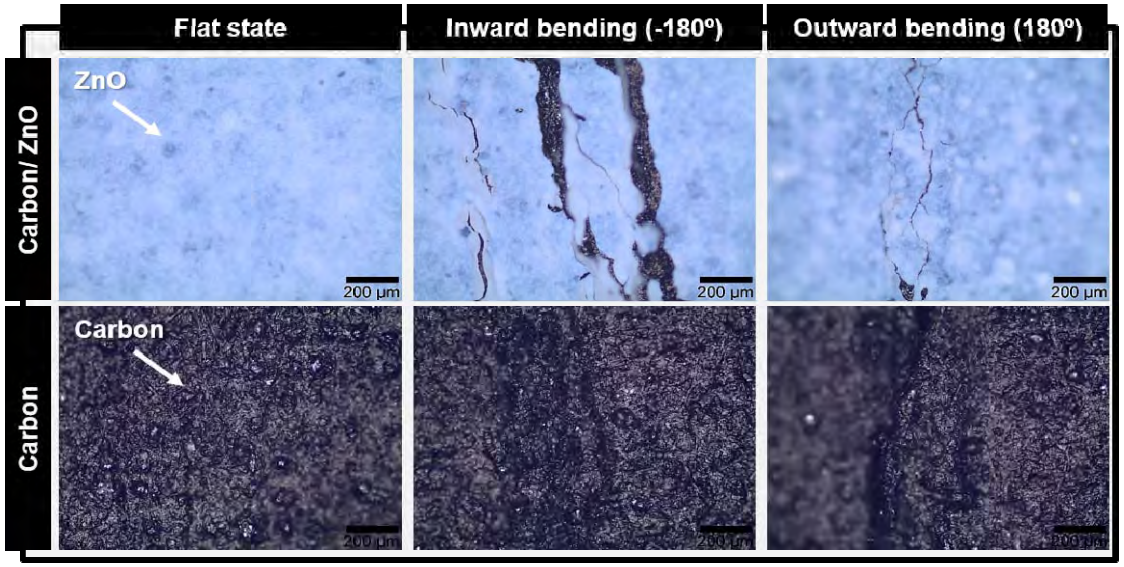
ZnO NPs 40 wt.% into a solution of 3 wt.% of CMC in water

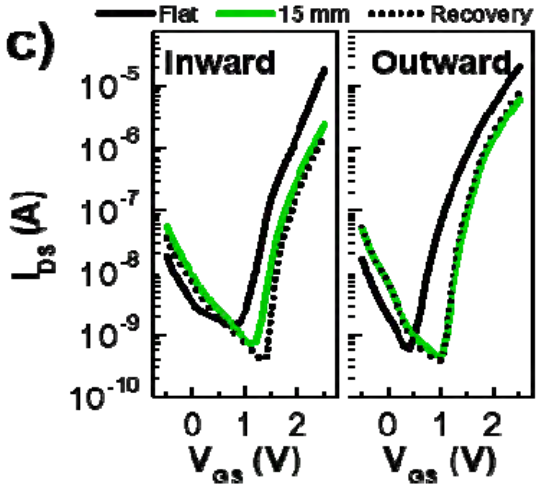


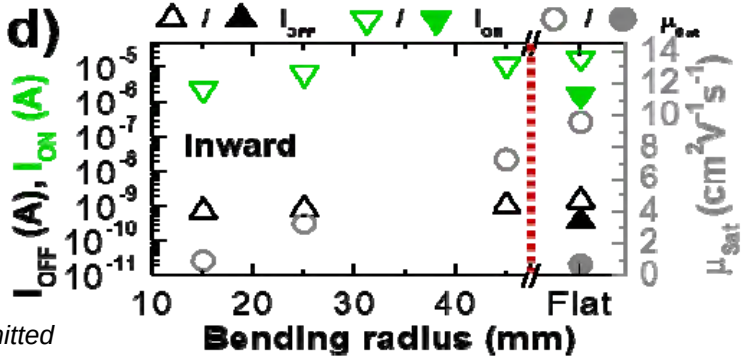
"Office" paper substrate

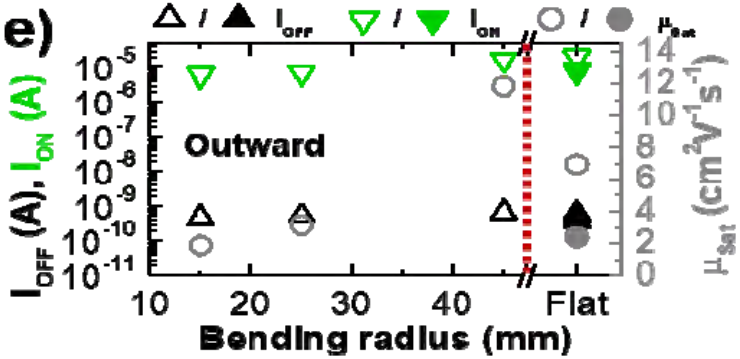
Printed EGTs

Fully printed EGTs on paper









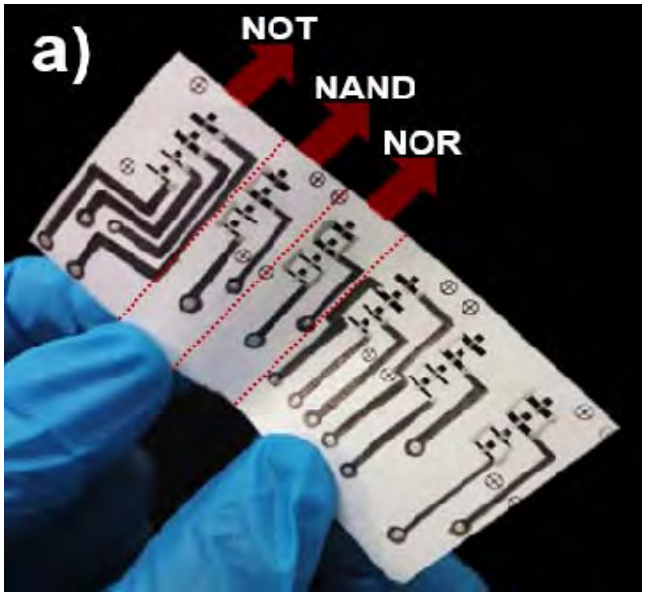
Cunha et al, submitted

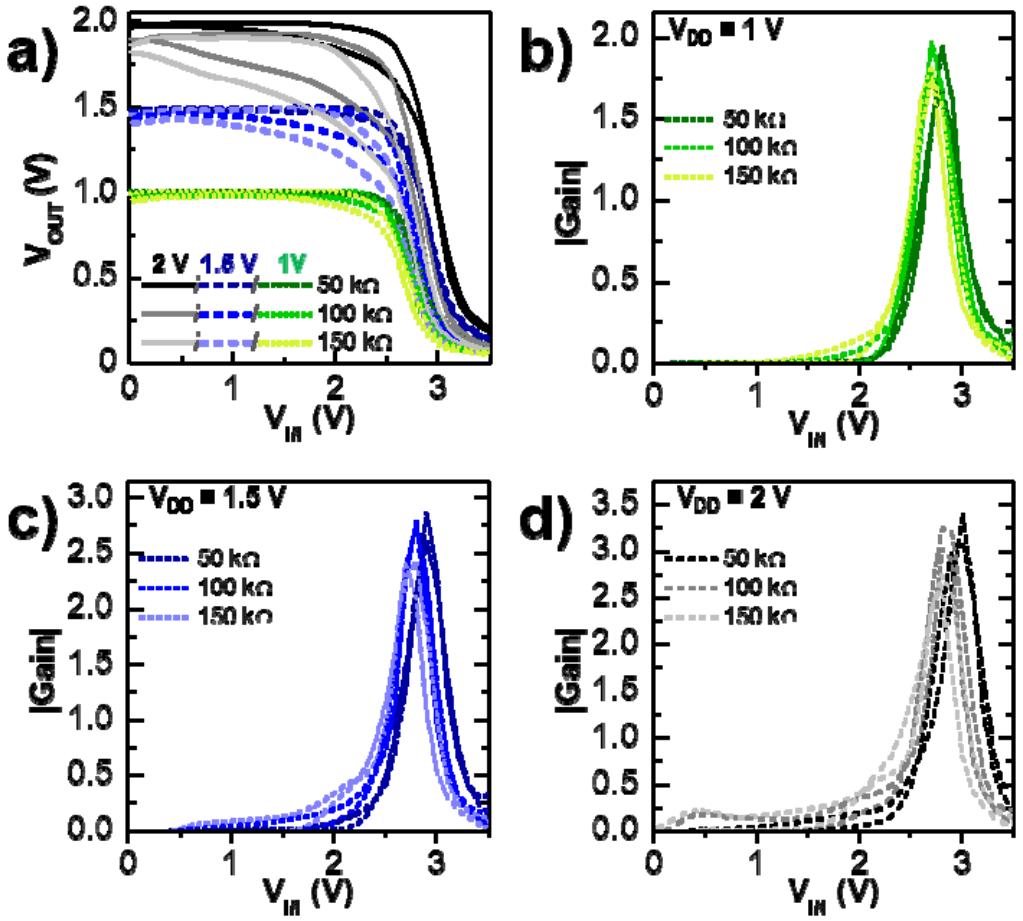
Cellulose/ZnO NPs inks

ZnO ink formulation and transistors printing

Fully printed logic gates on paper

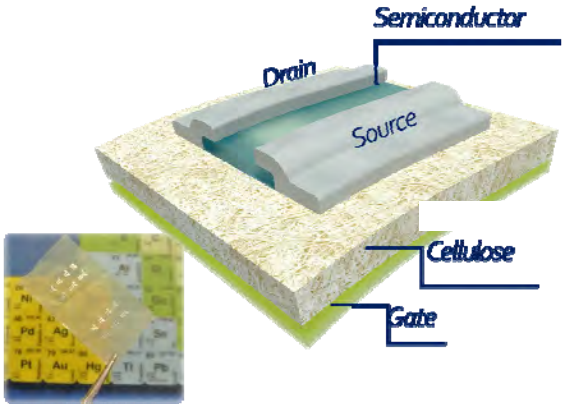
Ex: NAND





Cunha et al, submitted

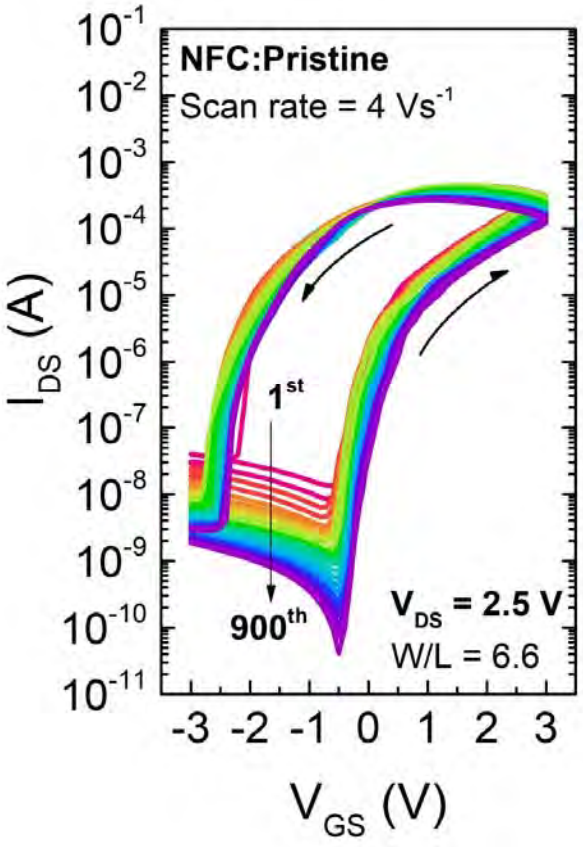
“Paper like” membranes

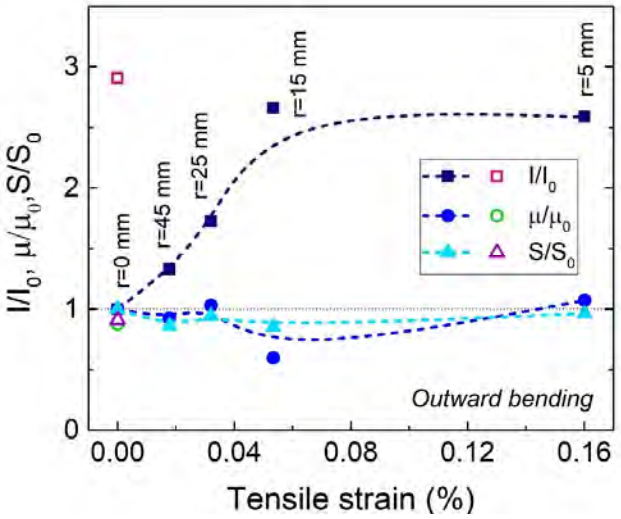


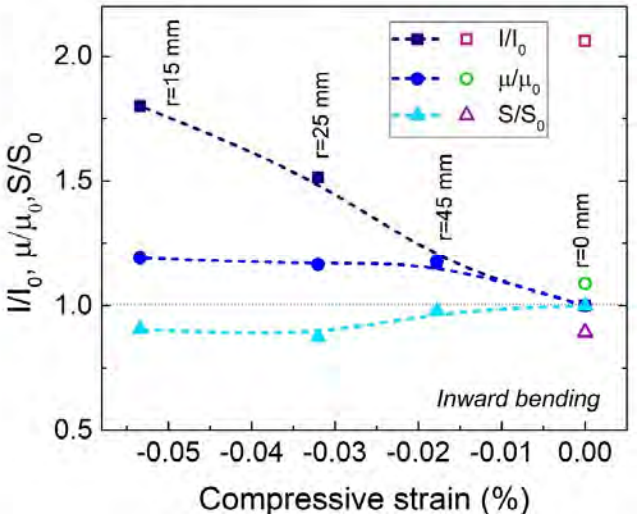
D. Gaspar at Session 8: Poster Session and Student Poster Competition

“Paper like” membranes

Nanofibrillated cellulose FETs







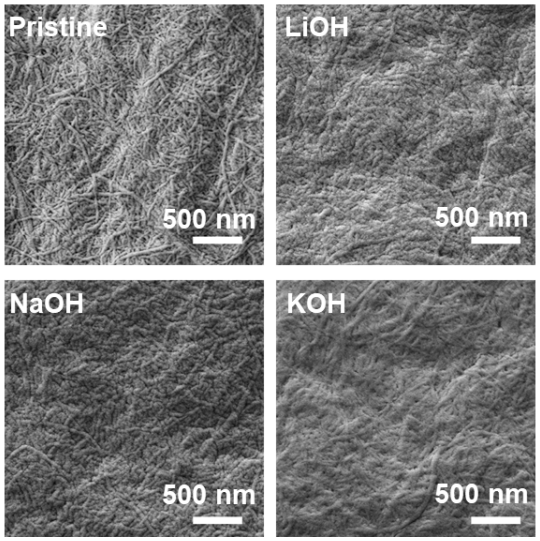
Highlights:

- Low operation voltage
  - decreased to V_{DS}=2.5 V and V_{GS}=[-3,3]V
- Proper operation after electrical endurance test even for fast scan rates
  - S and μ remain nearly unchanged
- Flexible
  - Devices operating under tensile or compreesive strains

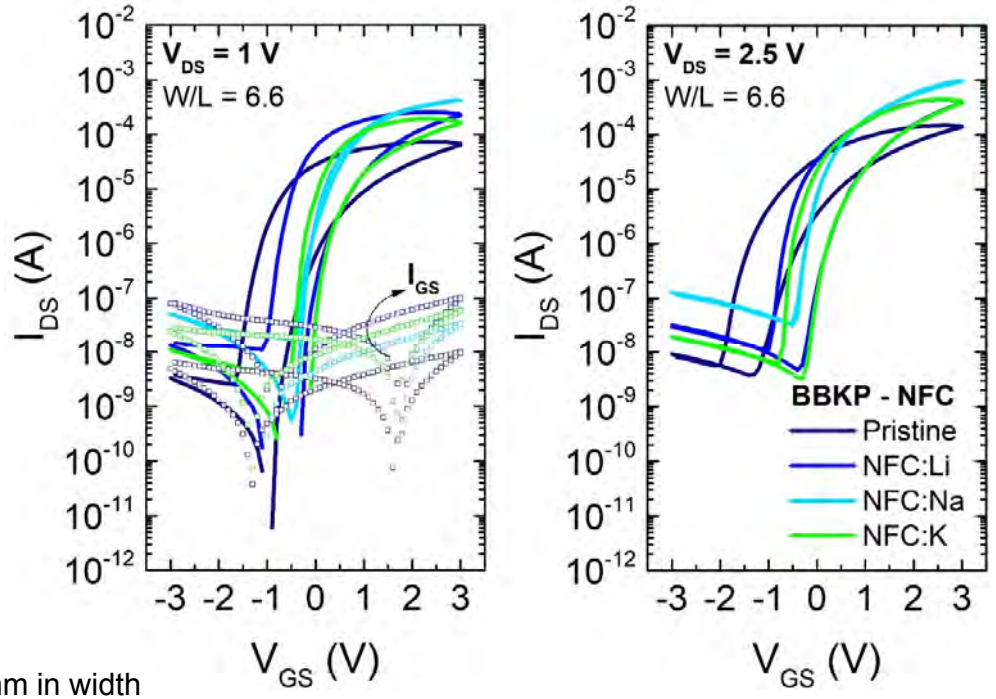
“Paper like” membranes

Alkali-doped NFC membranes

Bleached birch kraft pulp nanofibrillated cellulose



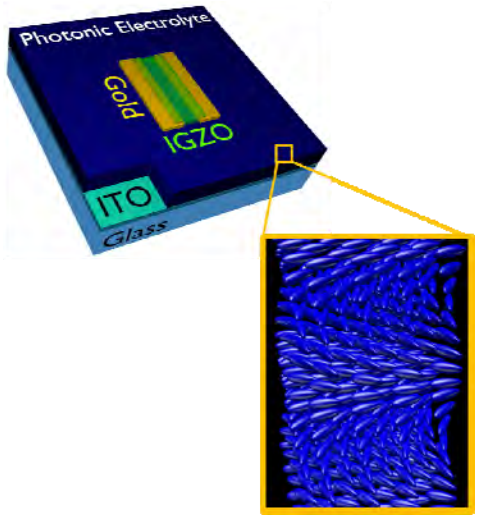
Fibrils:
Length: 1-2 µm / Width: 50 nm in width
Roughness RMS: 44 to 69 nm



	Pristine	NFC:Li	NFC:Na	NFC:K
µ ($cm^2\ V^{-1}\ s^{-1}$)	4.32	4.98	17.00	13.20
V_{on} (V)	-1.4	-0.3	-0.6	-0.3
I_{On}/I_{Off}	3.6×10^4	5.4×10^4	2.7×10^4	1.2×10^5
S ($V\ dec^{-1}$)	0.29	0.18	0.17	0.15

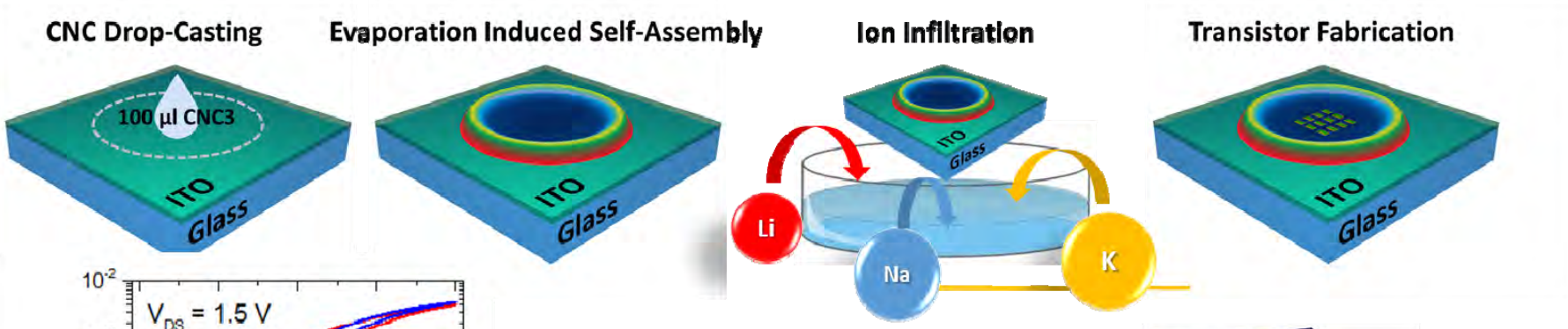
CNC membranes as dielectric

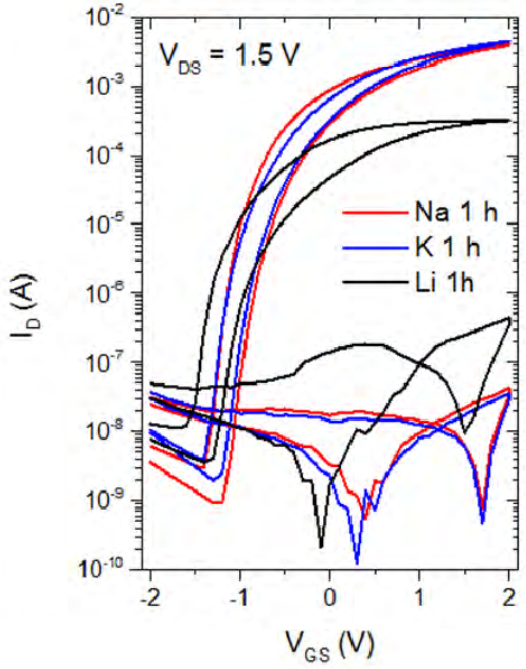
P. Grey at Session 20: Photonics



CNC membranes as dielectric

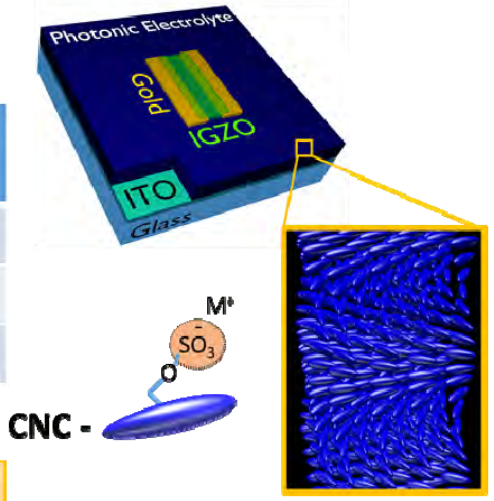
EGTs





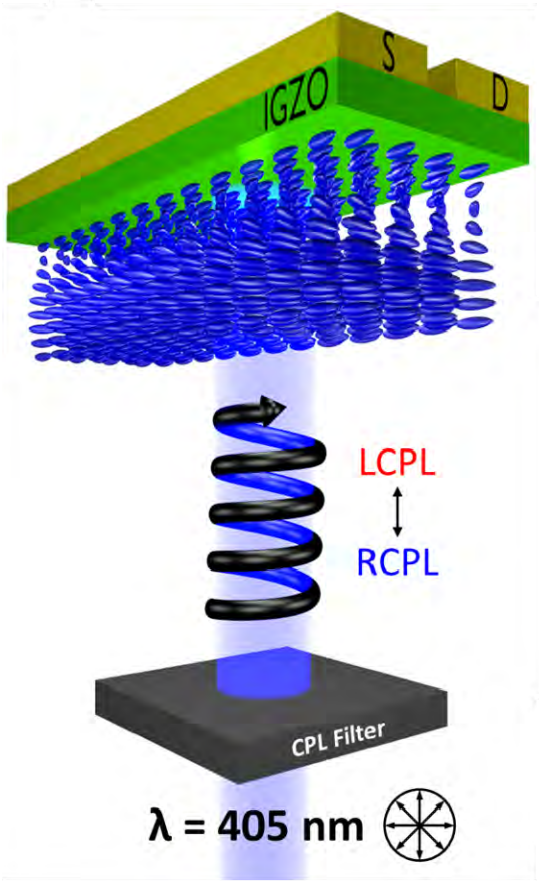
	On/Off ratio	SS (V/dec)	Mob ($cm^2V^{-1}s^{-1}$)
Li 1 h	$8.94x10^4$	0.11	1.05
Na 1 h	$4.34x10^6$	0.09	7.83
K 1 h	$2.25x10^6$	0.10	9.31

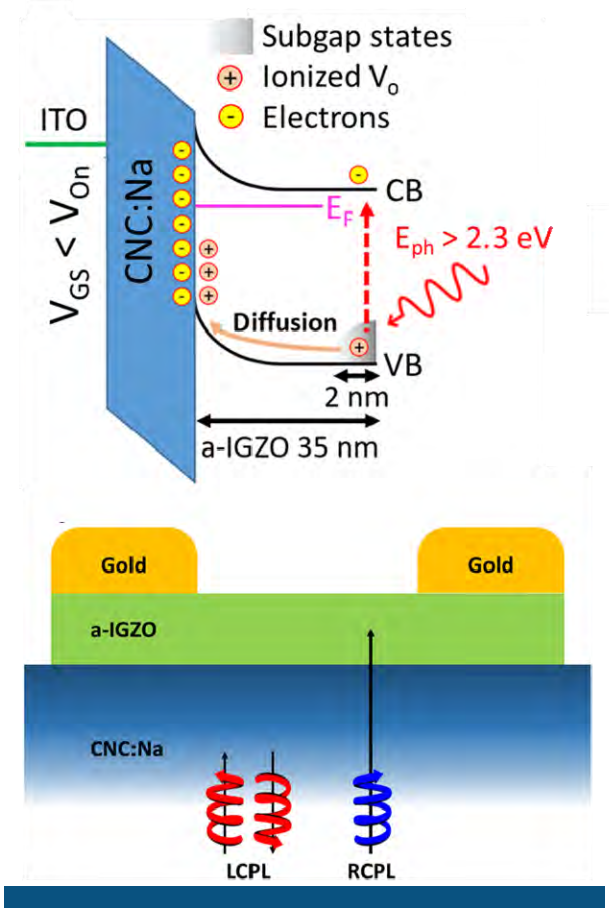
Theoretical MOSFET limit of SS is 0.06 V/dec
Potassium: always lowest hysteresis, lowest I_G

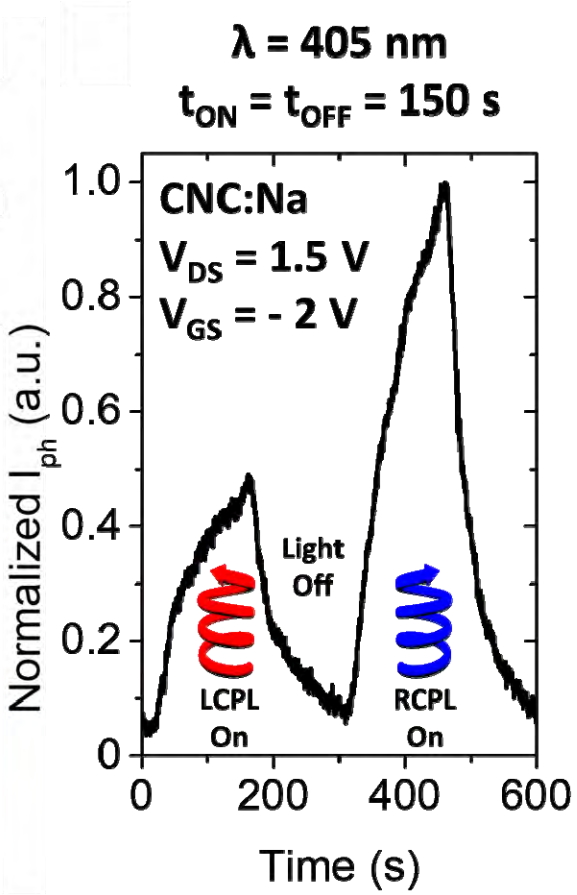


CNC membranes as dielectric

Photodetectors – CPL detectors







Summary

- Development of recyclable and reusable hydrogel electrolytes based on cellulose using LiOH and NaOH
- The membranes exhibit interesting mechanical and electrochemical properties for application in flexible electrochemical devices.
- Successful application in IGZO-EGTs on paper substrates
- Implementation of fully printed logic gates by combining ZnO NP + CMC printable inks
- Ion doping of fiber based membranes can be used to improve electrical performance of EGTs using then as dielectric

Acknowledgements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Associação para a Inovação e Desenvolvimento da FCT

QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL PORTUGAL 2007.2013

HORIZON 2020

erc

FCT
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Thank you

PRESENTED BY:
Luis Pereira
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