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PROJECT FULLFLEX: A MULTIFUNCTIONAL FLEXIBLE ELECTRONIC LABEL

Jean-Christophe P. Gabriel

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Printed and Flexible Electronics Congress 2017

21st-22nd Feb 2017

London, UK

London Heathrow Marriott Hotel

Abstract: We will present a CEA joint effort that delivered a multifunctional label prototype that integrates flexibles: (i) photovoltaic cells; (ii) a nanoparticle based Li-battery; (iii) a battery management system; (iv) a tension regulator; (v) a temperature sensor; (vi) a light sensor; (vii) a silver nanowire based transparent capacitive touch sensor; (viii) four LEDs; (ix) an electronic motherboard integrating a micro-controller.

Jean-Christophe P. Gabriel

CEA/DRE/DPNS

Jean-Christophe.gabriel@cea.fr

DE LA RECHERCHE À L'INDUSTRIE



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PROJECT FULLFLEX:

A MULTIFUNCTIONAL FLEXIBLE ELECTRONIC LABEL

Dr. Jean-Christophe P. Gabriel
Dep. Director Nanoscience & **ChimTronic**
Programs

Printed & Flexible Electronics Congress

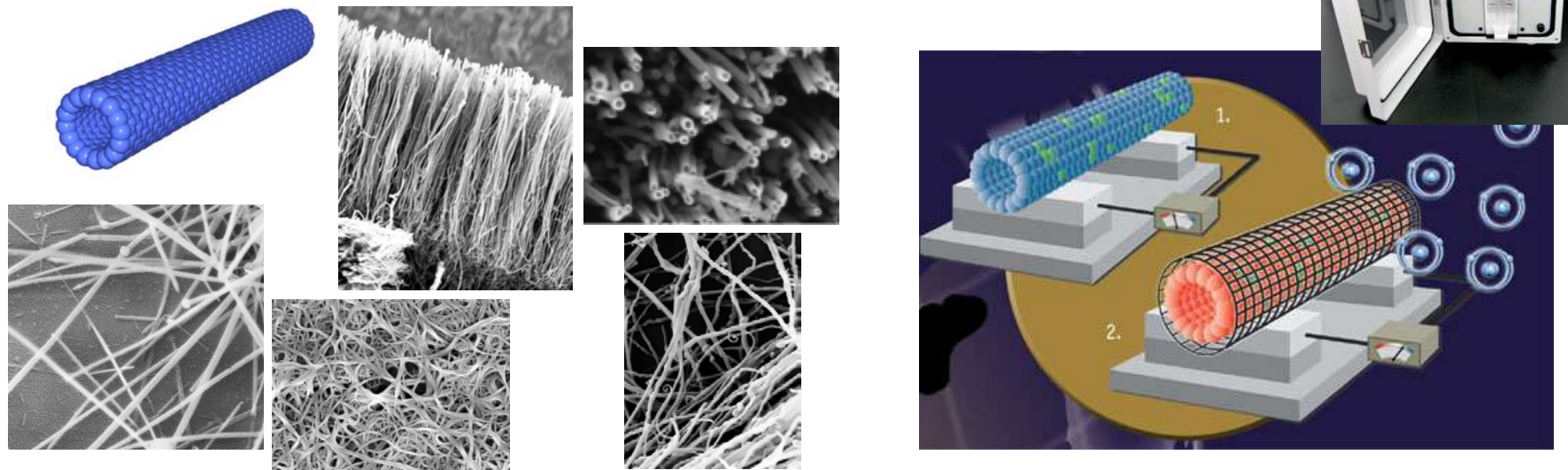
February 21st, 2017

CEA Key Figures (2015)



CAN A LOT BE DONE FROM NEW PARADIGMS? THE EXAMPLE OF CNTS

- 2001-2007 @ Nanomix (nano.com): CNT integration – Chemical sensors



Molecular Wires for Molecular Sensing

- First commercial sensors in 2005: H₂ sensor on Si wafers
- Printed NT sensors deployed in West Africa during Ebola crisis in 2015.
- \$36M raised over 15 years!!!

Nature 413, 504-508, 2001, *Phys. Rev. Lett.* 91(21) 218301, 2003, *Adv. Mater.*, 16(22) 2049-2052, 2004, *J. Phys. Chem. B.* 110(42); 21014-21020, 2006; *Proc. Nat. Acad. Sciences* 103(4), 921-926, 2006, . *J. Phys. Chem. B.* 110(42); 21014-21020, 2006; C. R. Physique, 11(5-6), 362-374, 2010; *Appl. Phys. Lett.* 103, 051907, 2013 + ~50 patent applications
Copyright CEA, all rights reserved

- Leverage effect (period 2008-2013, 98 projects, budget 7M€) : **170%**
- Direct income: **7M€** (32 projets: ANR, FP7,...)
- Indirect incomes: **5M€** (15 projets: ANR, FP7, ERC,...)
- Overall awarded money (with partners) : **78M€**

260 articles de journaux sur 2009-2016 (4806 citations)

31% of articles (80) in top 10% (*according to ESI Physics criteria*)

6% of articles (16) in top 1%

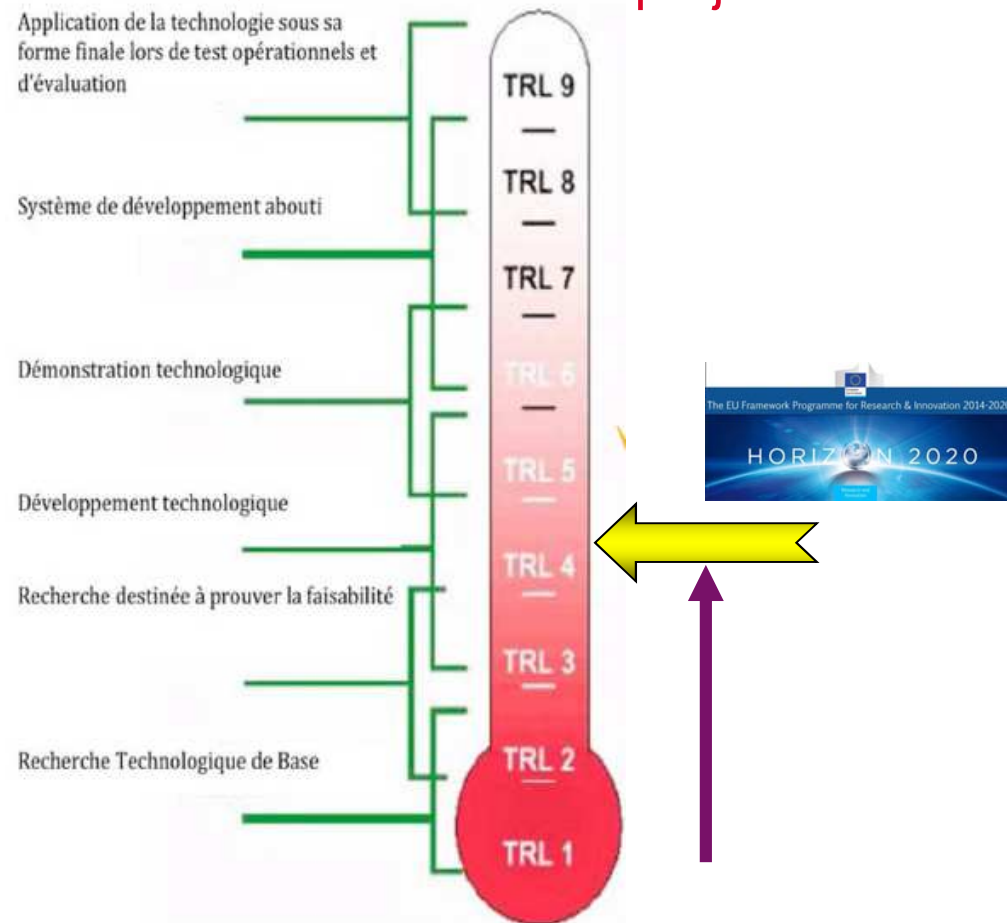
- **4 start-up** benefited directly from results initiated with program
- **29 patents** (2008-2013)

FULLFLEX PROTOTYPE CHALLENGE?

Objectif: go beyond germination!

Build a prototype Integrating technological components developed within Nanoscience & ChimTronic seed projects

- Reach higher TRL



FULLFLEX PROTOTYPE CHALLENGE?

Objectif: go beyond germination!

Build a prototype Integrating technological components developed within Nanoscience & ChimTronic seed projects

- ❑ Reach higher TRL
- ❑ Development of new technologies of flexible interconnects
- ❑ => A new prototype for CEA's Showroom



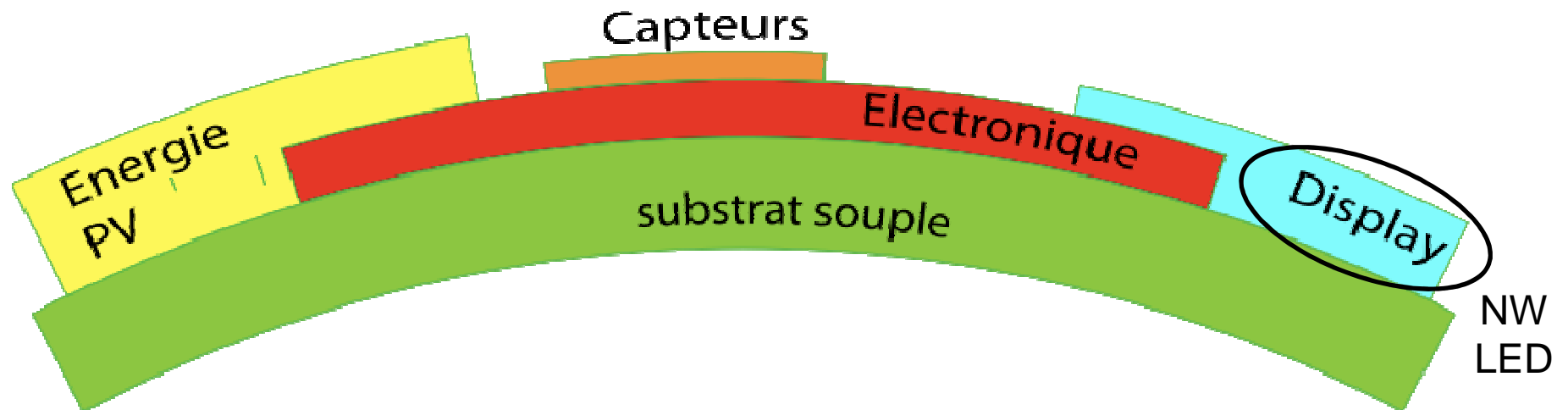
FULLFLEX PROTOTYPE CHALLENGE?

Objectif: go beyond germination!

Build a prototype Integrating technological components developed within Nanoscience & ChimTronic seed projects

- Reach higher TRL
- Development of new technologies of flexible interconnects
- => A new prototype for CEA's Showroom

Initial Concept: a flexible autonomous, multifunctions label



FULLFLEX: WHAT TEAM?

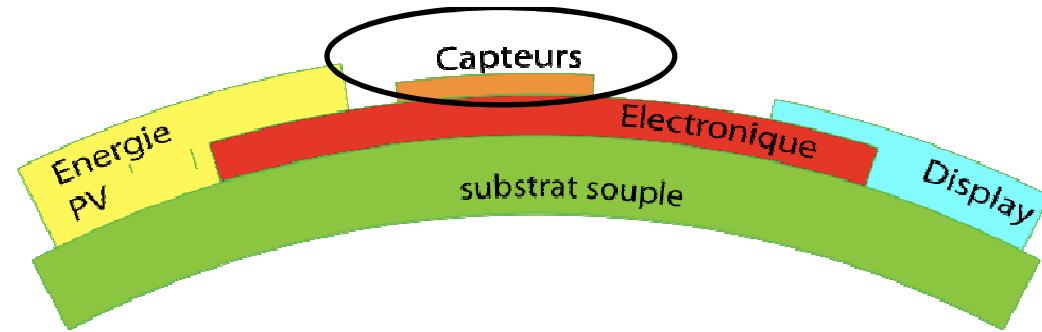
| Component | Investigators | Affiliation |
|--|---|--------------------------|
| Battery (Si NP) | Marc BRESTAZ | DRT/LITEN/DEHT/LCPB |
| | Séverine JOUANNEAU | DRT/LITEN/DEHT/LCPB |
| | Willy PORCHER | DRT/LITEN/DEHT/LCPB |
| | Axelle QUINSAC (NTE) | DSM/IRAMIS/SPAM/EDNA |
| | Yann LECONTE | DSM/IRAMIS/SPAM/EDNA/LFP |
| | Nathalie HERLIN | DSM/IRAMIS/SPAM/EDNA |
| PV organic | Rémi DE BETTIGNIES | DRT/LITEN/DTS/LMPV |
| | Nicolas GAUTHIER | DSM/INAC/SCIB/RICC |
| | Marinella MAZZANTI | DSM/INAC/SCIB/RICC |
| | Daniel IMBERT | DSM/INAC/SCIB/RICC |
| | Renaud DEMADRILLE | DSM/INAC/SPRAM/LEMOH |
| | Amélie REVAUX | DRT/LITEN/DTNM/LCSN |
| LED (NW) | Benoit AMSTATT + François LEVY & Alexandre LAGRANGE | DRT/LETI/DOPT/SCOOP/LCE |
| | Joël EYMERY + Benjamin GREVIN | DSM/INAC |
| Transparente Electrode (CNTs or NW) | Eléonore MOREAU | DRT/LITEN/DTNM/LCRE |
| | Jean-Pierre SIMONATO + Caroline CELLE | DRT/LITEN/DTNM/LCRE |
| | Benjamin GREVIN + | DSM/INAC |
| | Renaud DEMADRILLE | DSM/INAC |
| Printed Electronics | Abdelkader ALIANE | DRT/LITEN/DTNM/LCEI |
| | Romain COPPARD | DRT/LITEN/DTNM/LCEI |
| System /integration | Jean-François MAINGUET | DRT/LETI/DSIS/SIPP |
| | Tristan HAUTSON | DRT/LETI/DSIS/SIPP |
| | Pascale RIVIER | DRT/LETI/DSIS/SIPP |
| Pilotage | Jean-Christophe GABRIEL | DSM/DIR/DPNS |
| | Norbert DANIELE | DRT/LETI/DSIS/SIPP |
| | Tiana DELHOME | DRT/LETI/DSIS/SIPP |

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Printed Temperature Sensors

Abdelkader Aliane





PRINTED ORGANIC ELECTRONICS @CEA/LITEN

PLED (Polymer Light-Emitting Diodes)

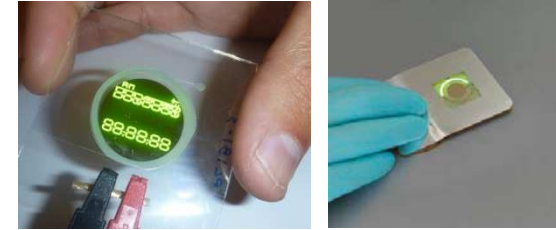
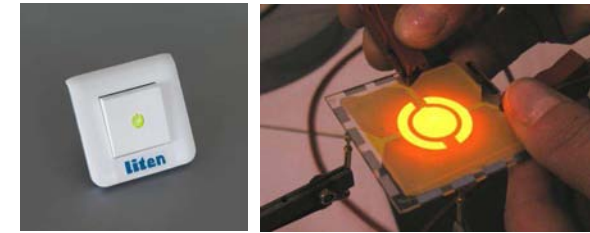
HMI, signage

Devices, systems

Single digit, matrix

Logos

cf Talk Tony Maindron (OLED)



Antennas

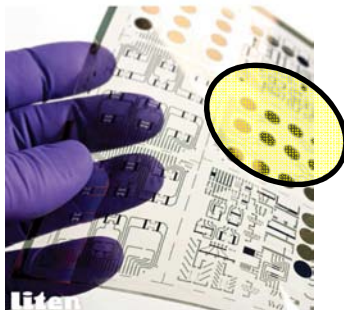


Sensors

Temperature (Resistors)

Capacitive

Pressure sensitive



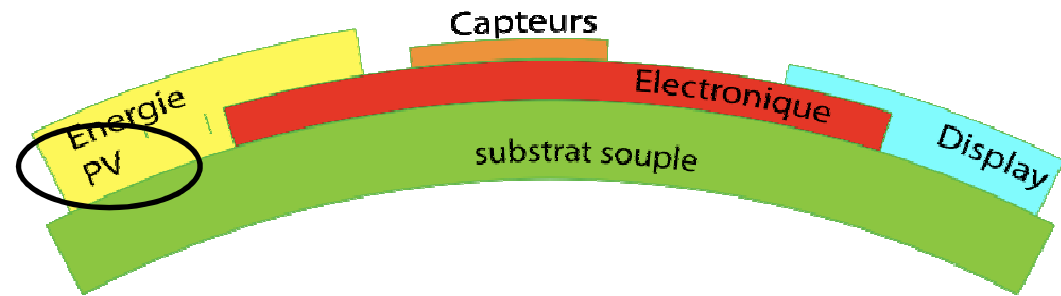
Large Surface Printing Platform (PICTIC):

- 50 researchers and technicians
- €9 million in investment
- 600 sq. m of clean rooms
- Slot-die, gravure, flexography process equipment
- Industrial partnerships, startup (ISORG)

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Photovoltaic flexible modules



Renaud DEMADRILLE – DRF / INAC / LEMOH

Solenn Berson – DRT/INES/SMPV

Bulk-heterojunction solar cells (BHJ) : Concept

Heeger et al. *Science*, 1992, 258, 1474.

- 2 Interpenetrated percolating networks
- Optimal phase segregation (10-20nm)

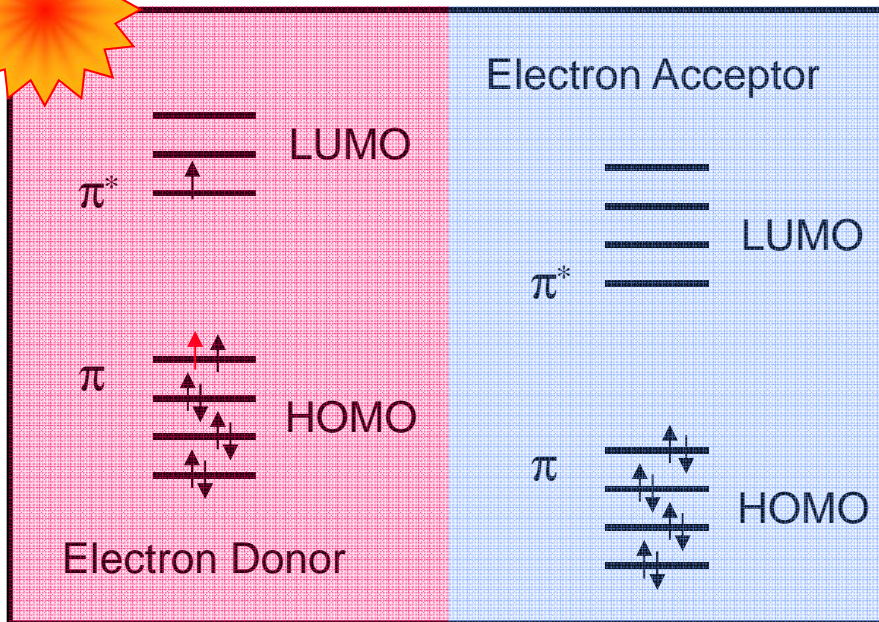
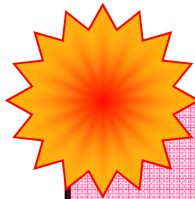


Photo-induced charge transfer

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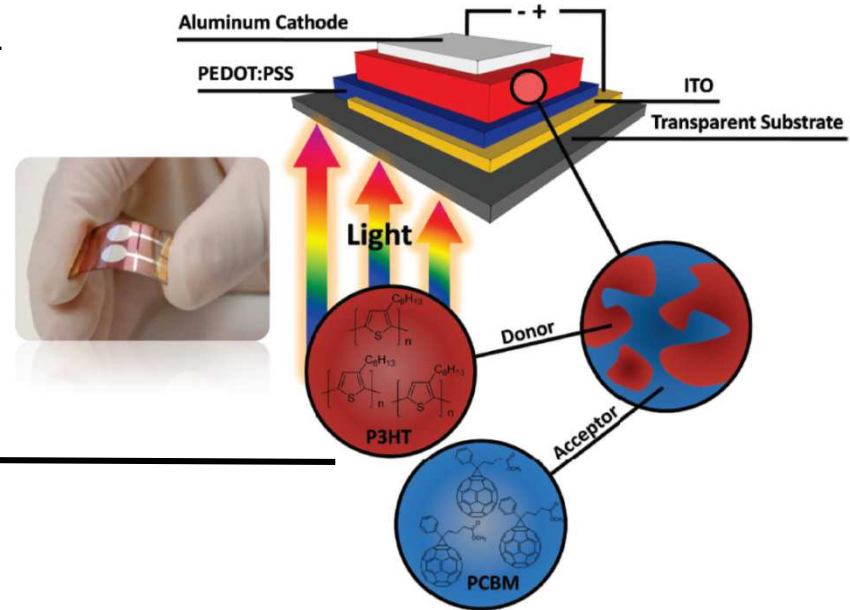
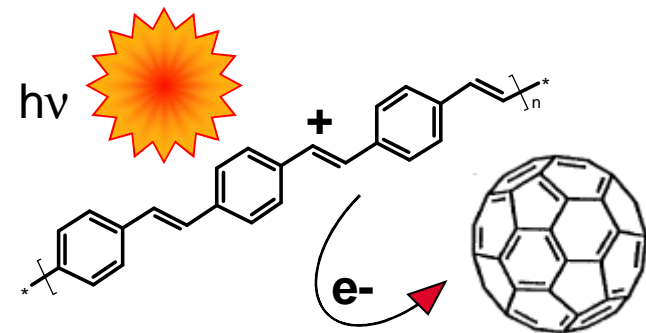
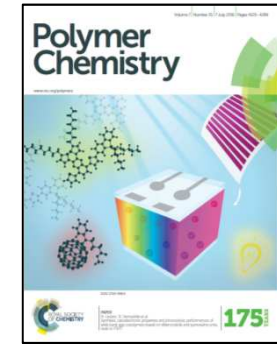
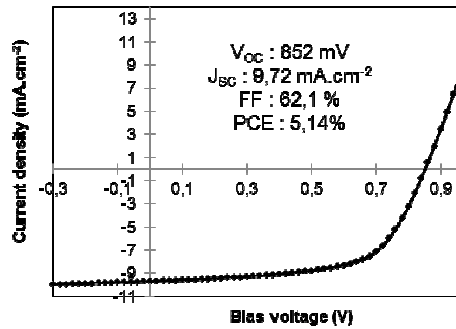
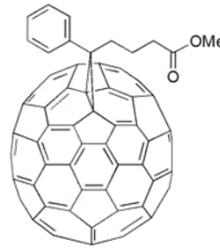
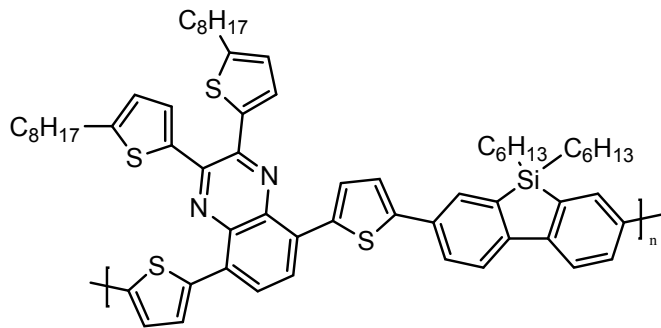


Photo-induced charge transfer $< 10^{-12}$ s



Development of new materials for use in the active layer



Polymer Chem., 2016, 7, 4160

Laboratoire des Modules Photovoltaïques Organiques (LMPO) – S. Berson (DRT-INES)



Development of OPV modules by printing techniques (ink-jet)
 First examples with P3HT

P3HT-Fullerene $S = 11,04 \text{ cm}^2$

PCE = 2,9%
 $V_{oc} = 1,61 \text{ V}$
 $J_{sc} = 3 \text{ mA/cm}^2$
 $FF = 60 \%$

PCE = 2,1%
 $V_{oc} = 4,9 \text{ V}$
 $J_{sc} = 1.1 \text{ mA/cm}^2$
 $FF = 40 \%$

P3HT-Fullerene

Printed modules : S.Berson, R. De Bettignies, DRT-INES

P = 30mW

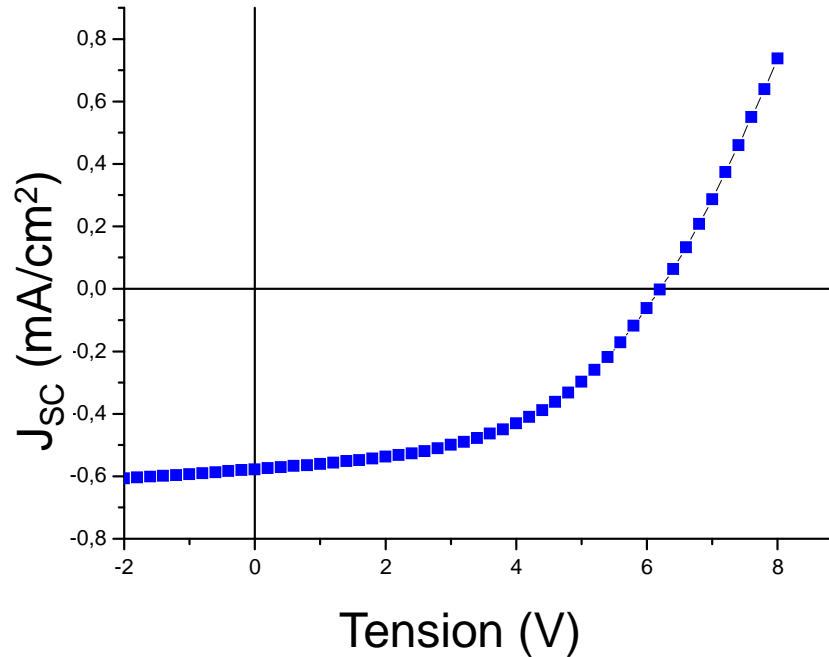
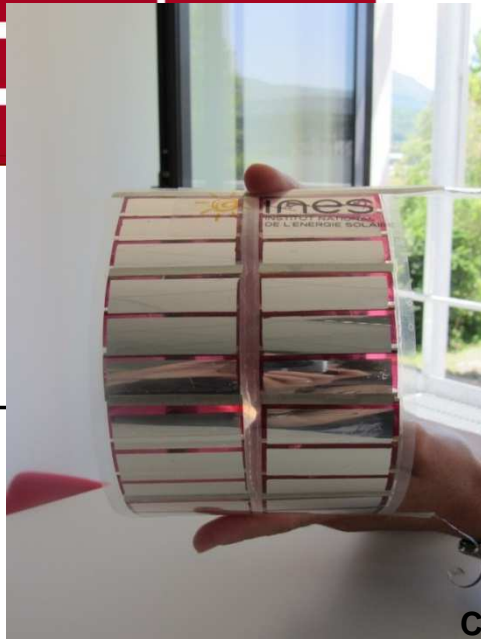
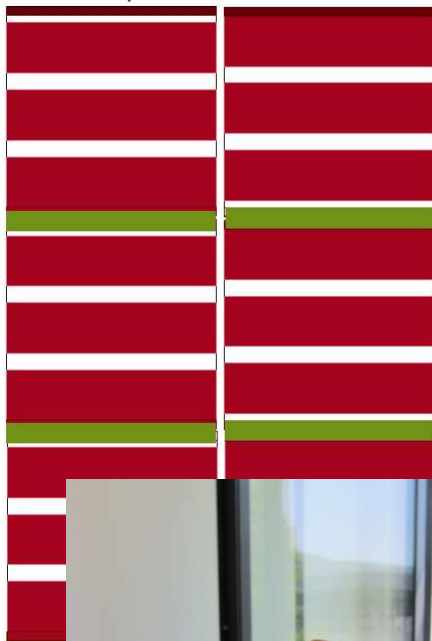
Cf talk Solenn Berson

Compatible with Li Ion batteries
 $V_{min} = 3.7V$

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PV DEVELOPED FOR THE LABEL

All Interconnects: conducting adhesive

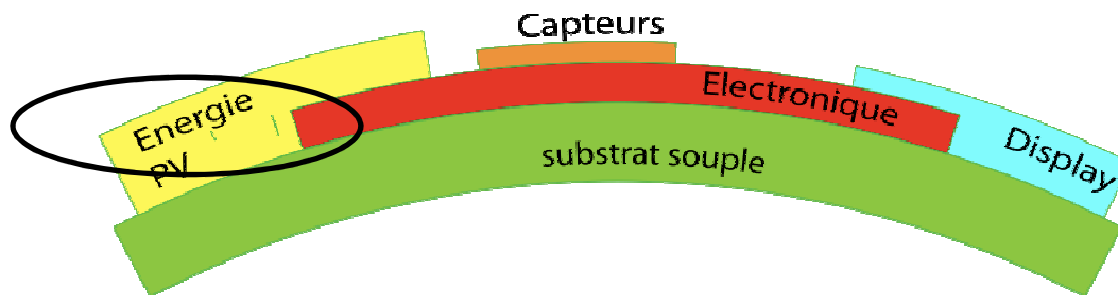


Voc= 6.2 V
Jsc= 0.577 mA/cm²
FF= 48.2 %
PCE= 1.73 %
Vmax = 4.1V
Imax = 35.8 mA

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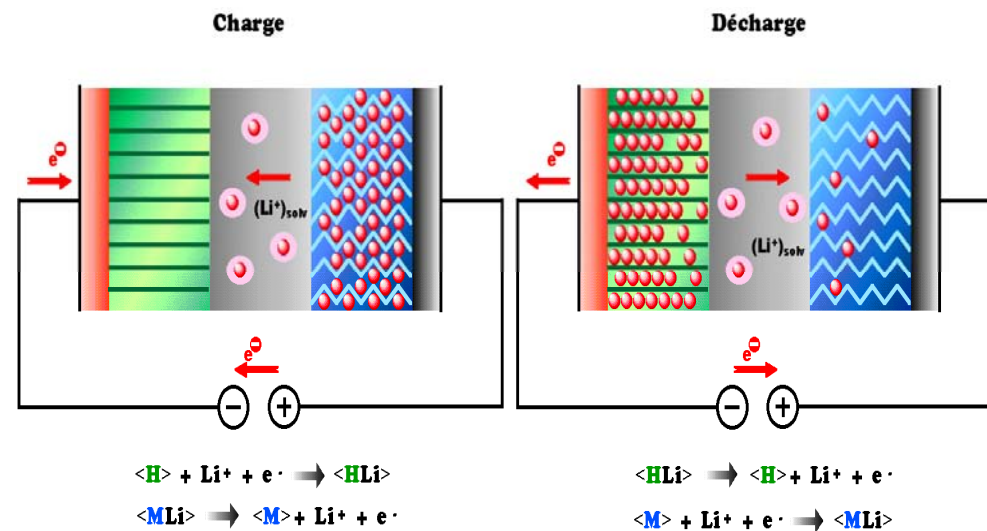
www.cea.fr



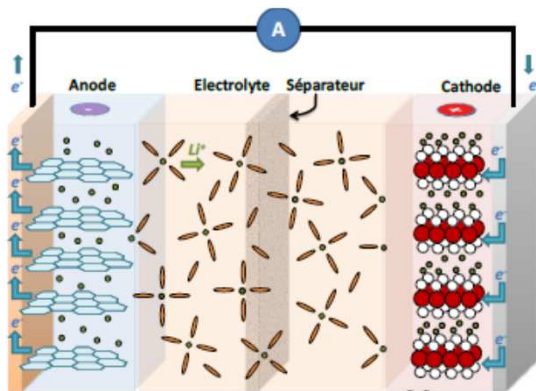
Silicium NP based battery

Nathalie Herlin, Séverine Jouanneau,

Willy Porcher



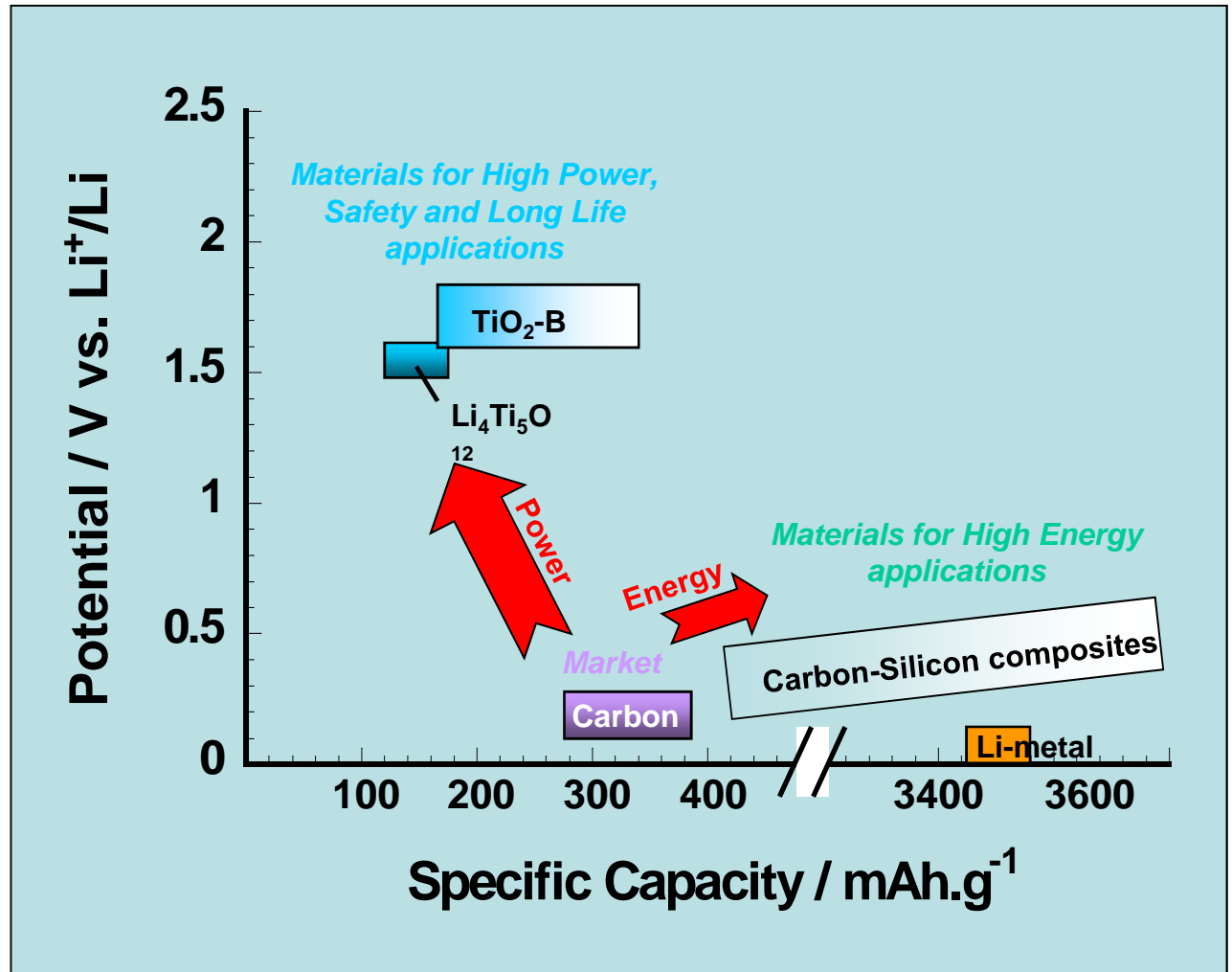
Batteries lithium-ion



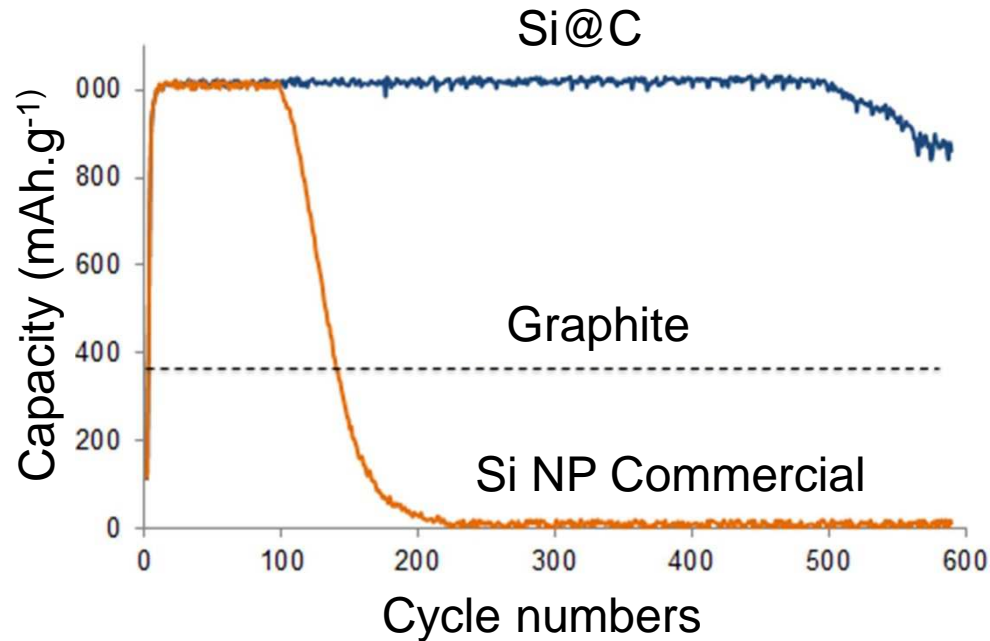
AVANTAGE :

Max = 3578 mAh/g (Si → Li_{3,75}Si) = 10x graphite

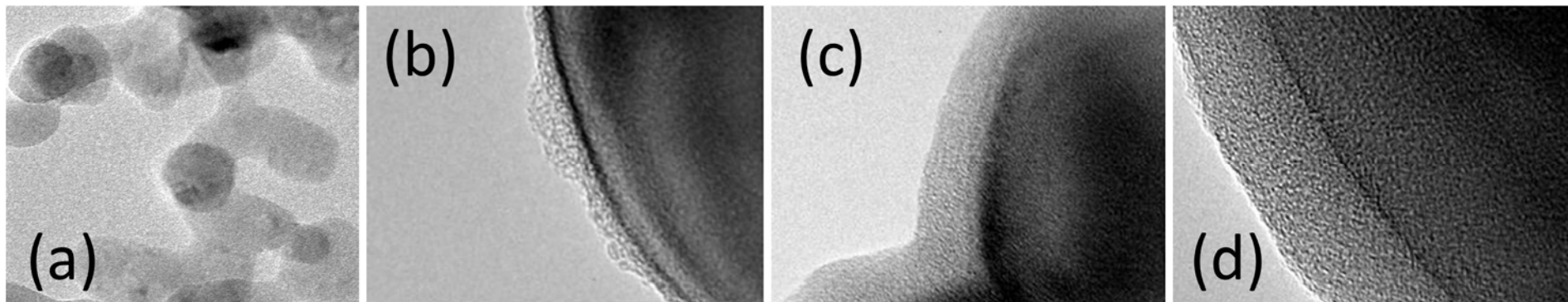
DISAVANTAGE: $V_{inc} = +280\%$



=> NP Si



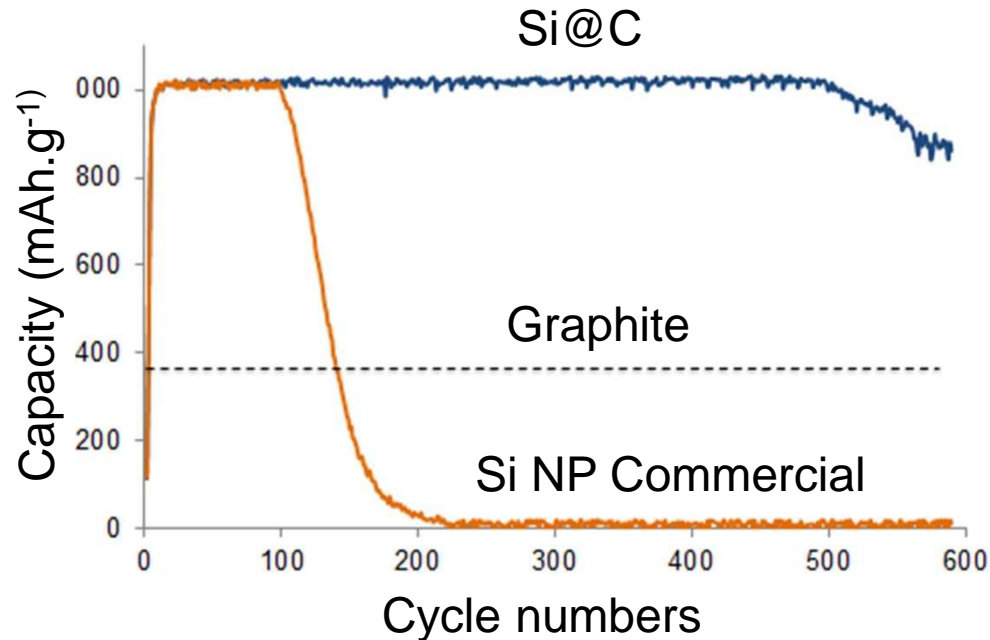
- Core-shell amorphous silicon-carbon nanoparticles for high performance anodes in lithium ion batteries
- *Journal of Power Sources* **328** (2016) 527-535
- Patent: US9205399 (2015), US20150299861, US20150303462
- 1 startup (Nanomakers)



NP Si@C: Amorphous C layer = 3nm

10 nm

15 nm



- Core-shell amorphous silicon-carbon nanoparticles for high performance anodes in lithium ion batteries
- *Journal of Power Sources* **328** (2016) 527-535
- Patent: US9205399 (2015), US20150299861 US20150303462
- 1 startup (Nanomakers)

Overall

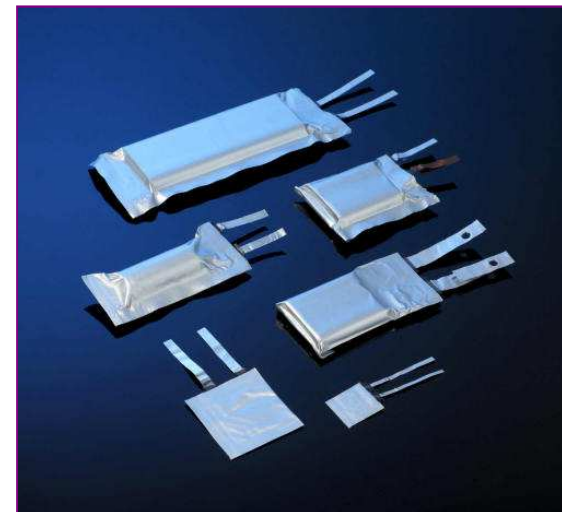
Positive Electrode: NMC ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$)

Ref. Element: 3Ah for 3x3 cm x 5 mm cell

Power < 3W

Surface capacity: 3 mAh/cm²

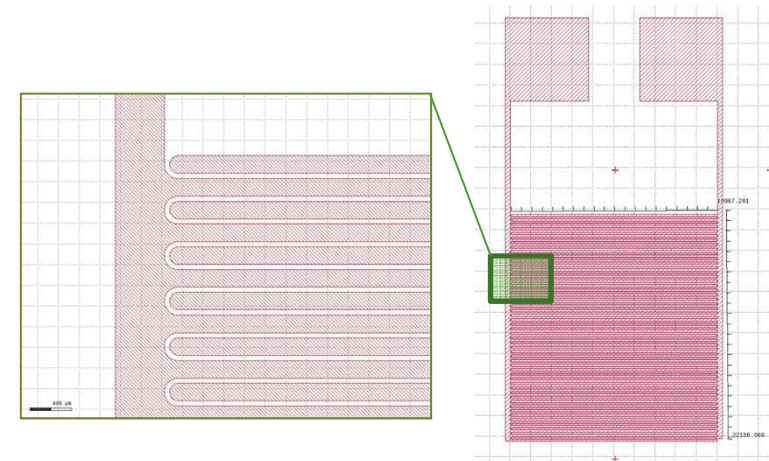
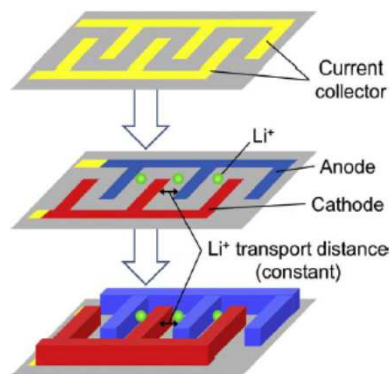
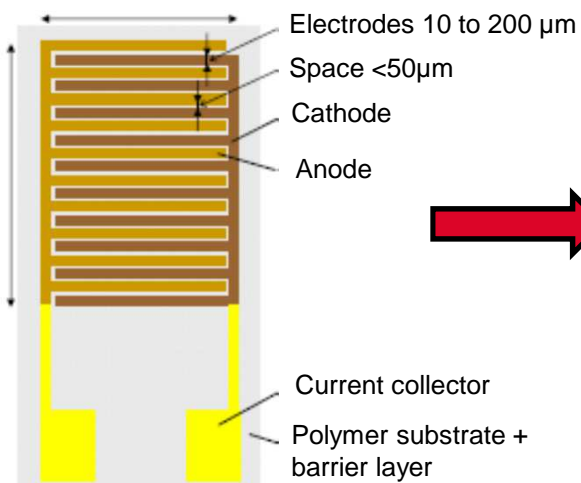
Voltage : 3,5 V



To simplify or solve several technological barriers, another battery architecture is possible:
the interdigitated planar design

- **The interdigitated concept reverses at 90 ° stacked architecture**
 - ✓ Architected current collectors on the same plane
 - ✓ Electrodes printed side by side on respective collectors
 - ✓ Separator printed between the electrodes printed on the entire surface
 - ✓ Gellified electrolyte
- **Constraints of the concept:**
 - ✓ High printing resolution(10µm +/- 1µm)

- Dimensions:
 - Width of lines : 200µm
 - Distance between lines : <100µm (target 50µm) → electrolyte compartment
- Solid electrolyte configuration
- No densification

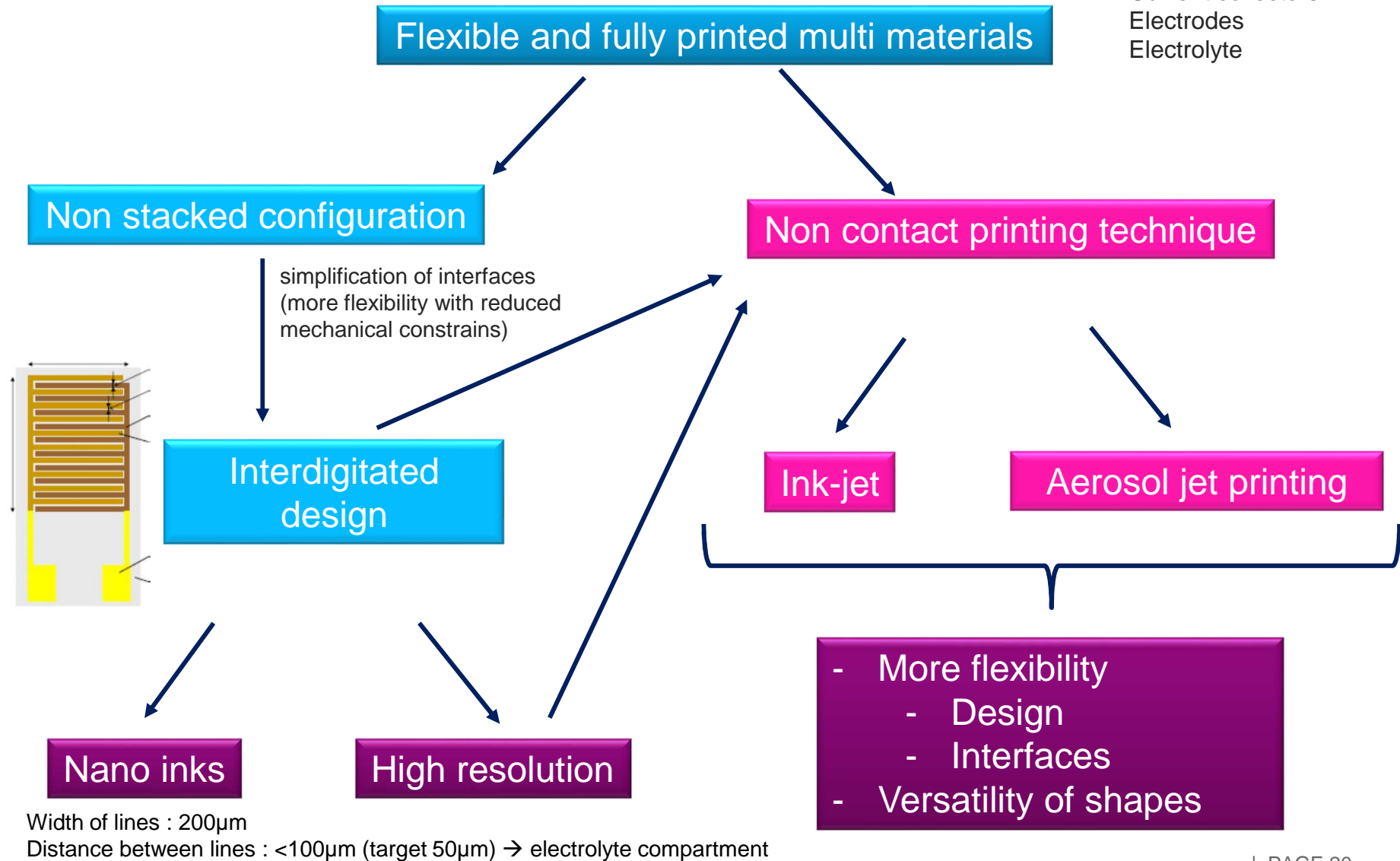


Patent BF3007206

=> Thomas Yohann

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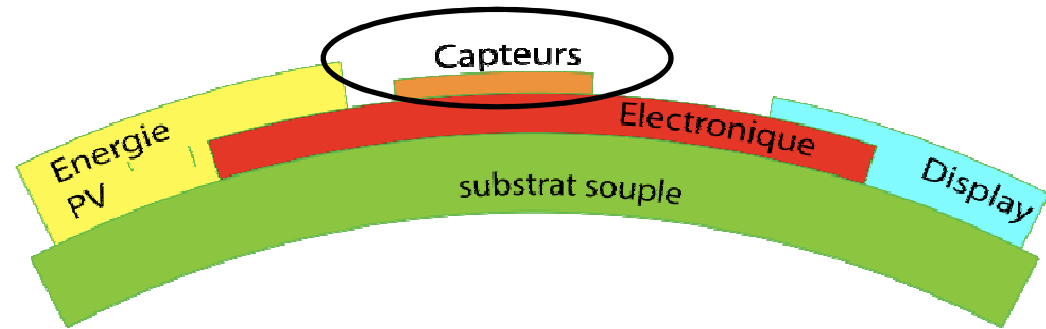
Current collectors
Electrodes
Electrolyte



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Transparent Electrode + Capacitive Sensors

JEAN-PIERRE SIMONATO

A NEW NEED FOR FLEXIBLE TRANSPARENT ELECTRODES



TCOs (ITO) have serious limitations

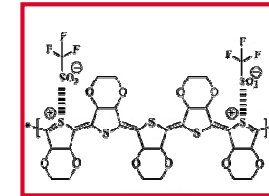
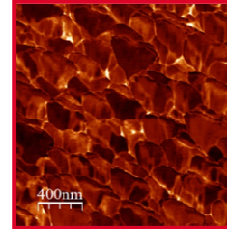
- × *Indium is a major critical raw material*
- × *High cost process (capex, material)*
- × *Brittleness*

Alternatives ?

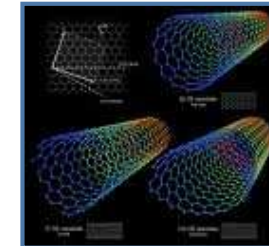
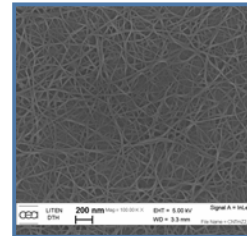
- ✓ *Conductivity / Transparency*
- ✓ *Flexibility / stretchability*
- ✓ *Low cost (material / process)*

SUBSTITUTION of ITO by Nanomaterials

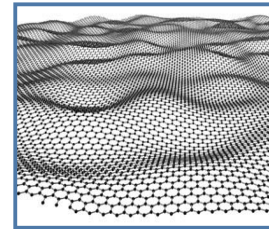
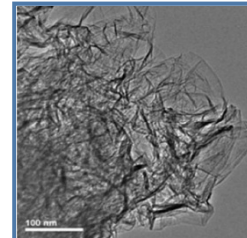
➤ Conducting polymers



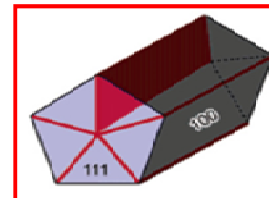
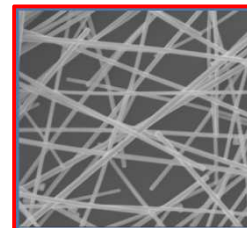
➤ Carbon Nanotubes



➤ Graphene

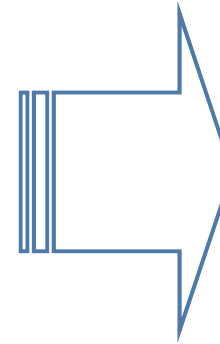
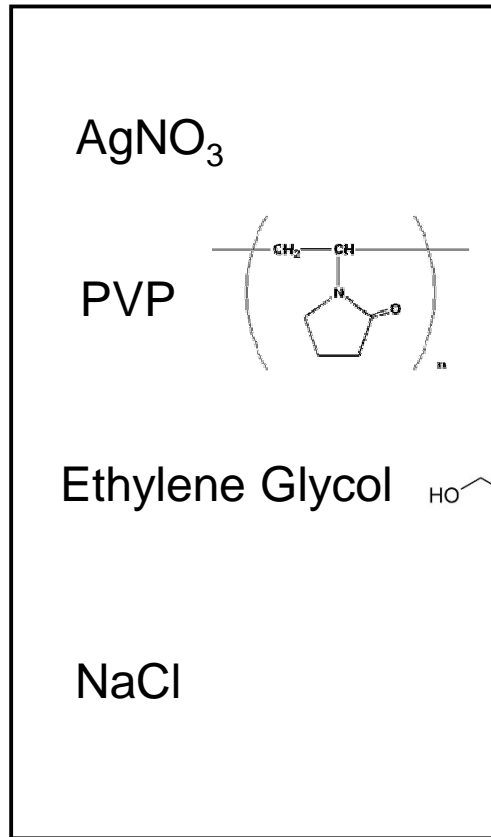


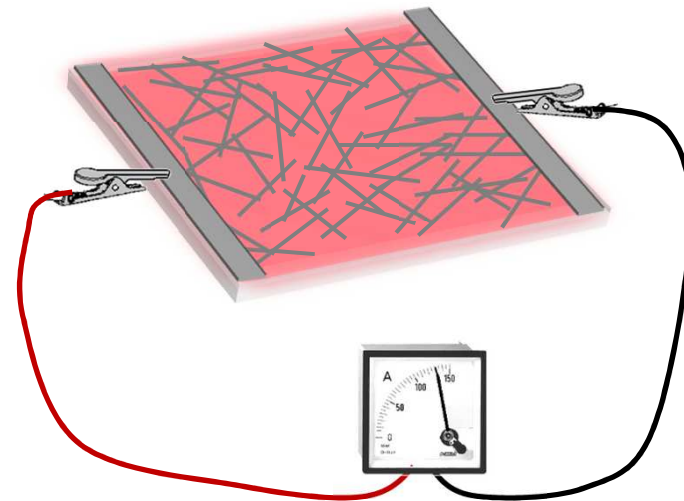
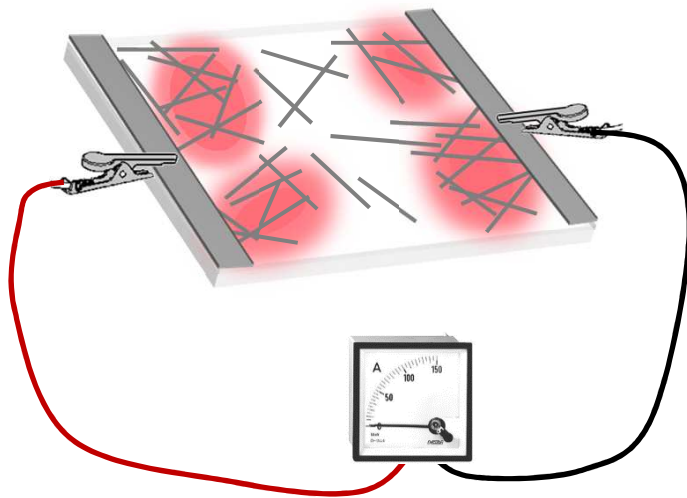
➤ Metallic nanowires



| | |
|-------------------------------------|--|
| <p>➤ Conducting polymers</p> | <p><i>J. Mater. Chem. C</i>, 2014 <i>Chemical Science</i>, 2015 <i>Chemistry of Materials</i>, 2016</p> |
| <p>➤ Carbon Nanotubes</p> | <p><i>Nano Letters</i>, 2003 <i>Carbon</i>, 2012 <i>Carbon</i>, 2014</p> |
| <p>➤ Graphene</p> | <p><i>Applied Physics Letters</i>, 2014 <i>Ultramicroscopy</i>, 2015</p> |
| <p>➤ Metallic nanowires</p> | <p><i>Nanoscale</i>, 2015 <i>Small</i>, 2016 <i>Nano Research</i>, 2012, 2014 <i>Nanotechnology</i>, 2013 x 2 <i>Nano Letters</i>, 2016</p> |

Ag NW SYNTHESIS: COMPLICATED?



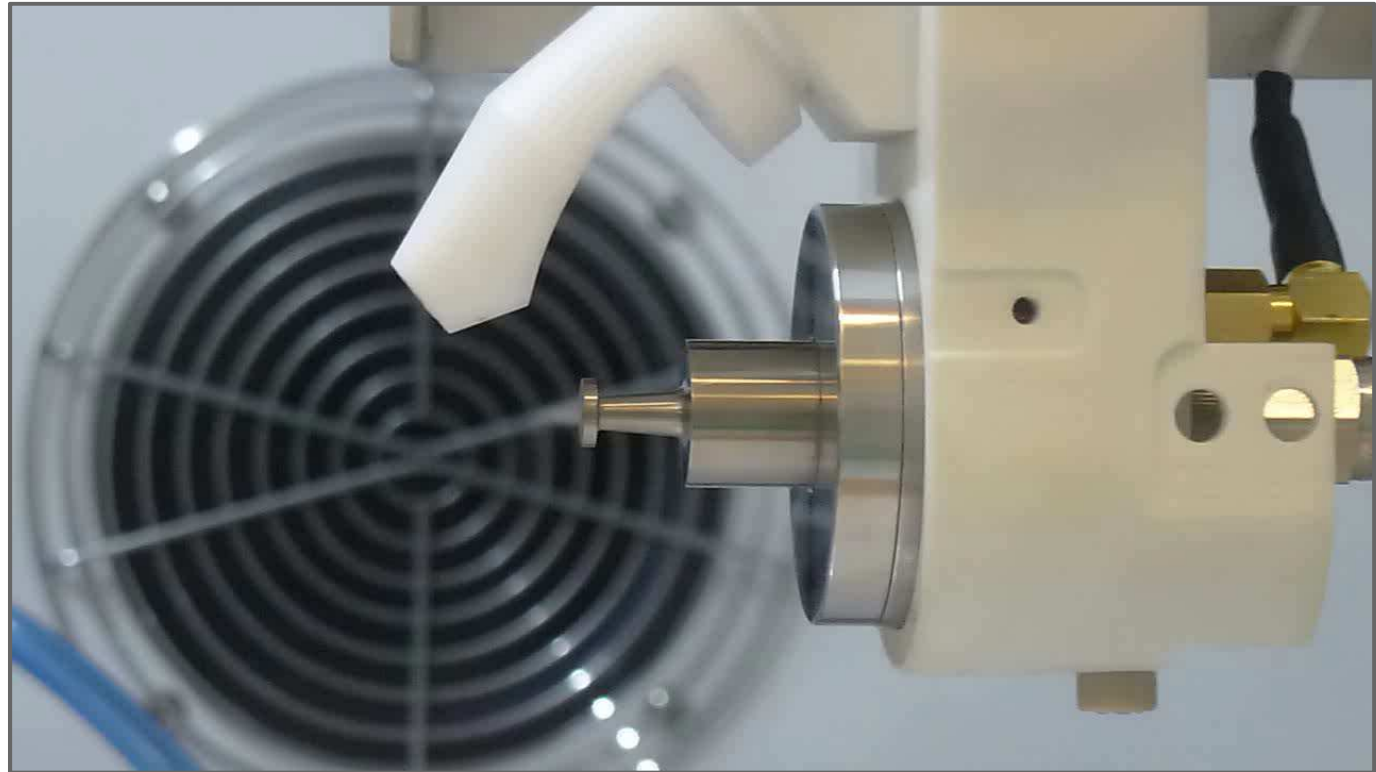


Percolation

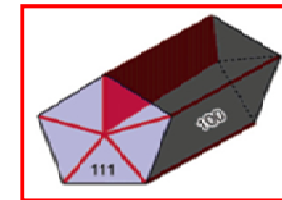
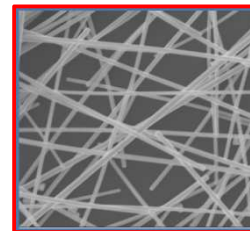
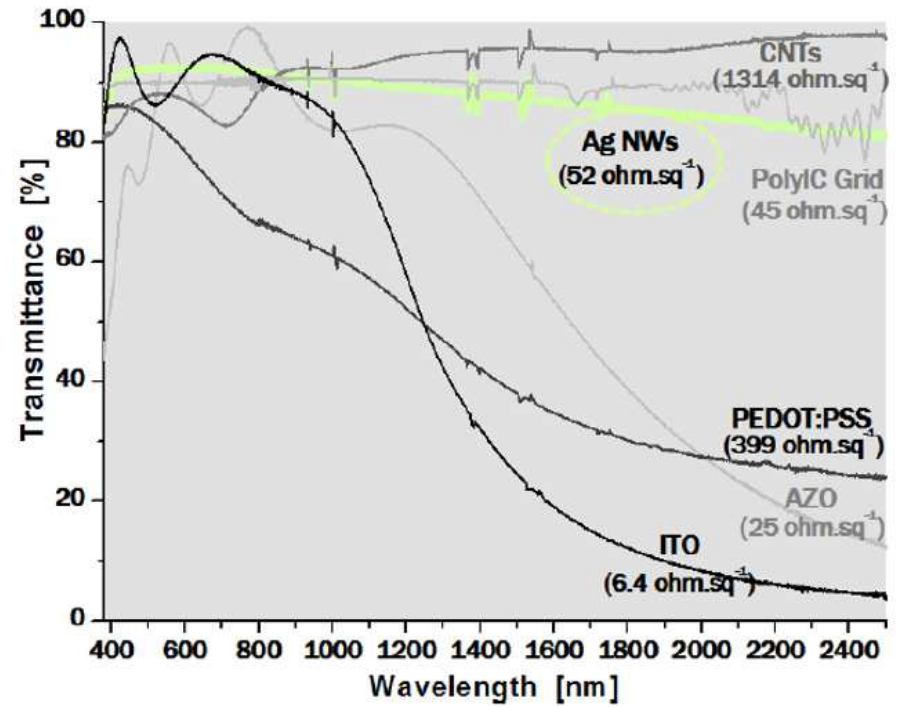
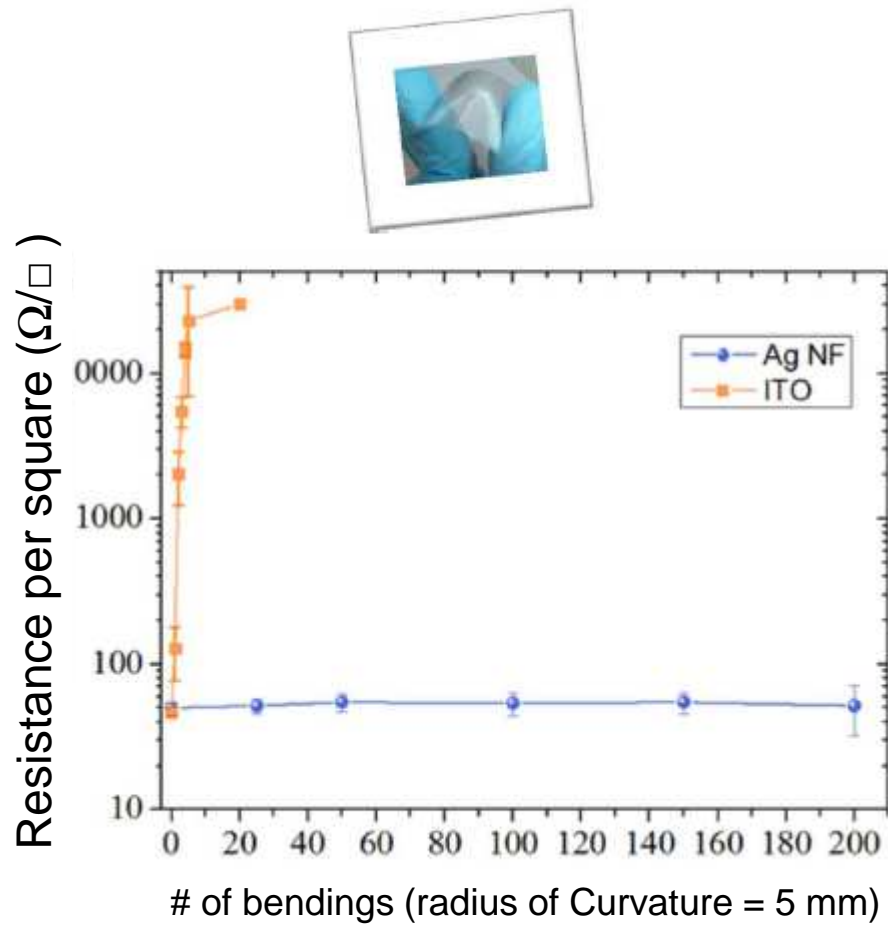
~ 15 PATENTS

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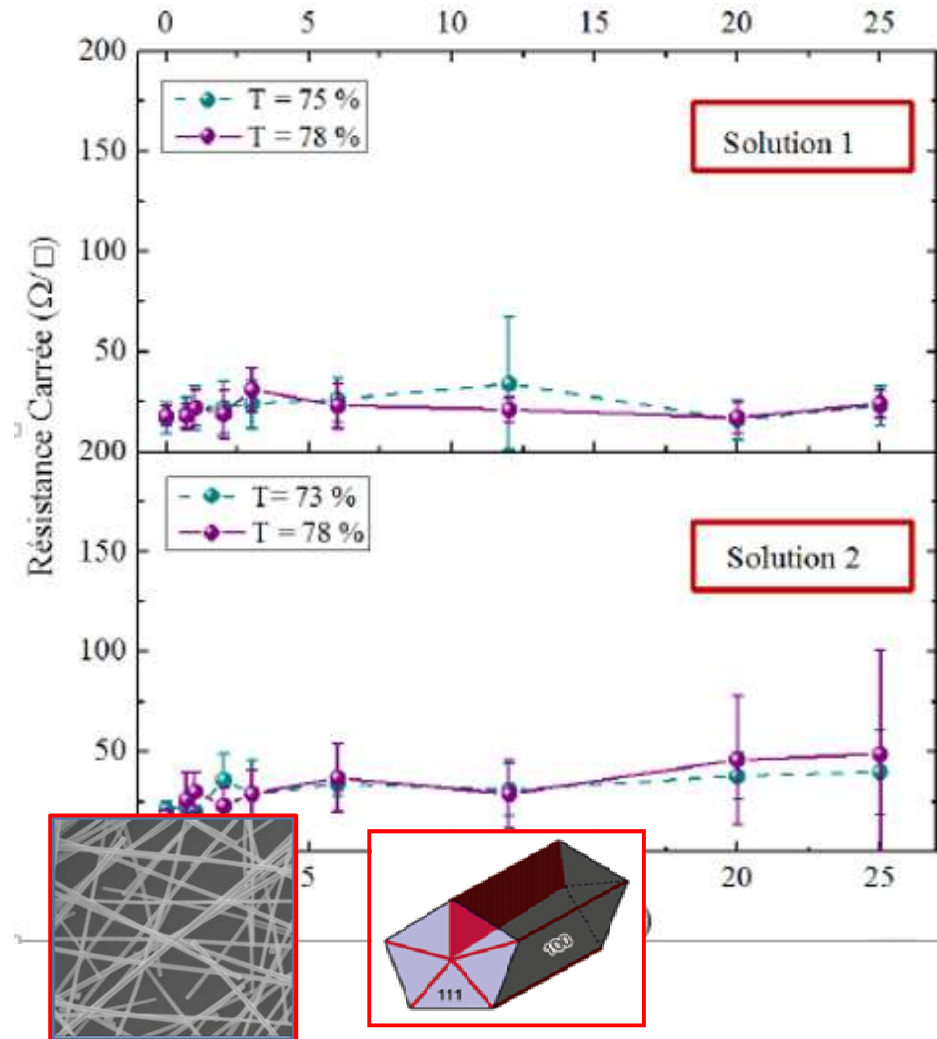
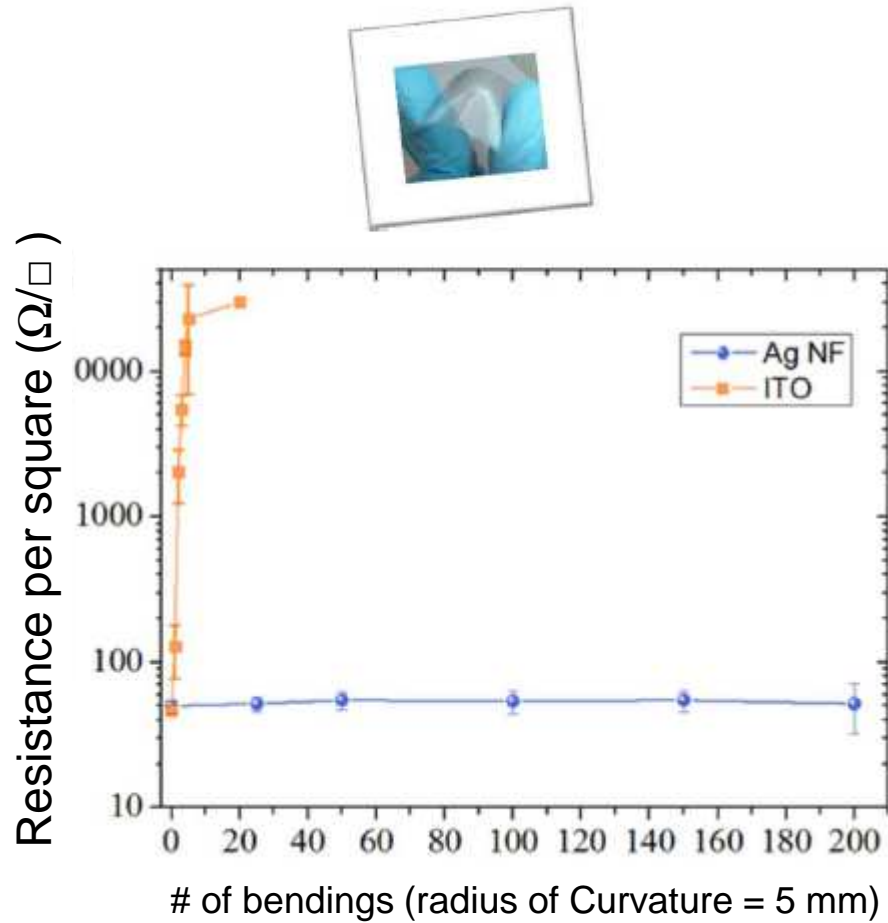
SPRAY-COATING, A METHOD OF CHOICE



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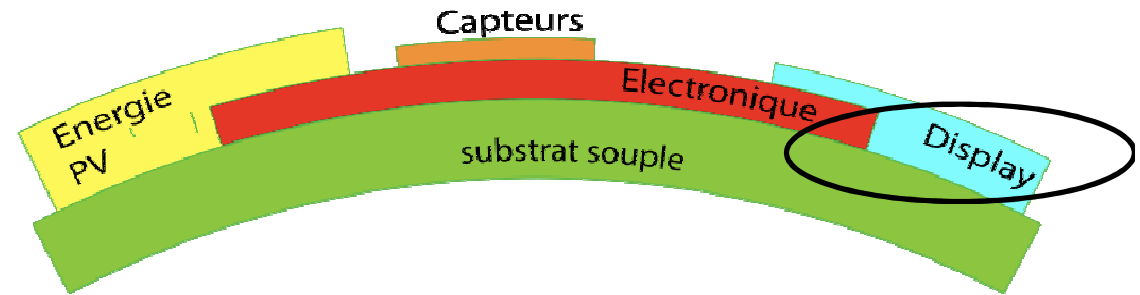
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Nanowire based LED

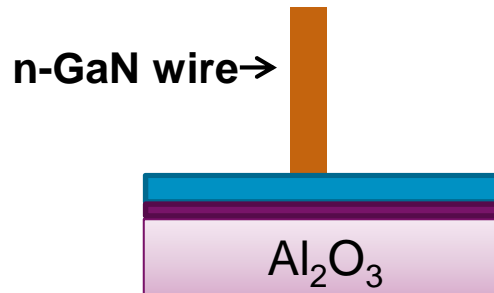
JOËL EYMERY, FRANÇOIS LEVY

NITRIDE NW BY CATALYST-FREE MOVPE

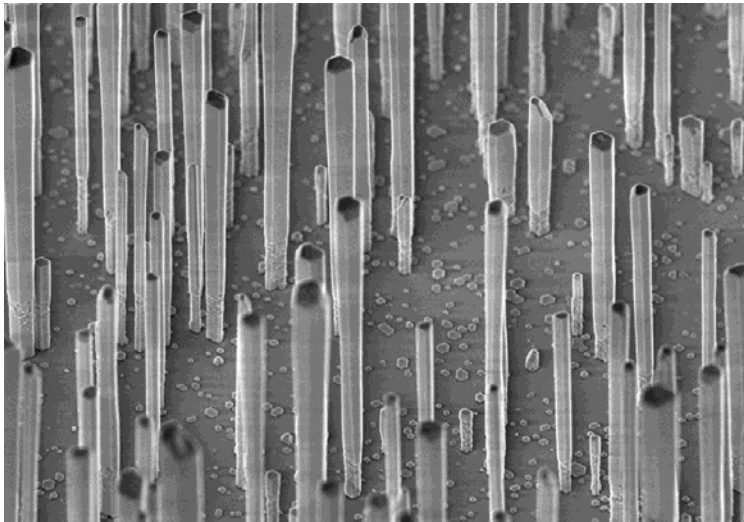
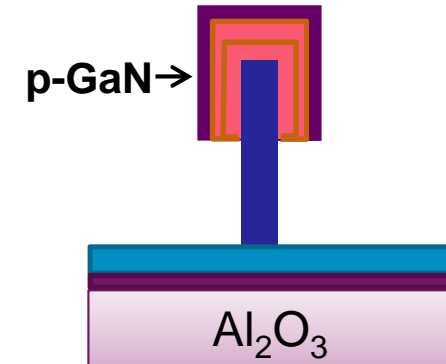
- 1 Nitridation under NH_3 and SiN deposition



- 2 Wire growth under Silane injection and low V/III ratio



- 3 InGaN QW growth and p-GaN capping layer



Nanowire morphology

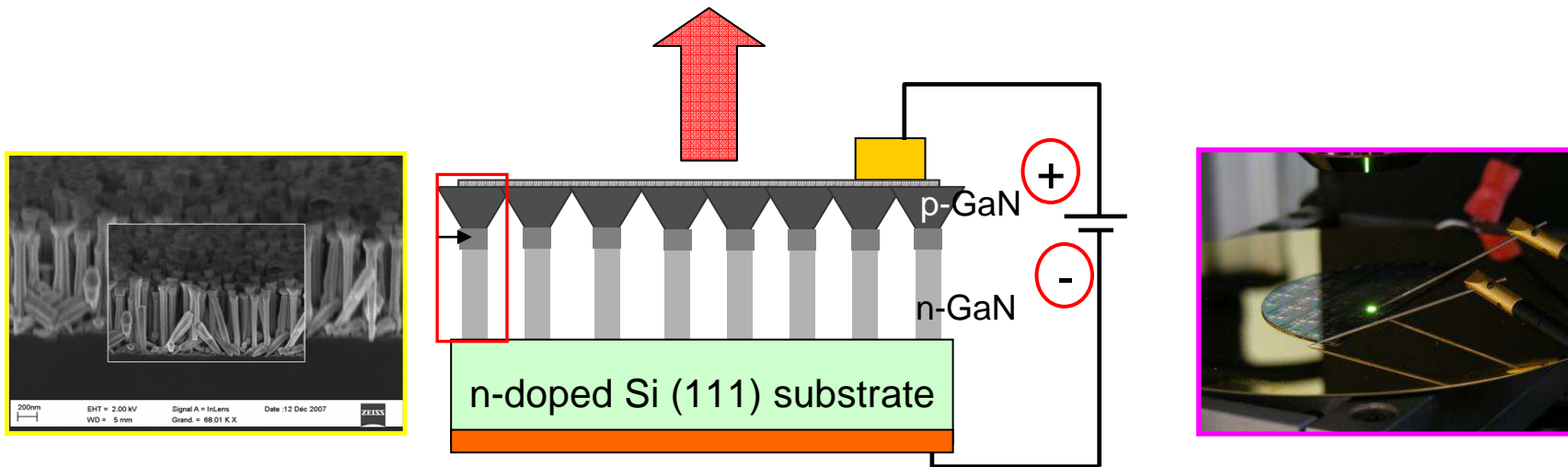
- **Diameter** : 500 nm – 2 μm
- **Height** : 10 – 30 μm
- **Density** : 10^7 cm^{-2}

Spontaneous growth – big surface available for process optimization

MOCVD growth by C. Durand, J. Eymery (CEA-Grenoble)

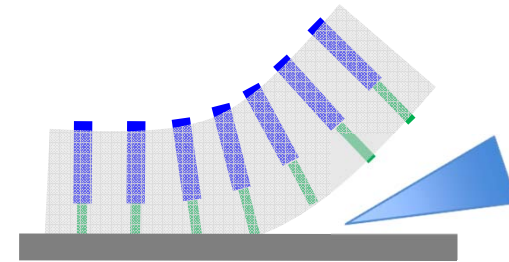
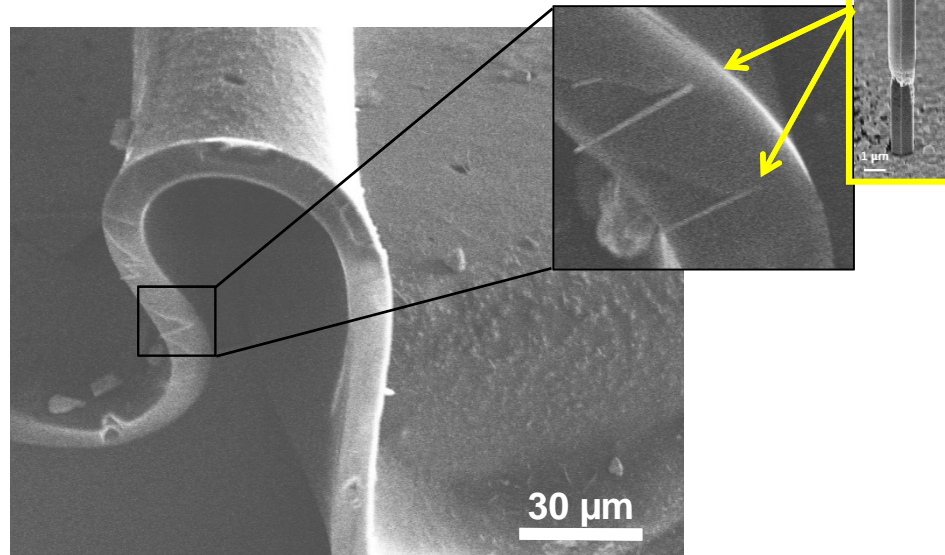
Koester et al., *Nanotechnology* 21, 015602 (2010)

GAN NW BASED LEDS: FROM SOLID SUBSTRATES...



A-L Bavencove et al., Nanotechnology 22 (2011) 345705
Submicrometre resolved optical characterization of green nanowire-based light emitting diodes

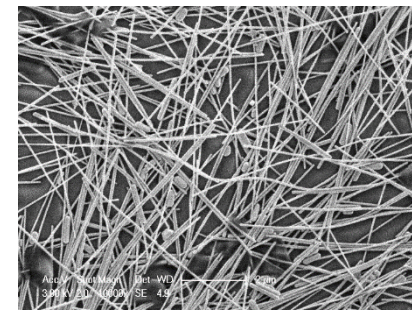
InGaN/GaN NWs / PDMS



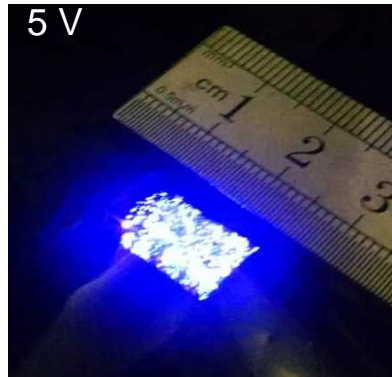
- GaN nanowires embedded into PDMS
- Mechanical lift-off of the composite film
- Back-side metallization and mounting on PET substrate

Main challenge – transparent flexible contact

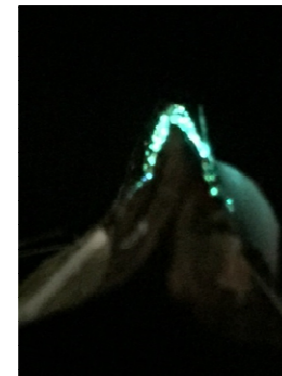
- Thin TCO layers
- Graphene and/or graphene μ -flakes
- **Silver nanowire mesh**



V. Neplokh, et al, Nanosc Res Lett 2015

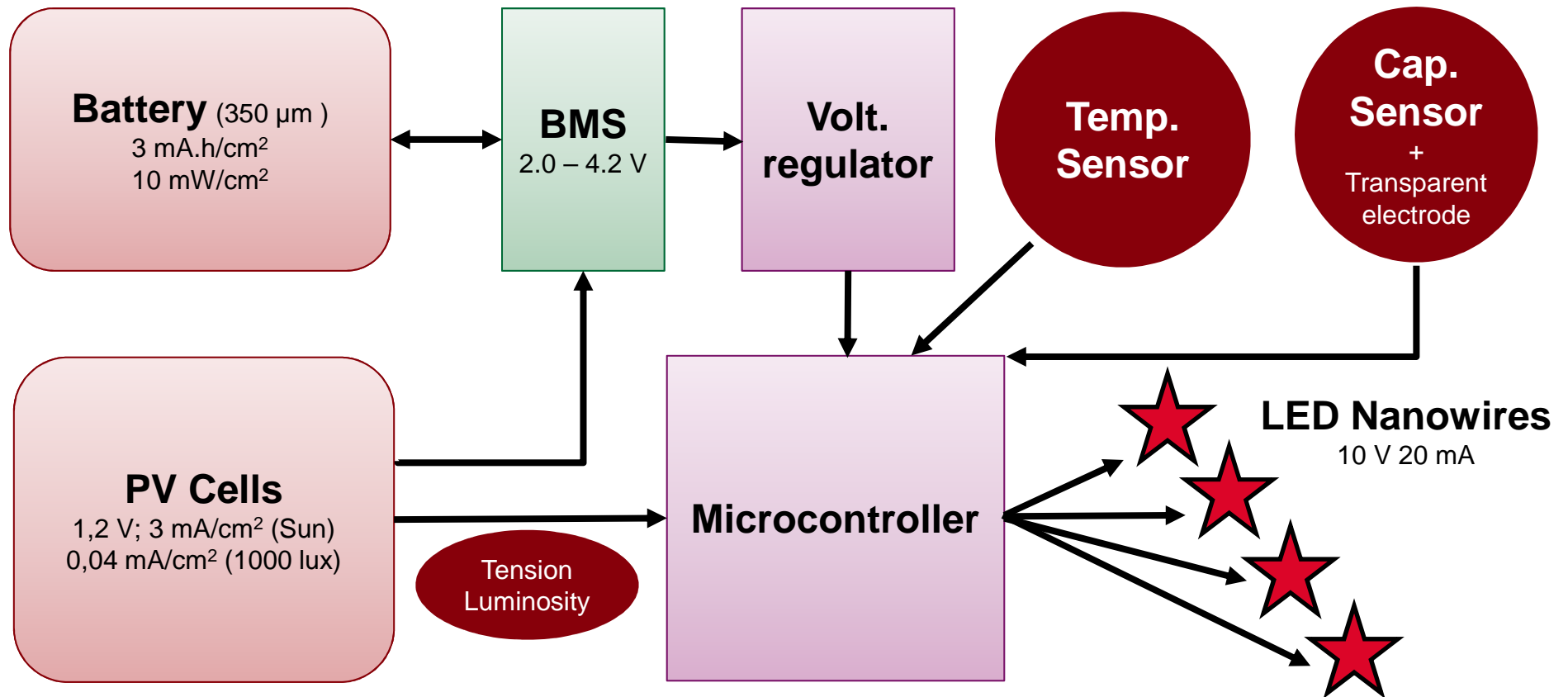


Blue LED



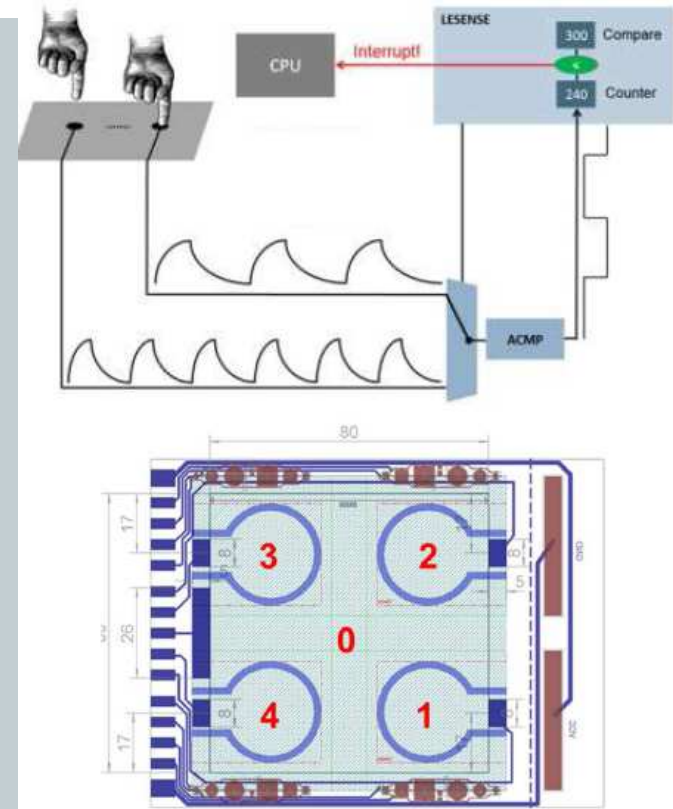
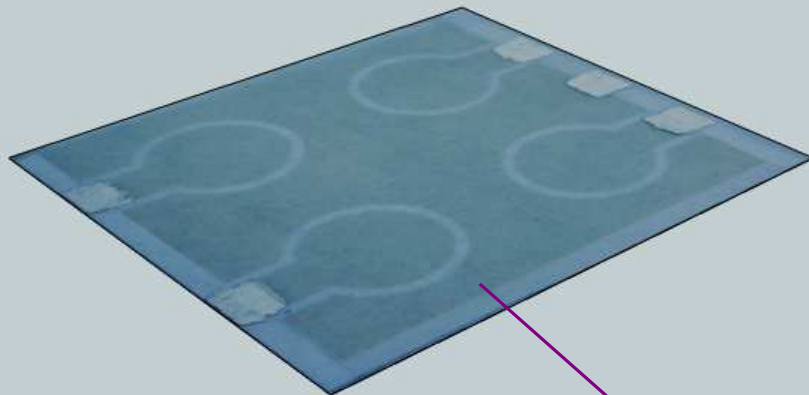
Green LED

- Large area flexible LEDs (active area of several cm²)
- No I-V or EL degradation after 10 bending cycles ($R_{\text{bending}} \approx 0.3 \text{ cm}$)
- Further improvement of emission homogeneity with organized NW arrays is under investigation

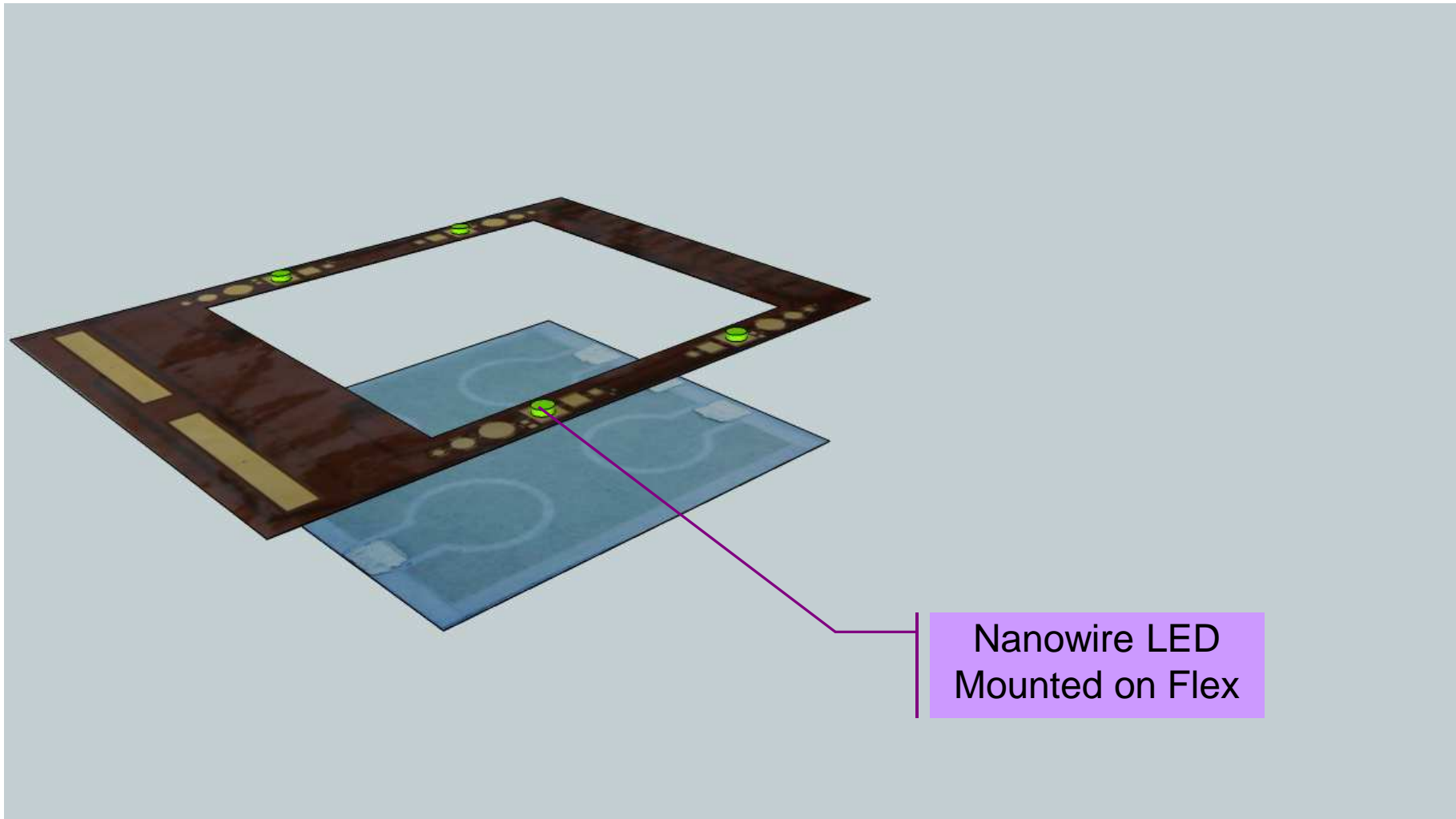


Three Sensors: Light, temperature, capacitive
Copyright CEA, all rights reserved

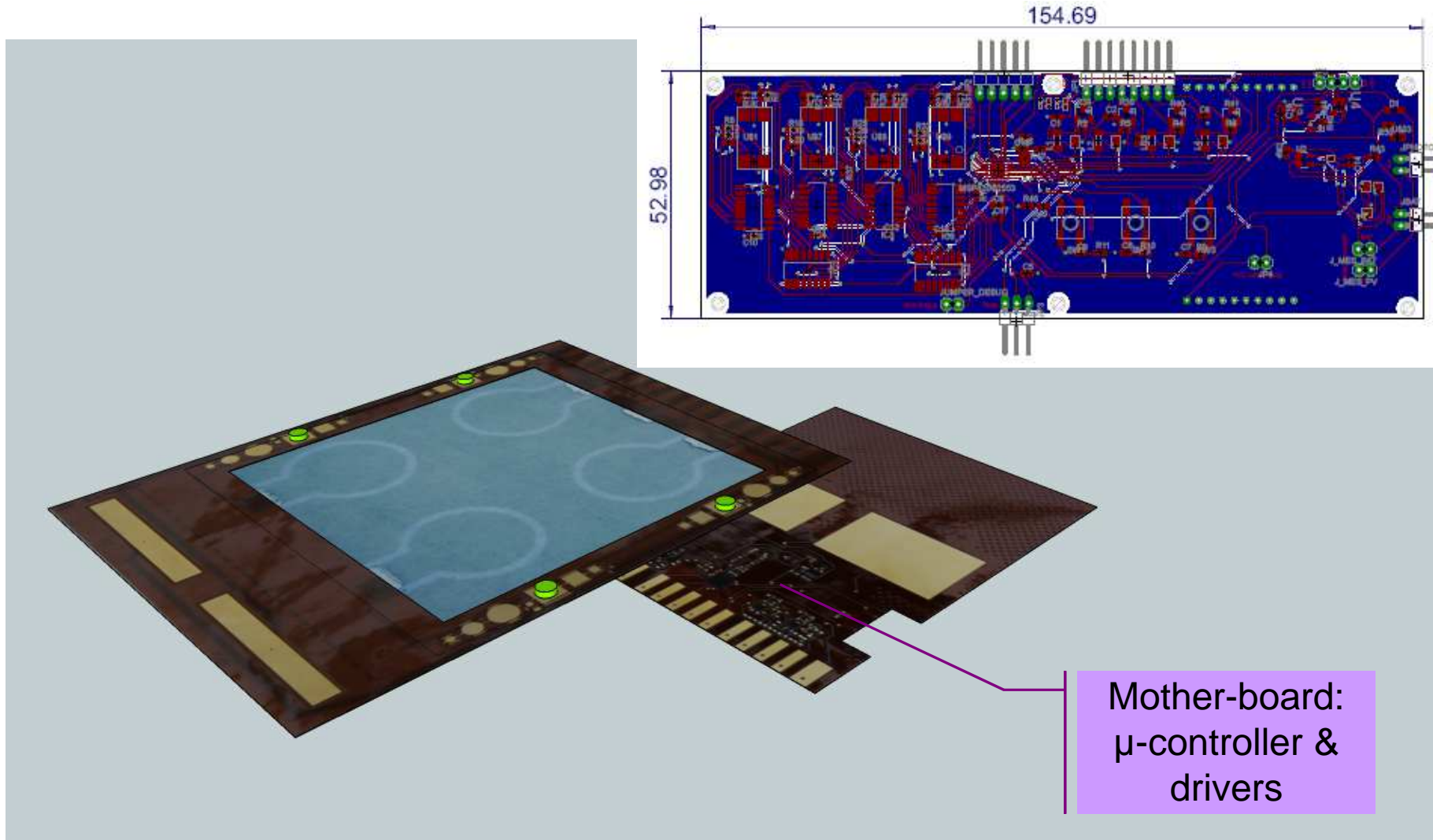
OVERALL ASSEMBLY?

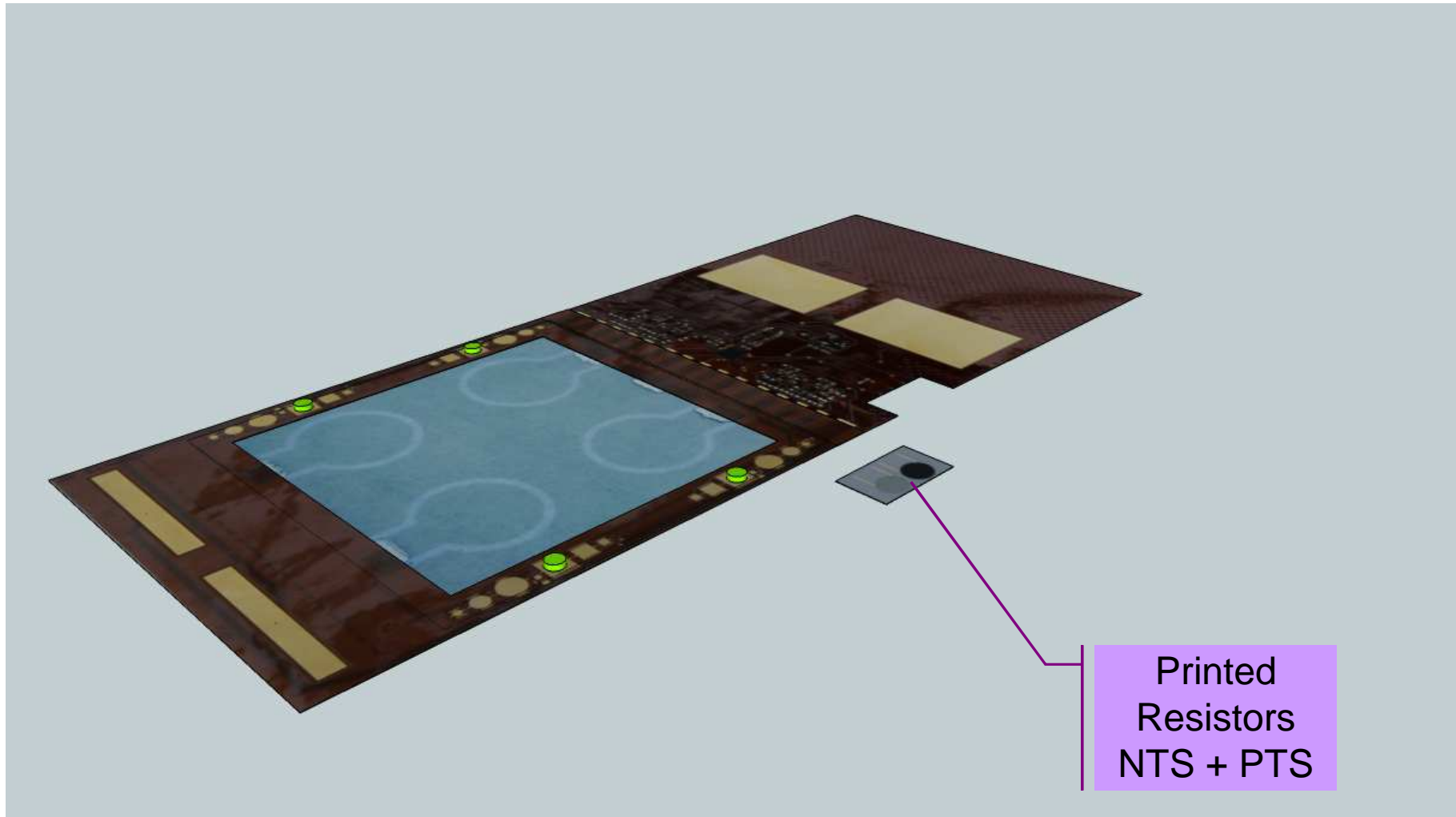


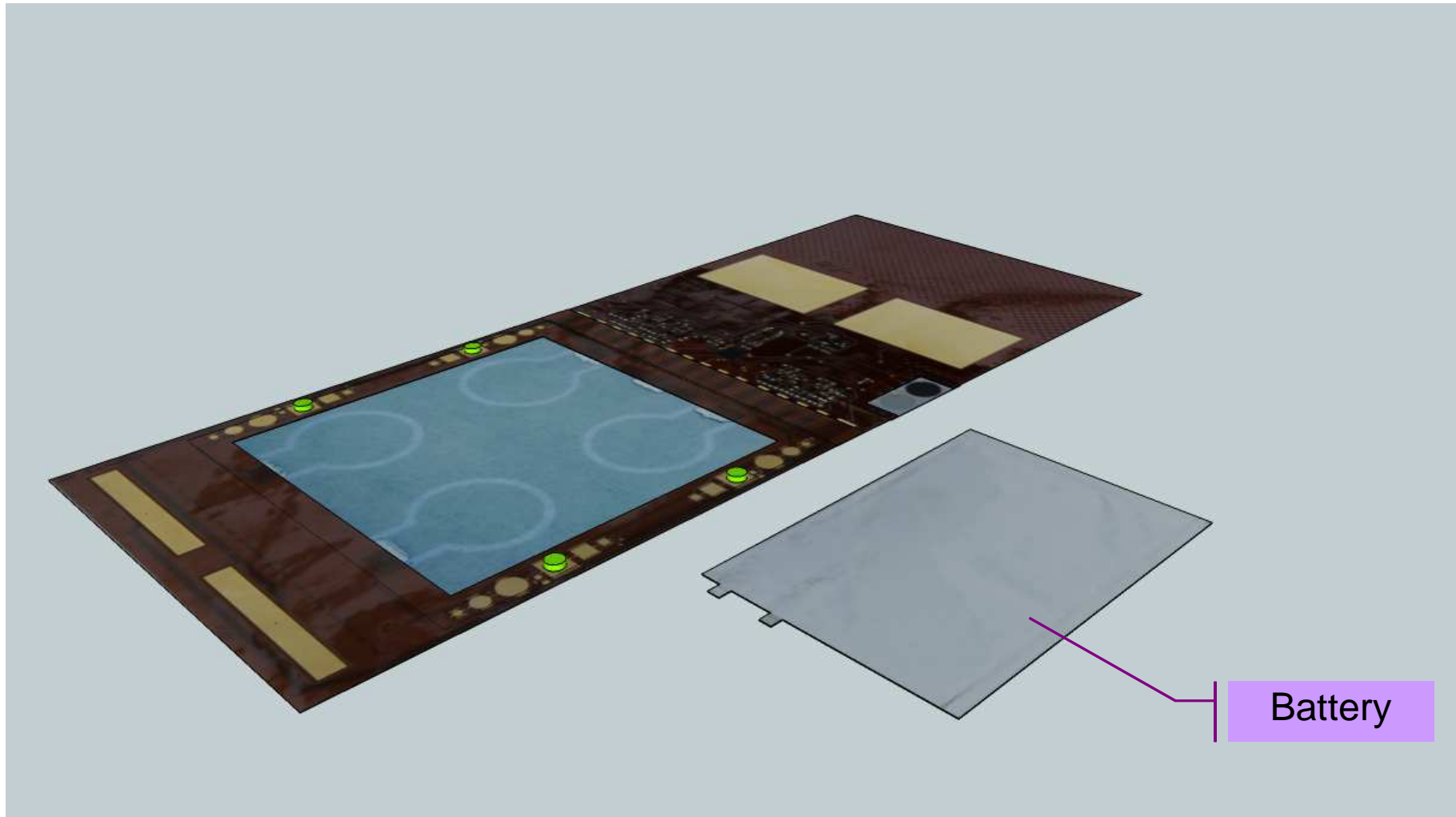
Silver Nanowires
Transparent electrode

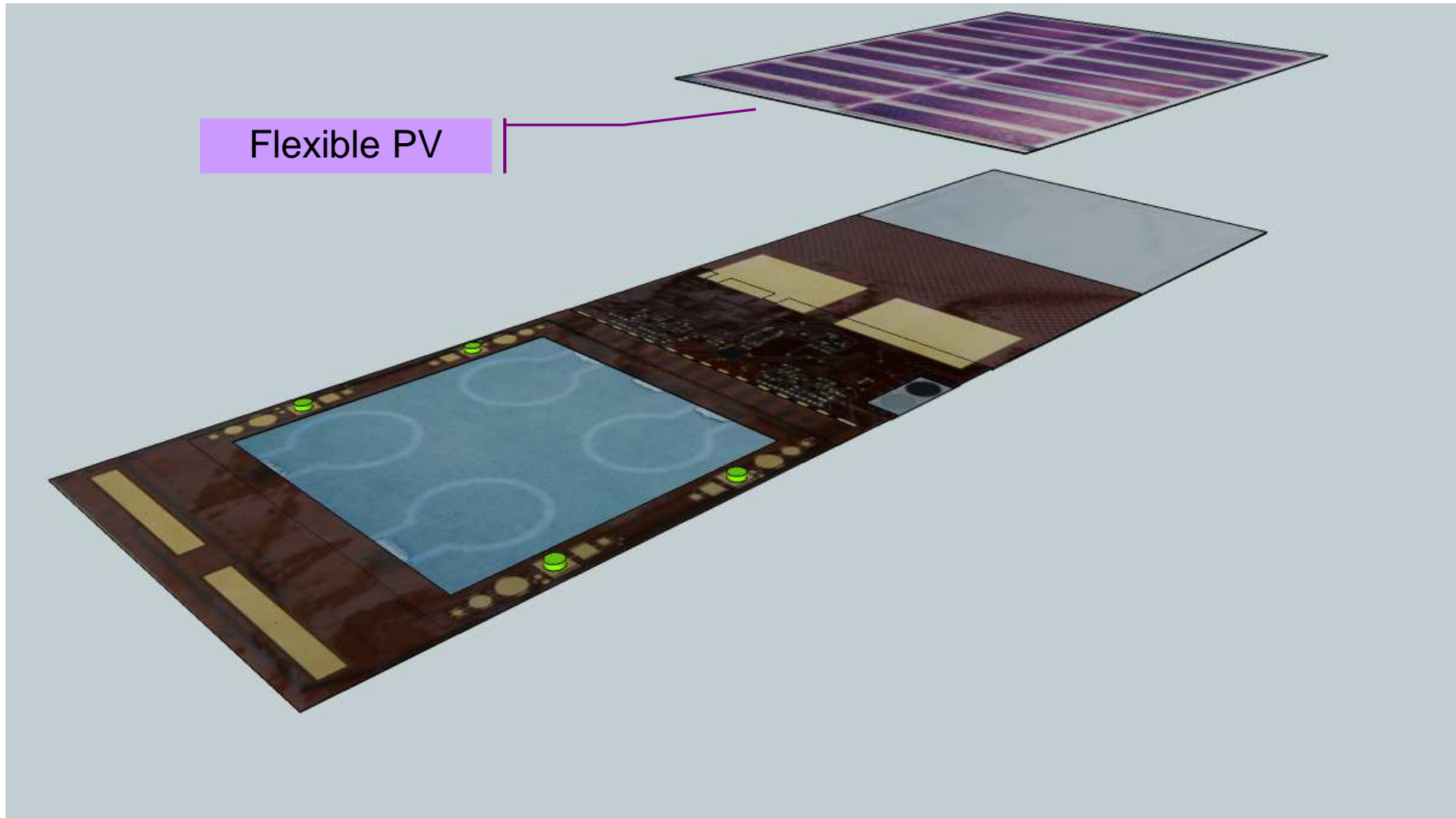


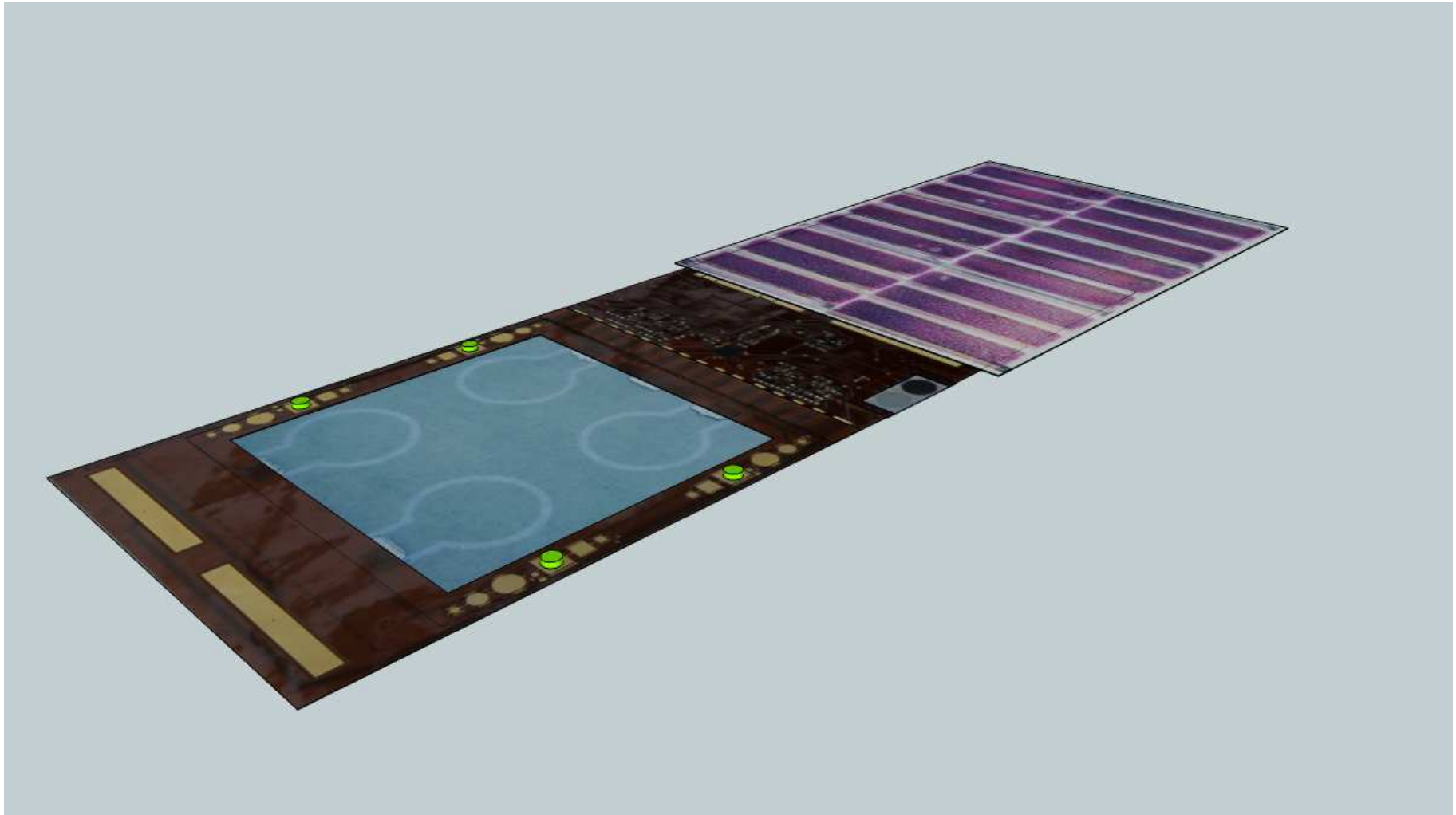
Flexible electronic mother board





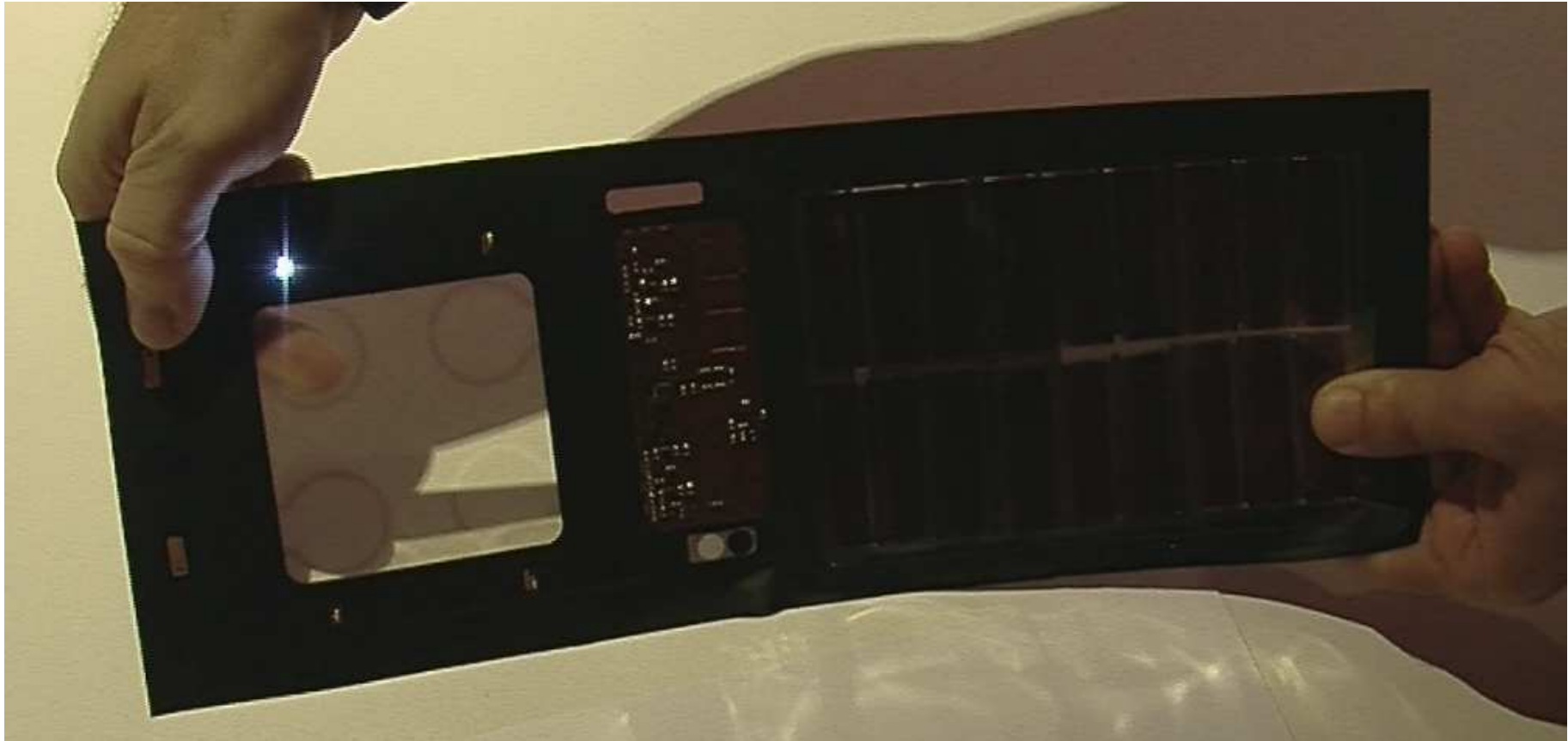






Assembled Flexible Multi-functional Label





- [Capacitive mode](#) (movie)
- [Temperature alarm mode](#) (movie)
- [Light mode](#) (movie)

- ✓ **1 year project, successfull**
- ✓ **Deadline met**
- ✓ **4 CEA's new techno. integrated**

Since then:

- ✓ **3 startups, 20 patents, numerous H2020 projects + industrial contracts**

More info:

jean-christophe.gabriel@cea.fr

QUESTIONS?



FULLFLEX: WHAT TEAM?

| Component | Investigators | Affiliation |
|--|---|--------------------------|
| Battery (Si NP) | Marc BRESTAZ | DRT/LITEN/DEHT/LCPB |
| | Séverine JOUANNEAU | DRT/LITEN/DEHT/LCPB |
| | Willy PORCHER | DRT/LITEN/DEHT/LCPB |
| | Axelle QUINSAC (NTE) | DSM/IRAMIS/SPAM/EDNA |
| | Yann LECONTE | DSM/IRAMIS/SPAM/EDNA/LFP |
| | Nathalie HERLIN | DSM/IRAMIS/SPAM/EDNA |
| PV organic | Rémi DE BETTIGNIES | DRT/LITEN/DTS/LMPV |
| | Nicolas GAUTHIER | DSM/INAC/SCIB/RICC |
| | Marinella MAZZANTI | DSM/INAC/SCIB/RICC |
| | Daniel IMBERT | DSM/INAC/SCIB/RICC |
| | Renaud DEMADRILLE | DSM/INAC/SPRAM/LEMOH |
| | Amélie REVAUX | DRT/LITEN/DTNM/LCSN |
| LED (NW) | Benoit AMSTATT + François LEVY & Alexandre LAGRANGE | DRT/LETI/DOPT/SCOOP/LCE |
| | Joël EYMERY + Benjamin GREVIN | DSM/INAC |
| Transparente Electrode (CNTs or NW) | Eléonore MOREAU | DRT/LITEN/DTNM/LCRE |
| | Jean-Pierre SIMONATO + Caroline CELLE | DRT/LITEN/DTNM/LCRE |
| | Benjamin GREVIN + | DSM/INAC |
| | Renaud DEMADRILLE | DSM/INAC |
| Printed Electronics | Abdelkader ALIANE | DRT/LITEN/DTNM/LCEI |
| | Romain COPPARD | DRT/LITEN/DTNM/LCEI |
| System /integration | Jean-François MAINGUET | DRT/LETI/DSIS/SIPP |
| | Tristan HAUTSON | DRT/LETI/DSIS/SIPP |
| | Pascale RIVIER | DRT/LETI/DSIS/SIPP |
| Pilotage | Jean-Christophe GABRIEL | DSM/DIR/DPNS |
| | Norbert DANIELE | DRT/LETI/DSIS/SIPP |
| | Tiana DELHOME | DRT/LETI/DSIS/SIPP |