New materials and technologies for next-gen smart, integrated energy harvesting/storage devices

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SUMMER SCHOOL NiPS/EnABLES

3rd – 6th September 2019

Hotel Giò , Perugia

CHOSE-Center for Hybrid and Organic Solar Energy

People

- 6 staff members
- 6 RTD A
- 12 PhD
- 12 Post Doc

Objectives

- Printed electronics
- Research and Development on organic and Perovskites photovoltaics
- Device design
- Technology transfer to Industry

Basic Research → CHOSE → Industrialization

Spin-off

cicci research

intellienergia s.r.l. renewablenergyengineering

TIBERLAB

INGEM S.R.L L'INGEGNERIA PER L'EMERGENZA

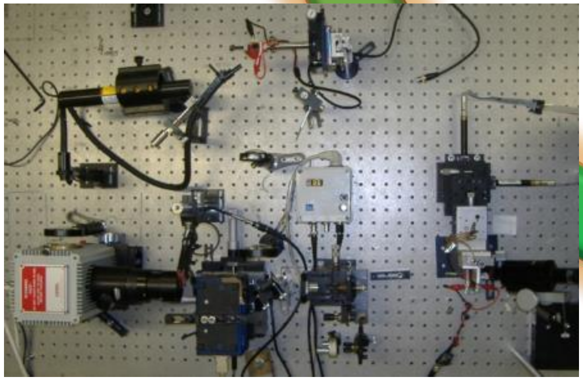
CHOSE- Facilities

CHOSE – TT
650 mq

ESTER
100 mq

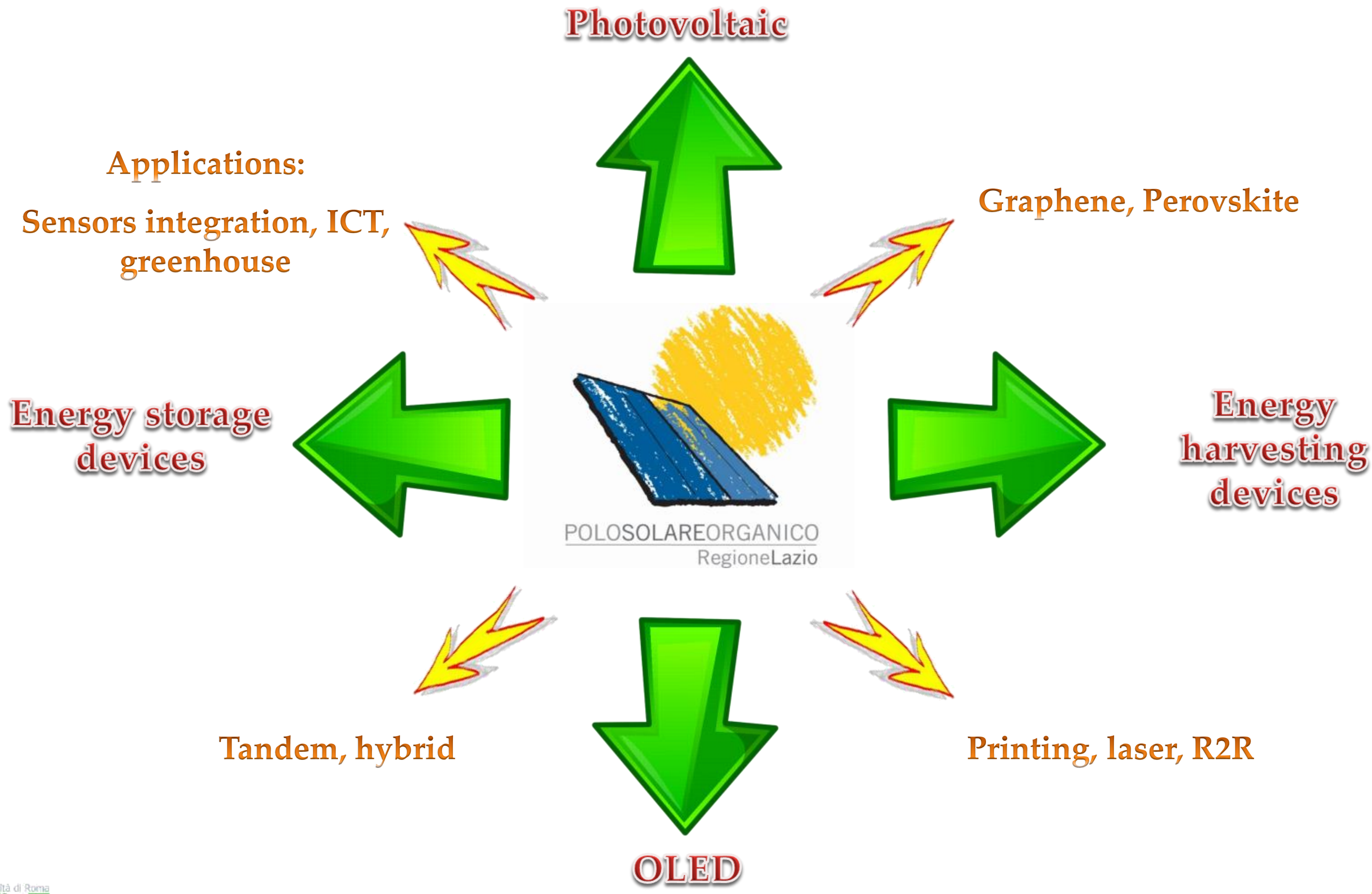
POLOSOLAREORGANICO
RegioneLazio

CHOSE –NT
70 mq

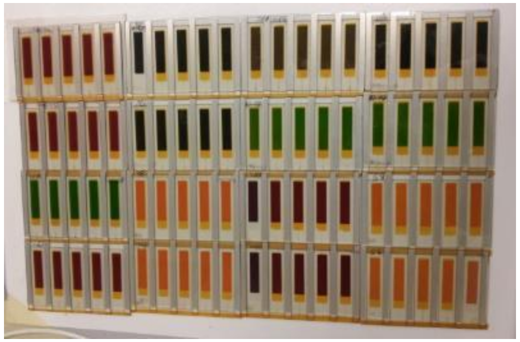
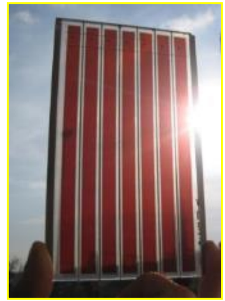
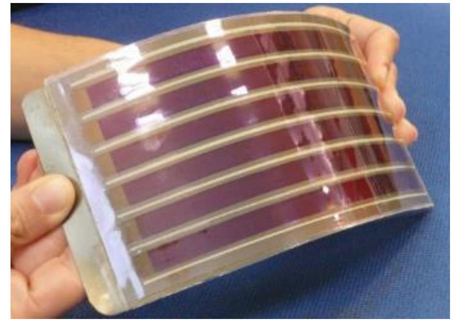


CHOSE –MI
200 mq

CHOSE ACTIVITIES



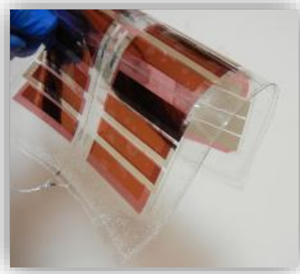
Fabrication lab

DSC

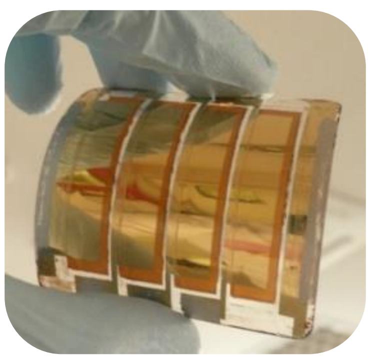
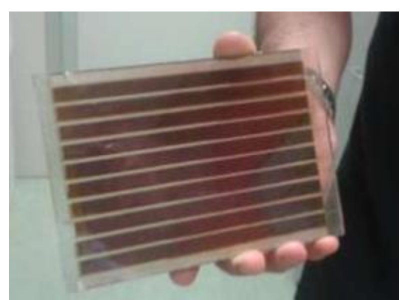
Rigid

flex


OPV

Grapene/CNTs electrodes

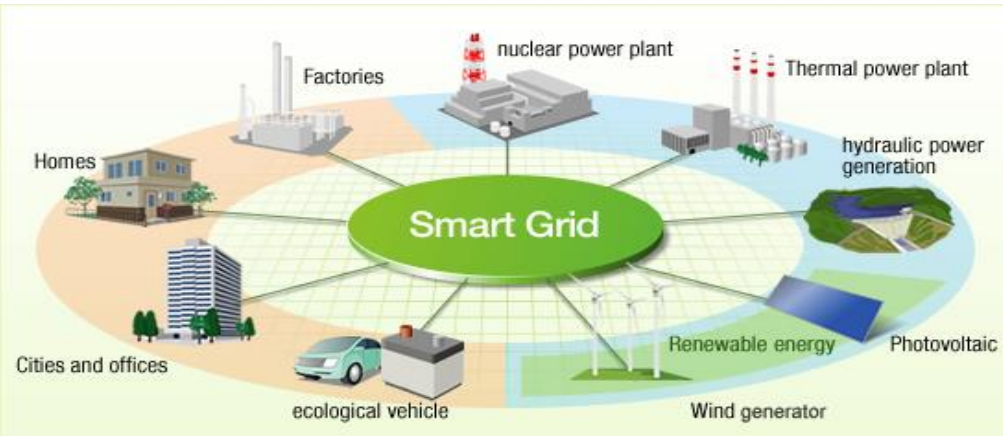
Mesoporous & Planar Perovskites

Outline

- Background and motivation
- Printing techniques for new generation energy harvesting/storage devices
- The role of substrates: rigid or flexible?
- Examples of printed energy harvesting system: the case of organic and perovskite solar cells
  - Working principles
  - Role of architectures
  - Material engineering for printing processes
  - Scaling up to large scale printed devices
  - Stability issue
- Examples of printed energy storage system: supercapacitors and batteries
  - What is the difference between a supercapacitor and a battery?
  - Working principles
  - Devices architecture
  - Material engineering for printing processes
  - Scaling up to large scale printed devices
- How to integrate solar cells and storage systems?
- Conclusions and future perspectives

Background

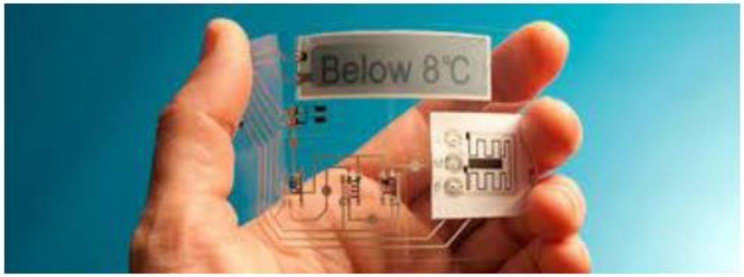
Sustainable energy supply is of paramount importance to support an expanding world with increasing living standards and growing energy needs. On the other hand, in the last few years, new generation of portable electronics devices have been enriching our professional and recreational lives to an extent that they have become indispensable for almost everyone. Flexible and stretchable devices can be used in a wide range of consumer applications, ranging from wearable electronics, to mobile healthcare, to Internet of Things (IoT) technology

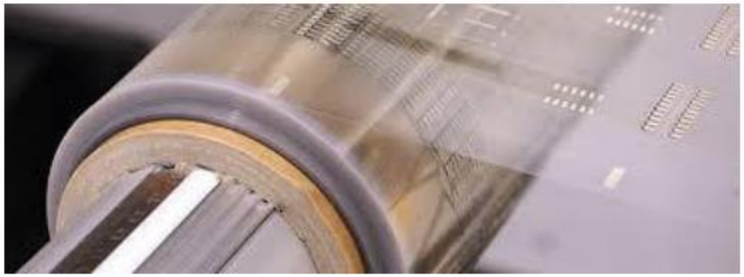


Smart man

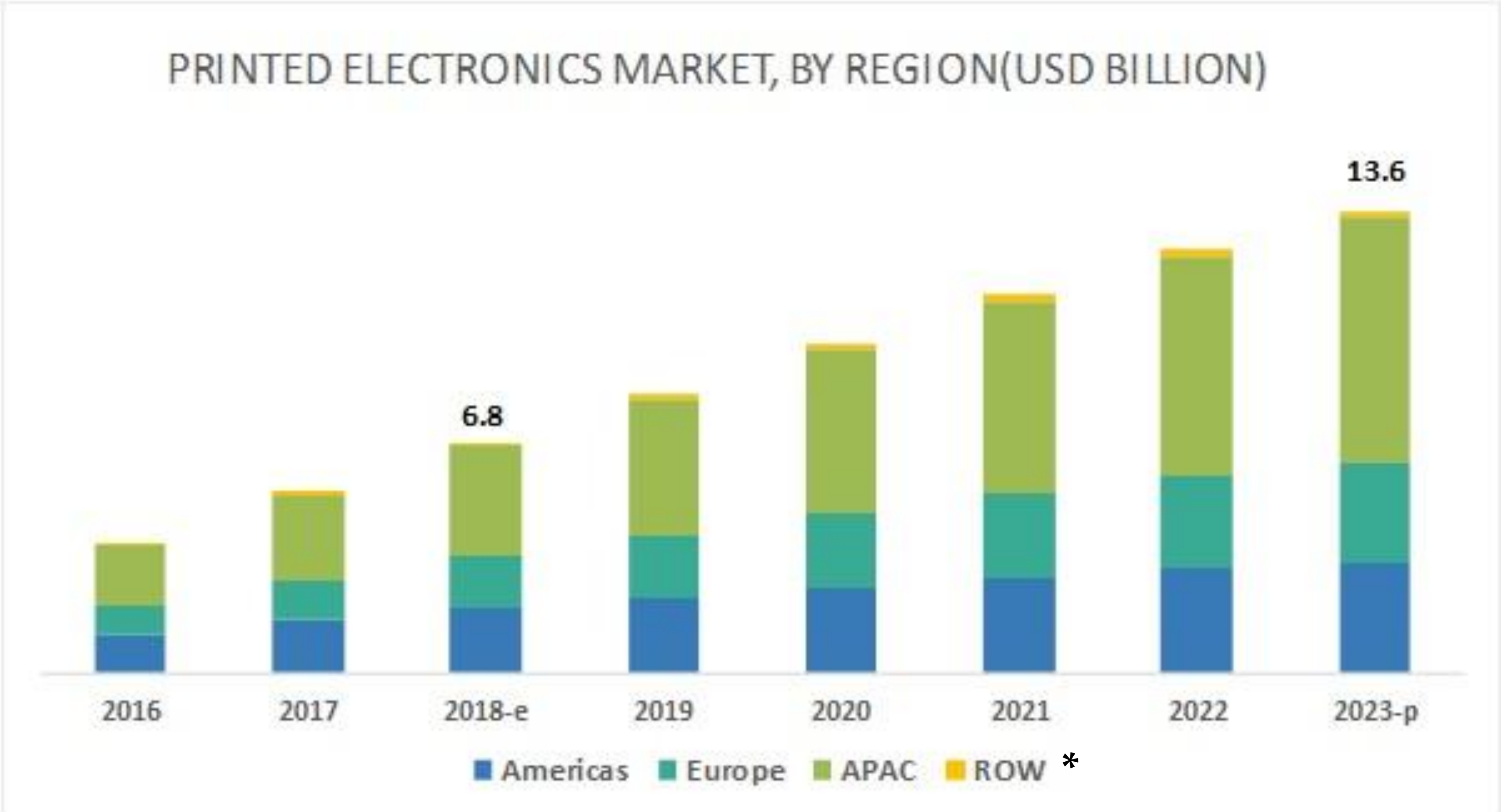
From conventional electronics to printed electronics

- Microelectronics changed the world by enabling many intelligent products
- A new field of electronics is emerging that cannot be made small, but must be big in order to interact with big things
- This is flexible, printed electronics and its most important feature is that it can conform to surfaces to impact a wide range of applications





Printed electronic market



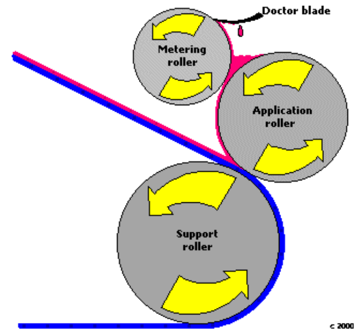
The overall printed electronics market is estimated to reach USD 13.6 billion by 2023 from USD 6.8 billion in 2018, at a Compound Annual Growth Rate (CAGR) of 14.92% during 2018–2023

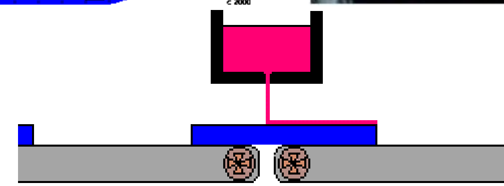
*** APAC =Asia Pacific, ROW= Rest of the World**

https://www.marketsandmarkets.com/Market-Reports/printed-electronics-market-197.html

Background: A paradigm shift in electronics

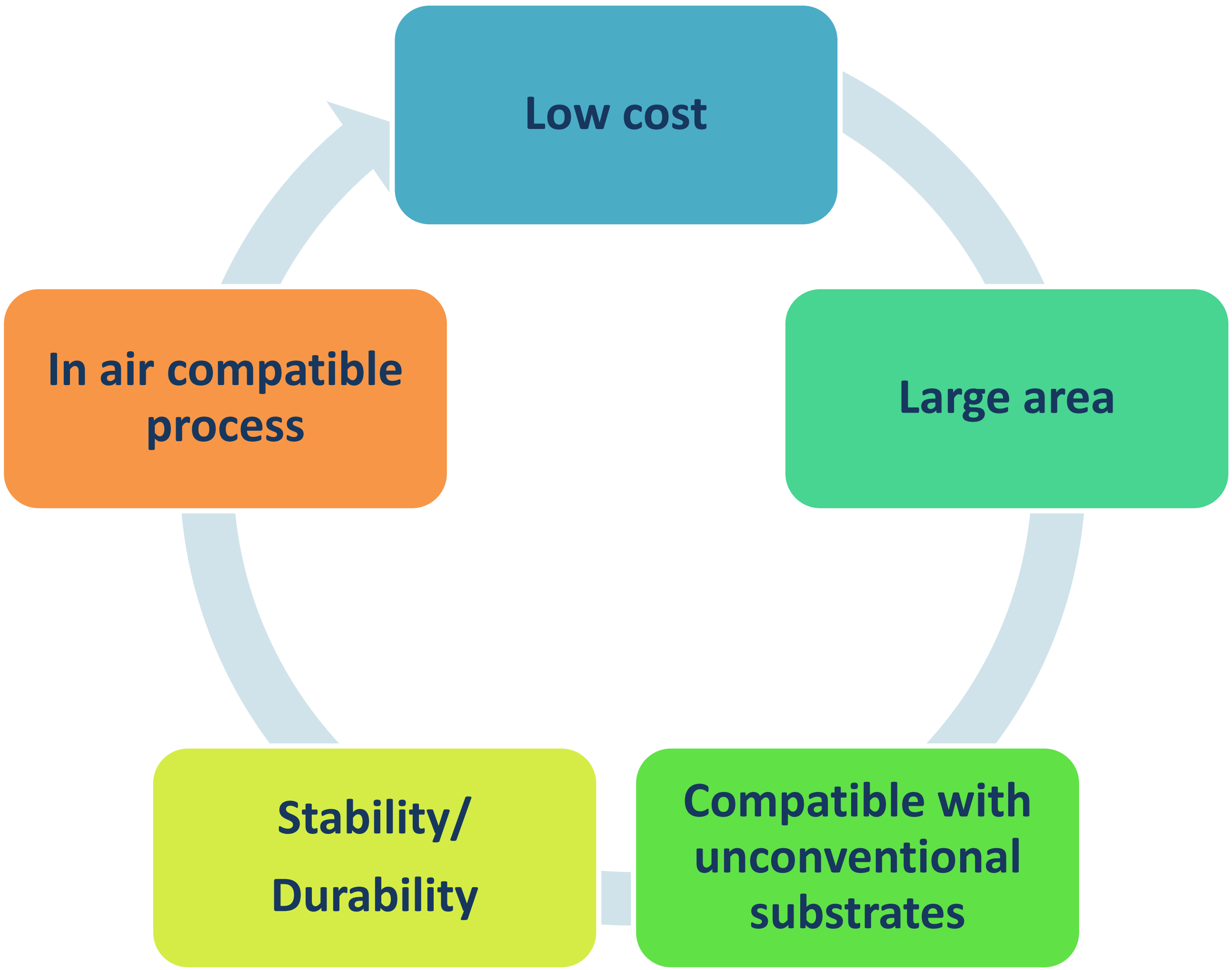
Conventional Electronics → Organic Electronics



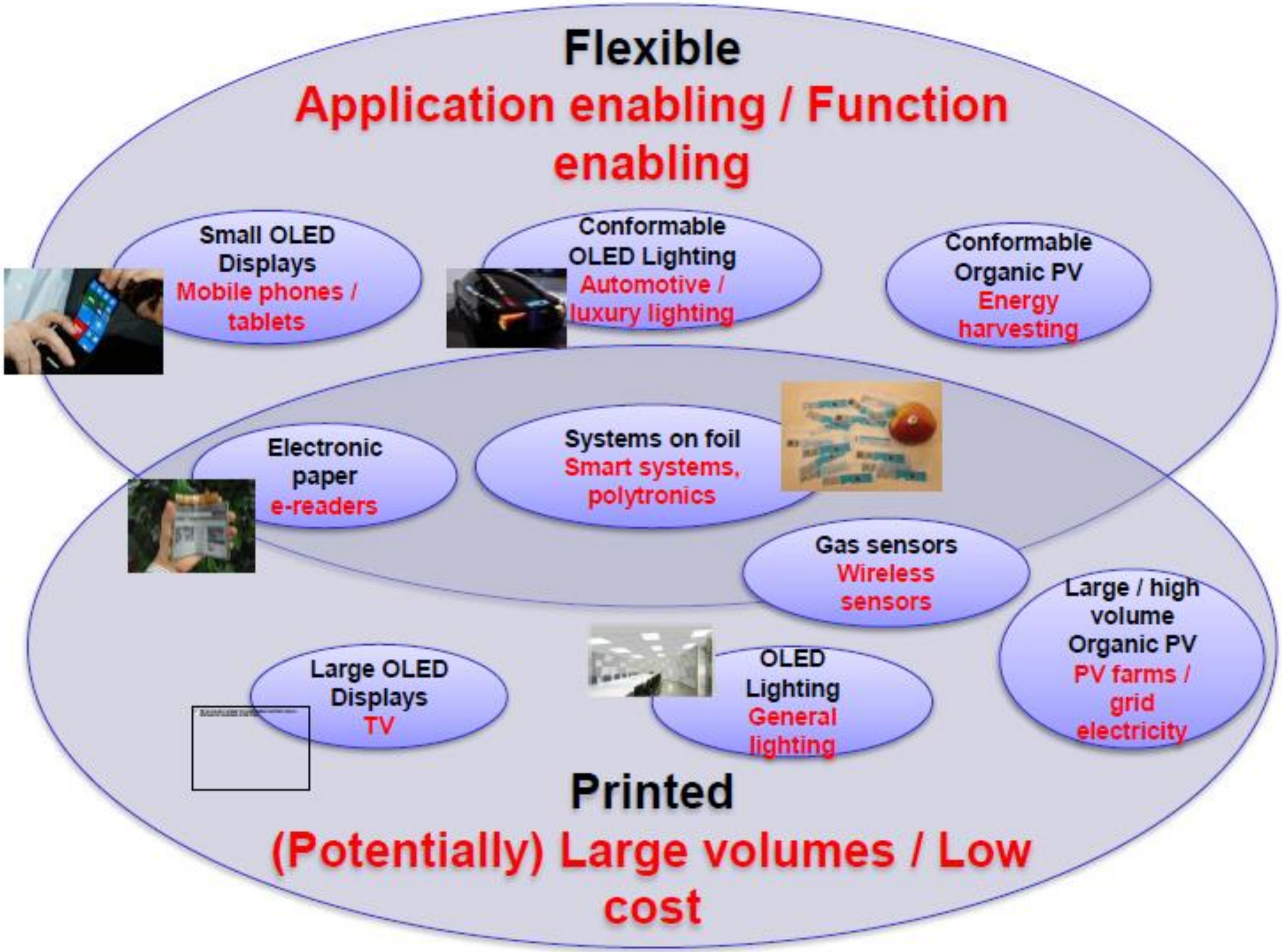


Conventional processing	Additive/printing processing
Subtractive batch processes (photolithography and wet/dry etching for layer definitions)	Additive continuous processes (printing, laser processing etc.) for layer definitions
Controlled (e.g., a vacuum environment)	Ambient temperature and pressure conditions
Fixed, long production runs of 'same product'	Flexible, short production runs - 'flexible' product functionality

What do we need for Printable Electronics?



Applications

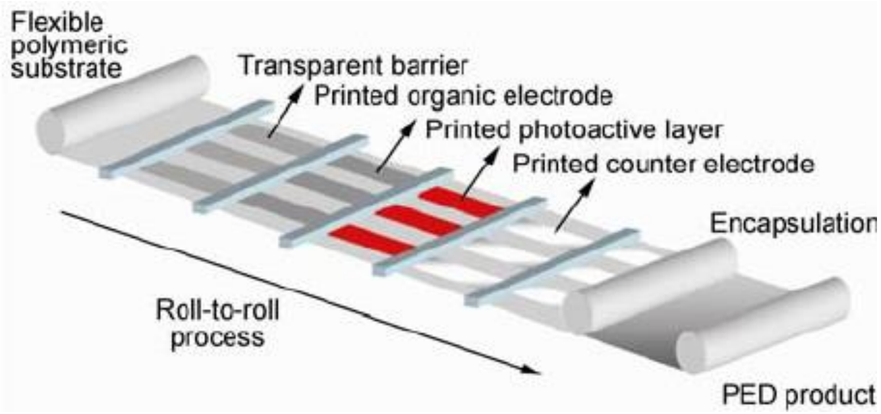


Printing technologies classification 1/2

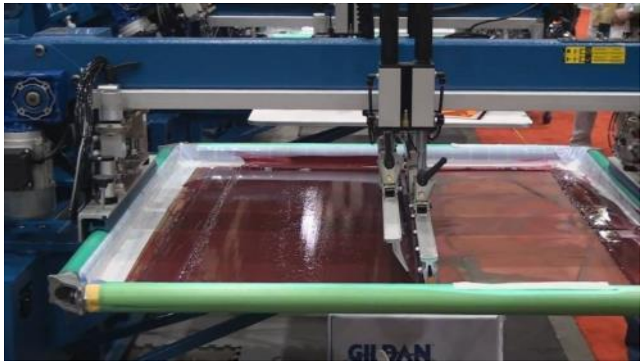
- Printing techniques
  - Contact printing techniques
    - Screen printing
    - Blade coating
    - Fexographic printing
    - Gravure printing
    - Slot die coating
    - Pad printing
  - Non-contact printing techniques
    - Laser Direct Writing
    - Aereosol/Spray coating
    - Inkjet printing

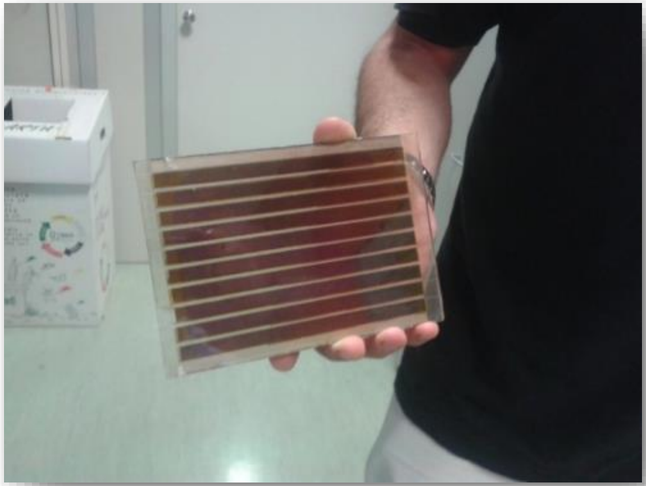
Printing technology classification 2/2

Roll to roll printing techniques

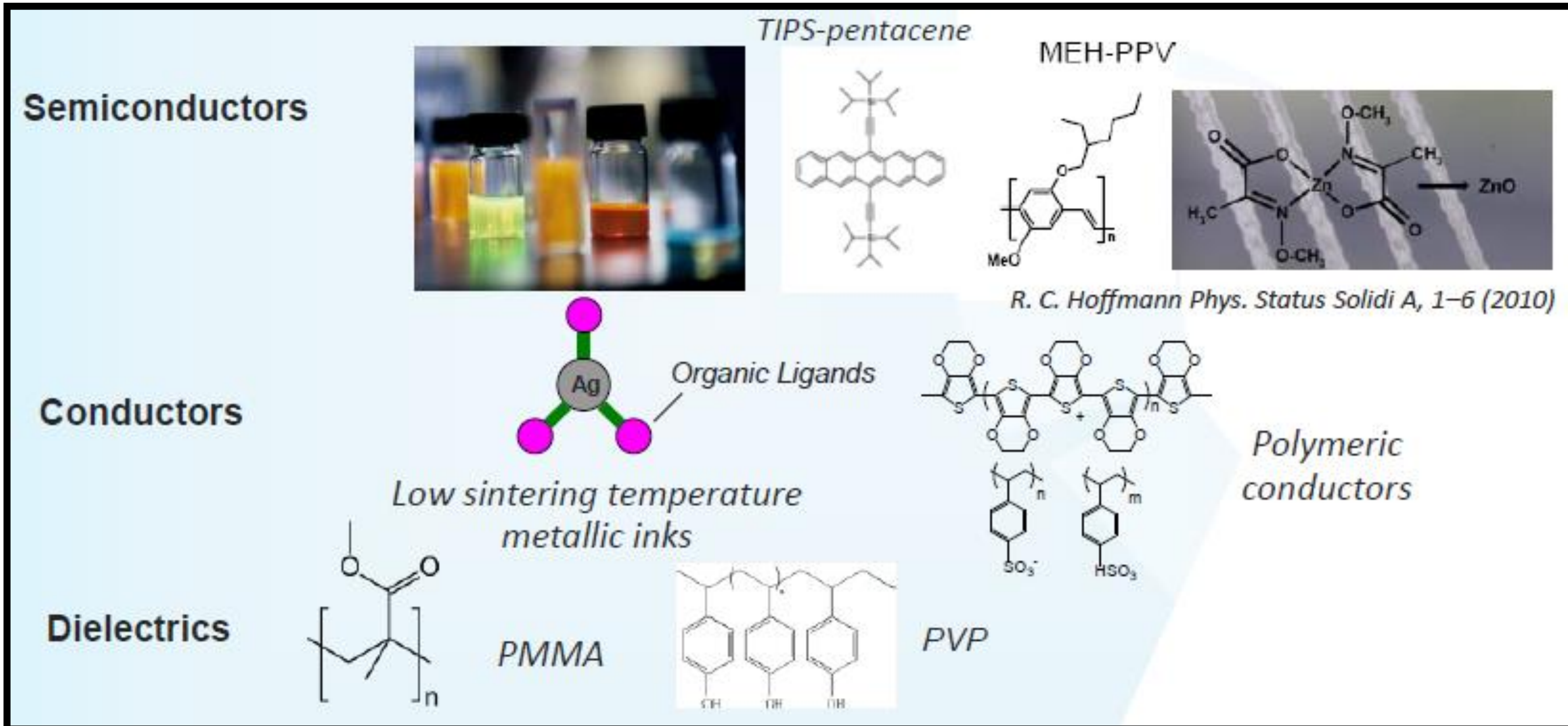


Batch printing techniques





Inks type



Both organic and inorganic inks have been developed for printed electronics

Inks characteristics

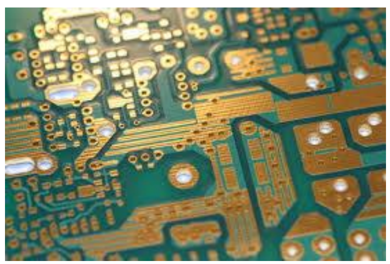
The most common types of inks are water, oil or solvents based. The general form of the ink consist of a mixture of compounds (pigments or dyes, resins, solvents, fillers, humectant and additives), in liquid or solid state, with specific proprieties adapted to the printing technology characteristic, such as viscosity, surface tension, etc., to be easily printed in a large variety of substrates.

THE INK FORMULATION REQUIRES THE USE OF GREEN AND SUSTAINABLE MATERIALS, FURTHERMORE HAS, IN SOME SPECIFIC CASES TO BE ADAPTED TO THE SUBSTRATE WHERE IT HAS TO BE DEPOSITED

- **Non halogenated solvents**
- **Non-toxic and with low volatile organic compounds (VOC)**
- **Boiling point ≤ 200°C**
- **Reduced environmental impact**

Printable substrates

Understanding the printing process and relationships between process parameters and printing quality (e.g., print resolution, uniformity and electrical conductivity of printed layer) is necessary for process optimization, as well as the suitability of the selected material in terms of adhesion and final applications; the appropriateness of the printed technology and ink, properties, the process deposition rate, etc. In this context the type substrate plays a fundamental role



- **Glass is rigid, heavy, typically hydrophobic, but is semitransparent, is a good barrier as encapsulant for organic materials and can survive to high temperatures**
- **Metal can be flexible and treated at high temperature is limited on the freedom of design and is high cost**
- **Polymers composites, such as, glass-reinforced epoxy laminates with flame retardant have been largely used in rigid printed circuit boards (PCB)**
- **Non-reinforced polymers such as, PET, PEN, PDMS, are flexible, lightweight materials, more economically processed, can be transparent. Their major drawback lies on the low surface energy, which, normally requires a prior surface treatment before printing and low processing temperatures.**
- **Paper, flexible reciclable, lightweight, low cost, compatible with most of the inks used for printed electronics. Main drawback, low processing temperature and durability**

Interaction between the ink and the substrate

Several factors influence the quality of the printed material

• Substrate properties (chemical composition, surface topography and porosity, etc.).

• Conductive ink properties (chemical composition, rheological behavior, the rate of solvent evaporation, etc.).

• The superficial tension (ST) of the ink and the surface energy (SE) of the substrate that will receive the ink, i.e., the difference between them.

• Functional groups and their intermolecular forces present in the ink/polymer system.

→ Superficial Tension (ST) refers to the amount of cohesive forces between liquid molecules.

→ The SE describes the degree of energy with which the molecules of the surface of a solid draw and allow adherence of a fluid

The transfer and distribution of the ink on a substrate depends on the wettability, spreadability and adhesion capabilities.

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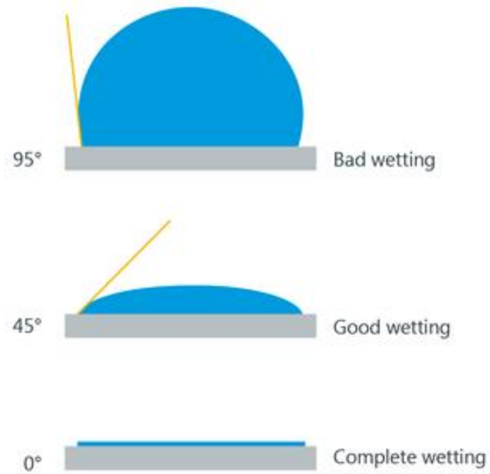
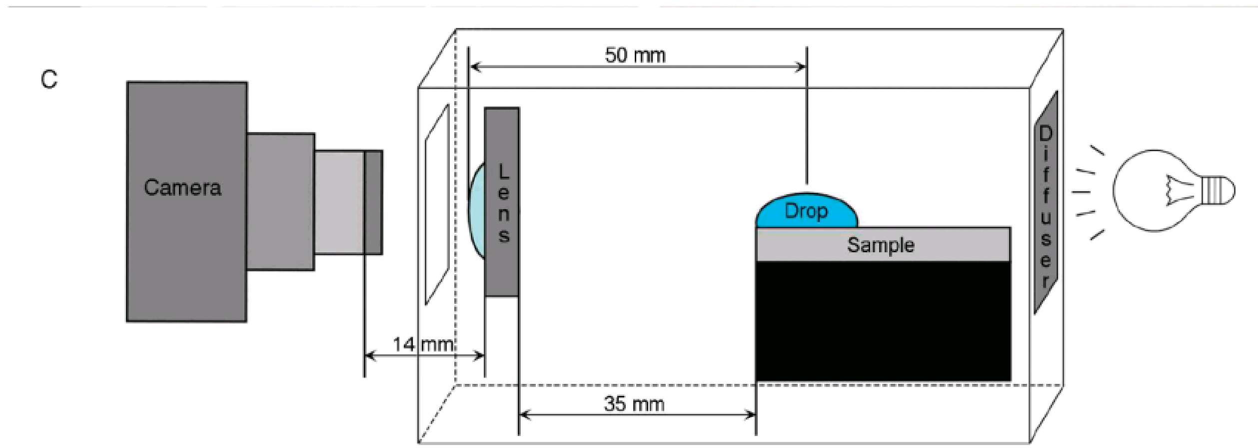
Wettability and contact angle

The contact angle measurement allows to evaluate the surface wettability, spreadability and adhesion.





How to increase the wettability?

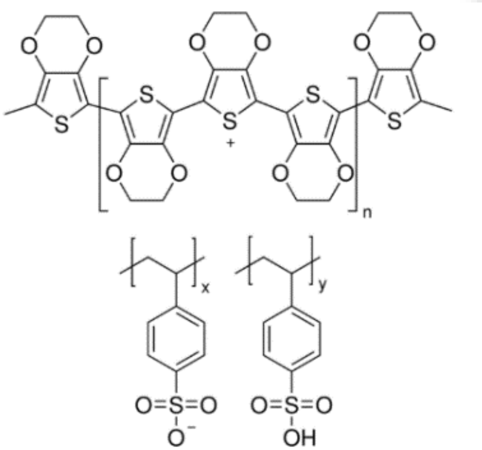
→ **Inks formulation**

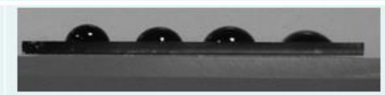
→ **Surface treatments**

- → **Plasma treatment**
- → **Chemical or mechanical induced roughening of the surface**
- → **Use of a primer (Silanization for example)**

Contact angle: the case of PEDOT:PSS on glass

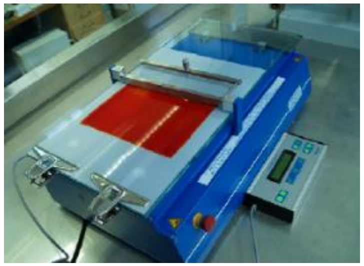
Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is a printable polymer commonly used in organic electronics for several application: as conductive electrode or hole transporting material in solar cells and OLED, for printed RFID tags, as component for sensor, for RF shielding. It has several formulation, in terms of additive used in the solution that allow to change its properties and in general can be purchased in water based suspensions



UV	70°	
Plasma	<20°	No plasma Plasma treated 
VPAI +0.1%HEX	38°	
HCV4	>90°	
HCV4+5%DMSO	90°	
HCV4+5%DMSO +0.1%hexafor	60°	
CPP105D+5%DMSO	**30°**	

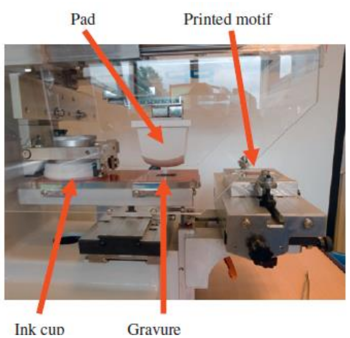
Large area coating techniques

There is a huge amount of film-forming techniques, and each of it can have specific characteristic and can be applied to the realization of printed electronic device



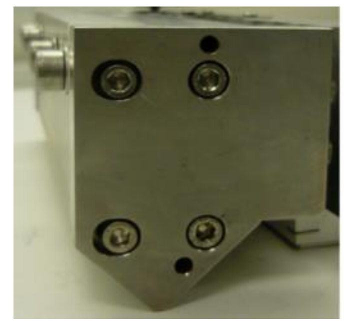
SCREEN-PRINTING

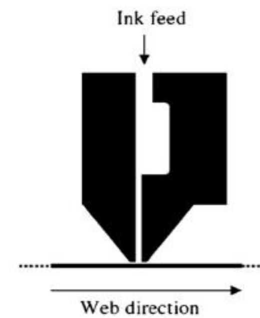
DOCTOR BLADING



PAD-PRINTING

SLOT-DIE





SPRAY-COATING

INK-JET PRINTING

F.C. Krebs / Solar Energy Materials & Solar Cells 93 (2009) 394–412

Y. Galagan et al. Adv. Eng. Mater. 2018, 1701190

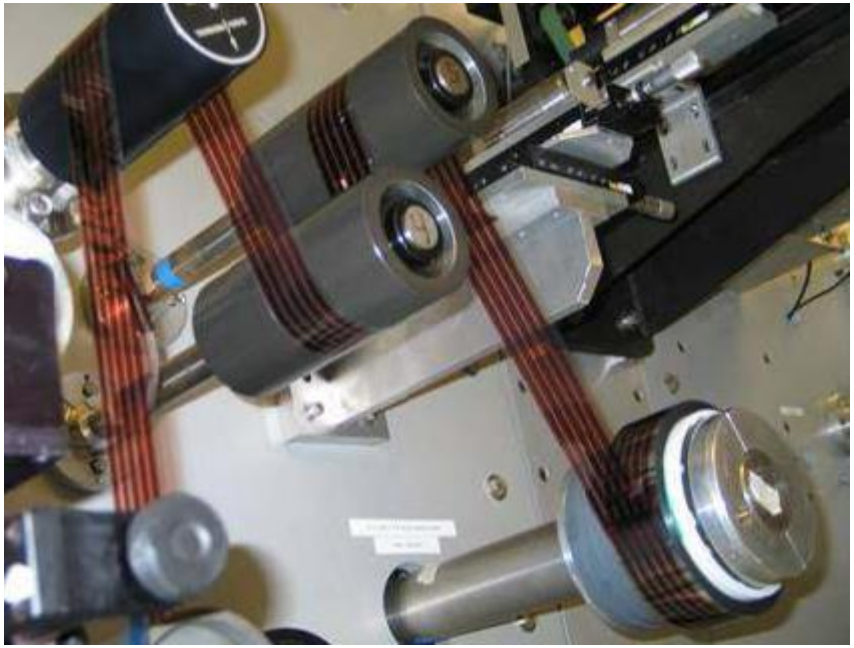
Lab scale vs high volume processing

Typically on lab scale small substrates are used → Mostly used techniques are: spin coating, doctor blading, casting

On large scale, a roll-to-roll coating, in which the substrate can be imagined as a continuous roll of material on which the different substrates are deposited, is currently under development.

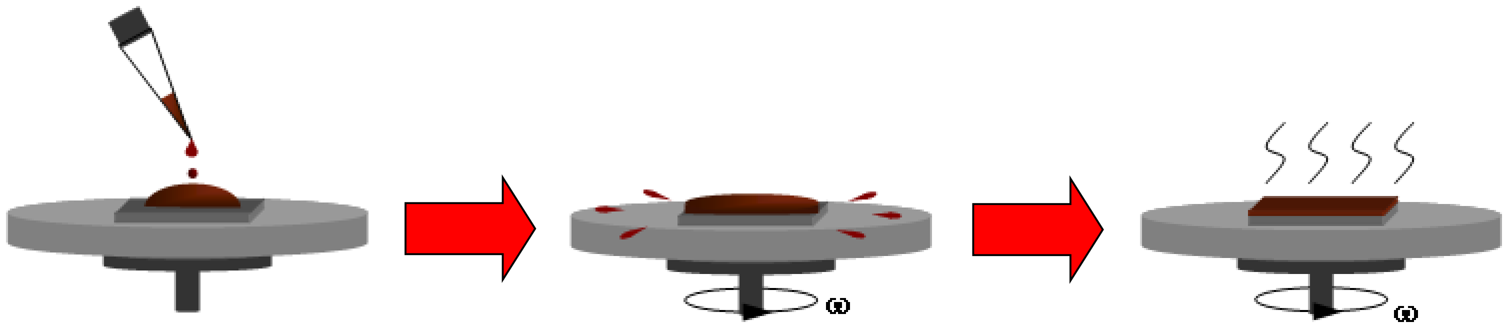
The ideal process on large area

- Solution processing of all layers on flexible substrates controlling the film thickness, uniformity and shape
- Few coating and printing steps, high speed
- Small amount of materials
- Free from costly indium, toxic solvents and chemicals
- Low environmental impact and a high degree of recyclability.
- Low costs



Spin coating

This is a batch deposition technique, used typically in lab to test new materials for several type of printable devices (solar cells, photodetectors, OLED, OTFT, sensors



First step
material deposition

Second step (spin-up)
ramp acceleration

Third step
costant rotation speed
(film levelling, solvent evaporation)

$$d = k\omega^{\alpha}$$

ω = rotation speed

K and α = empirical constants that depend on the physical properties of the solvent (viscosity, volatility and diffusivity), of the solute (molecular weight) and of the concentration of the solute

K. Norrman, A. Ghanbari-Siahkali, N.B. Larsen, Rep. Prog. Chem. Sect. C 101 (2005) 174–201.

Spin coating

Advantages:

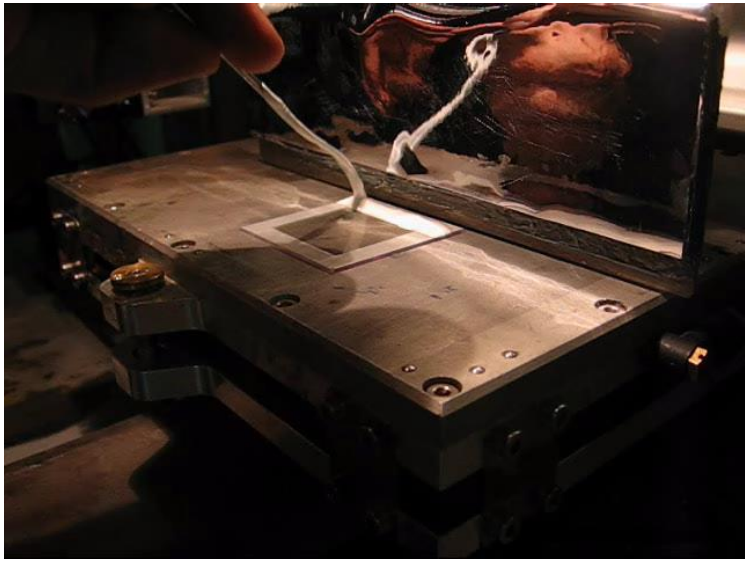
- **Highly reproducible films homogeneous on large area (max dim. 1,5m x 1,5)**
- **Well established coating technique**

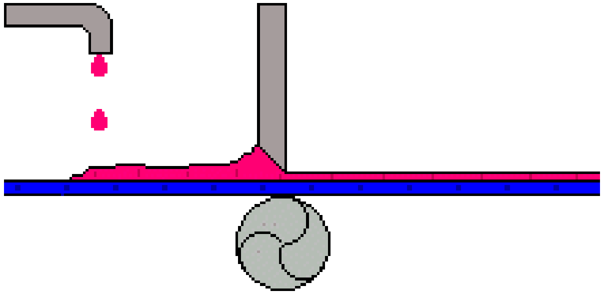
Disadvantages:

- **High waste of materials**
- **Serial technique for which each substrate have to be handled separately**
- **No patterning allowed**

Good on lab scale to optimize devices and materials

Blade Coating





The doctor blade technique is widely used in laboratory fabrication due to its simplicity.This process relies on a coating being applied to the substrate which then passes through a 'gap' between a moving or fixed 'knife' and a fixed or moving support. As the coating and substrate pass through, the excess is scraped off. This process can be used for high viscosity coatings and very high coat weights. There are innumerable variants of the relatively simple process which is rugged, hard-working and somewhat inaccurate.

Doctor blading

$$d = \frac{1}{2}\left(g\,\frac{c}{\rho}\right)$$

g= gap distance

c= concentration of the solid material

ρ=density of the material in the final film

The final thickness of film depends on:

- **The gap between the blade and the film**
- **The concentration of the solid material, density of the material**
- **Surface energy**
- **Surface tension of the coating solution**
- **Meniscus formed between the blade and the wet film**

F.C. Krebs / Solar Energy Materials & Solar Cells 93 (2009) 394–412

Doctor blading

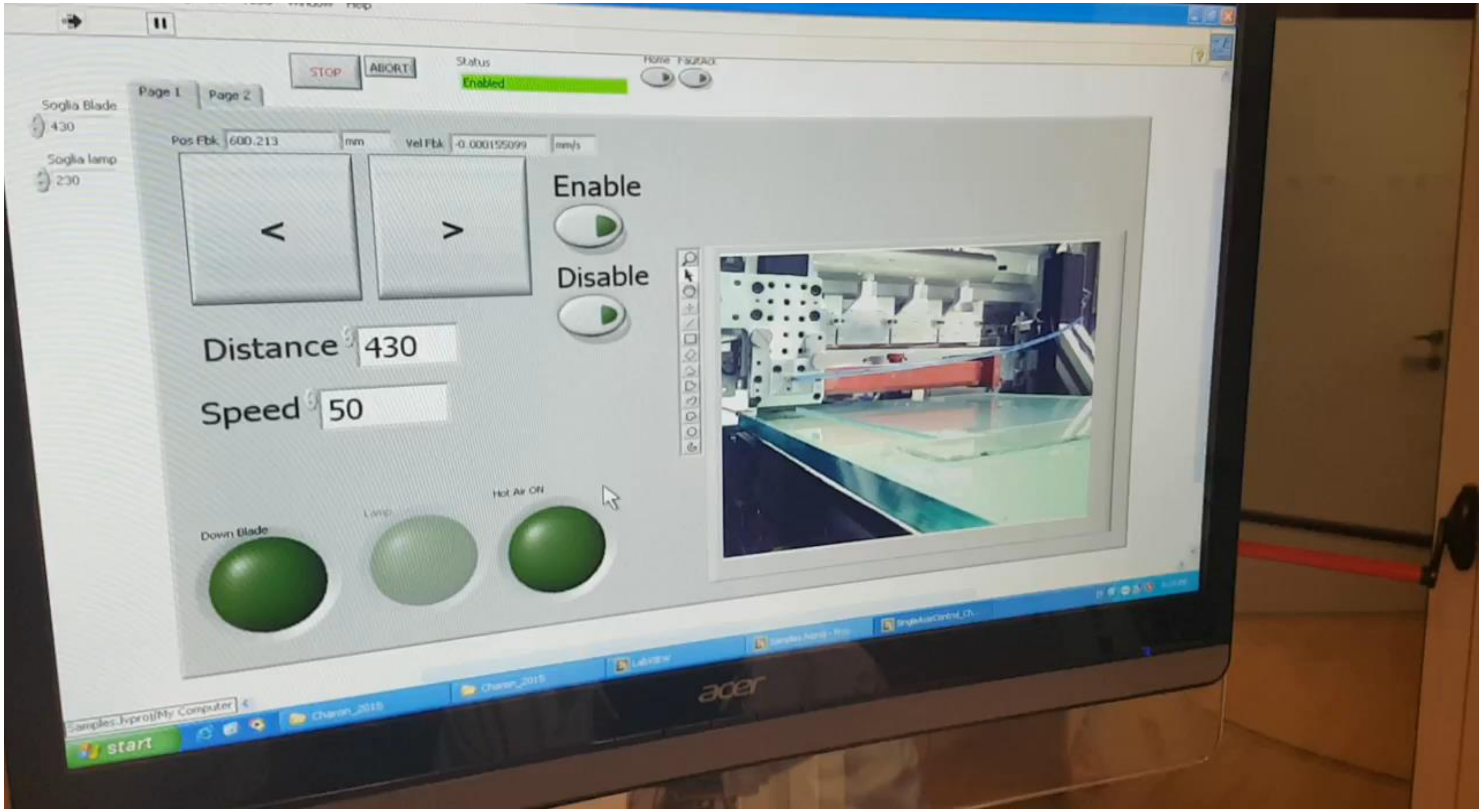
<u>**Advantages:**</u>

- **Simple technique**
- **Less waste of material respect to spin coating (< 5%)**
- **No degradation of the multilayer organisation occurs with successive depositions**
- **Possible application to R2R process in his knife over edge configuration**

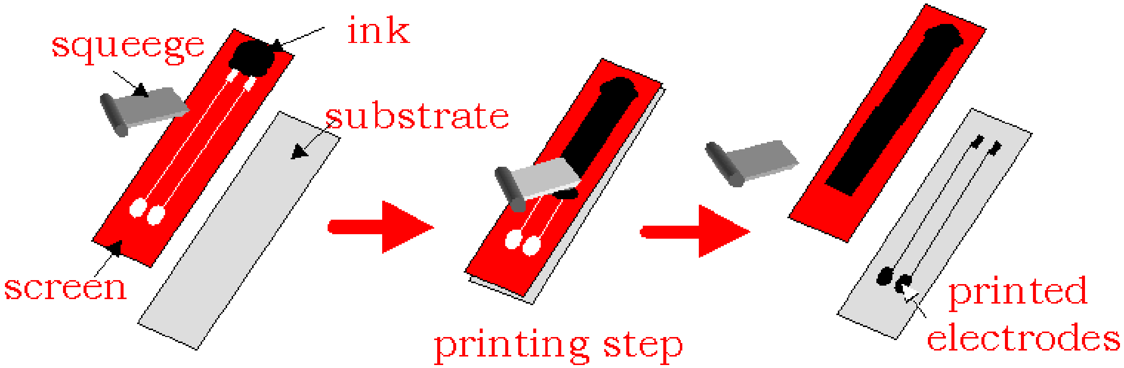
<u>**Disadvantages:**</u>

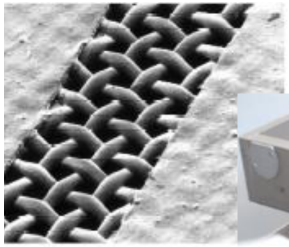
- **Slow technique**
- **Problems with the crystallization of the material during the deposition**
- **No patterning allowed**

Blade Coating



Screen Printing





Step 1 - Preparing the screen

A fine fabric mesh is coated with a photosensitive emulsion. The mesh is stretched over a frame.

Step 2 - Creating the stencil

The positive films are laid directly on top of the mesh. Ultraviolet light is shown onto the assembly. Where there is an image on the positive film, no light gets through to the emulsion on the screening assembly beneath, leaving it unexposed. Where the film is clear, the light passes through and hits the emulsion, causing it to harden. When the development process is complete, the unexposed, soft areas of emulsion are washed away, leaving only the porous fabric mesh.

Step 3 - Printing

The stencil is placed directly on top of the item that will receive the ink. Ink is poured on top of the stencil, and a squeegee is scraped over the top, forcing ink through the image area of the stencil, and onto the printable surface.

Step 4 - Drying

It is typical that the ink will be cured thermally or with ultraviolet light, so that subsequent layers can be applied without difficulty, and so that printed items can be stacked on top of each other immediately.

Screen Printing

Parameters:

- **Ink:**
  - **High Viscosity**
  - **Surface tension**
  - **Low volatility**
- **Squeegee:**
  - **Hardness**
  - **Speed**
  - **Pressure**
- **Screen:**
  - **Nominal thread diameter**
  - **Mesh count**
  - **Open area**

Film thickness

$$d = V_{screen} k_p \frac{c}{\rho}$$

V_{screen}=theoretical paste volume of the screen

k_p= pick-out ratio

c=concentration of the solid material

ρ=density of the material in the final film

F.C. Krebs / Solar Energy Materials & Solar Cells 93 (2009) 394–412

Screen Printing

Advantages:

- **Applicable for any soluble or dispersible polymer**
- **Smooth areas possible (<5 nm deviation)**
- **Large areas possible (up to 1 m^2)**
- **Low cost equipment**
- **Proceeds at ambient temperatures**
- **Almost no loss of material during the deposition**

Disadvantages

- **Batch operated (semi-continuous process)**
- **Screens have to be cleaned often**
- **Ink on the screen can pick up contamination**
- **Many parameters for tuning layer thickness and smoothness**

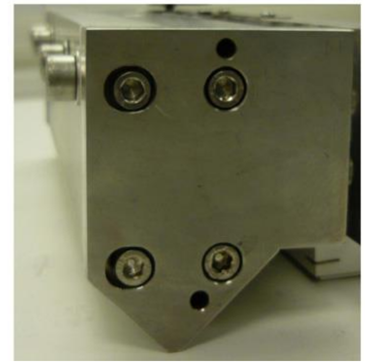
Screen Printing

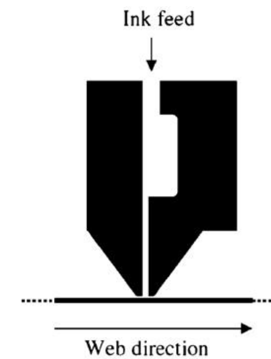
Slot-die Coating

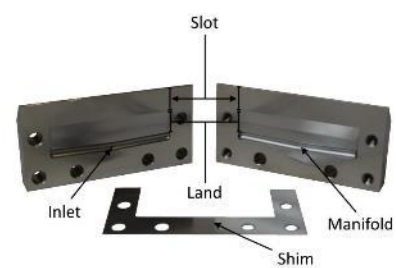
The slot-die coating is a **contact printing technique** where the slot head allows, thanks to the specific design of the internal mask, the deposition of patterns with several line dimension.

$$d = \frac{f}{S\,w} \cdot \frac{c}{\rho}$$

- d= thickness (cm),
- f= flowrate (cm^3 min^{-1}),
- S=web speed (cm min^{-1})
- w= coated width (cm)
- c= solid content in the inking (cm^{-3})
- R=density of the dried ink material (g cm^{-3})







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Slot-die Coating

Advantages:

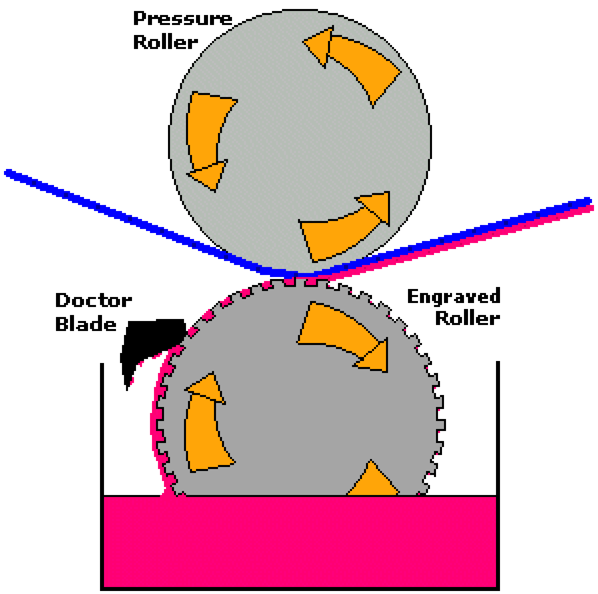
- **Applicable for any soluble or dispersible polymer with low viscosity**
- **Smooth areas possible (<5 nm deviation)**
- **Large areas possible (up to 1 m^2)**
- **Proceeds at ambient temperatures**
- **Almost no loss of material during the deposition**
- **Thicknesses up to 50 microns**
- **Easy in changing the pattern**

Disadvantages

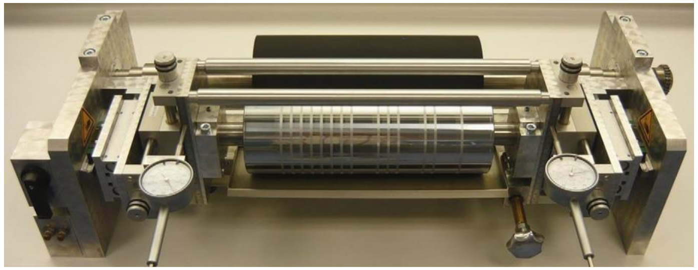
- **Design of the head is very complex**
- **Meniscus has to be controlled very carefully**
- **Many parameters for tuning layer thickness and smoothness**

Gravure printing

Rotogravure (**roto** or **gravure** for short) is a type of printing process, which involves engraving the image onto an image carrier, which in this case is a cylinder. It uses a rotary printing process.



Gravure coating



One printing unit consists of the following components:

- **an engraved cylinder (also known as "gravure cylinder") whose circumference can differ according to the layout of the product being made.**
- **an ink fountain**
- **a doctor blade assembly**
- **an impression roller**
- **a dryer**

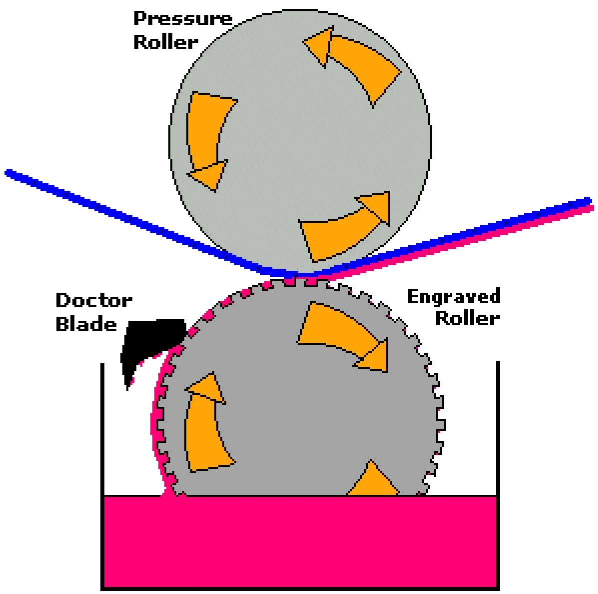
Gravure printing

Advantages:

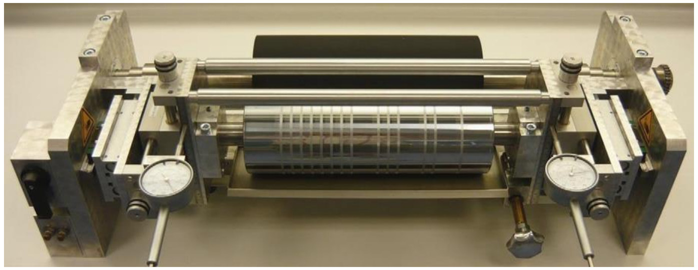
- printing cylinders that can last through large-volume runs without the image degrading
- good quality image reproduction
- low per-unit costs running high volume production

Disadvantages

- high start-up costs: hundreds of thousands of copies needed to make it profitable
- rasterized lines and texts
- long lead time for cylinder preparation, which is offsite as the techniques used are so specialized



Gravure coating



Inkjet printing

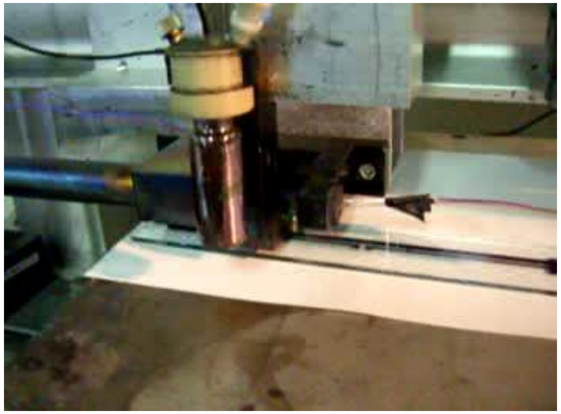
$$d = N_d V_d \frac{c}{\rho}$$

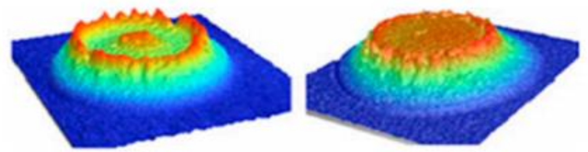
N_d= Number of droplets

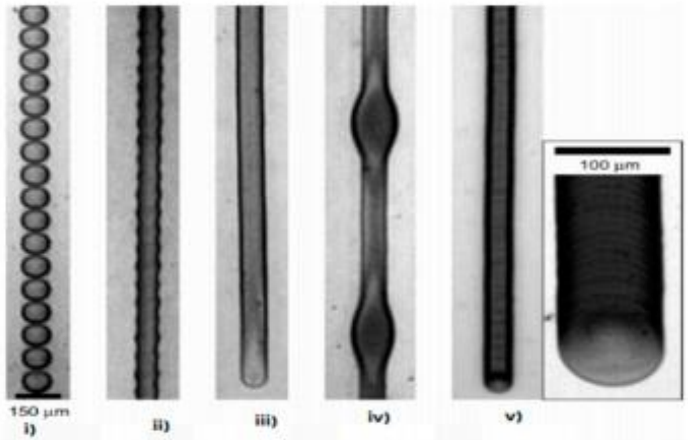
V_d= Droplets volume

c=concentration of the solid material

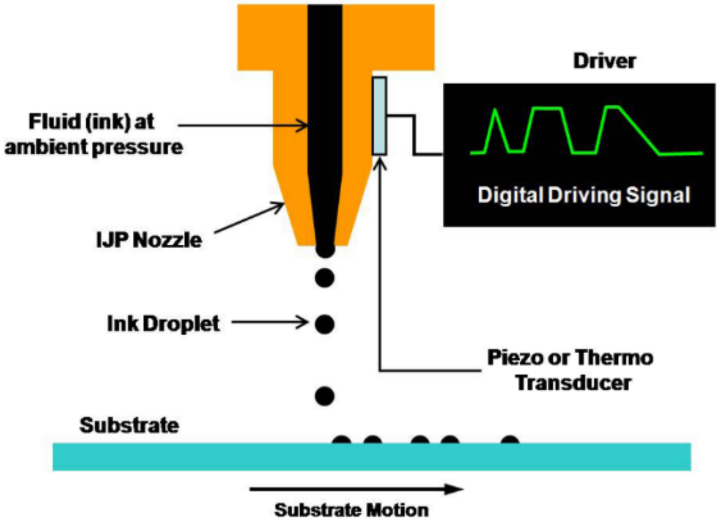
ρ=density of the material in the final film







Inkjet printing



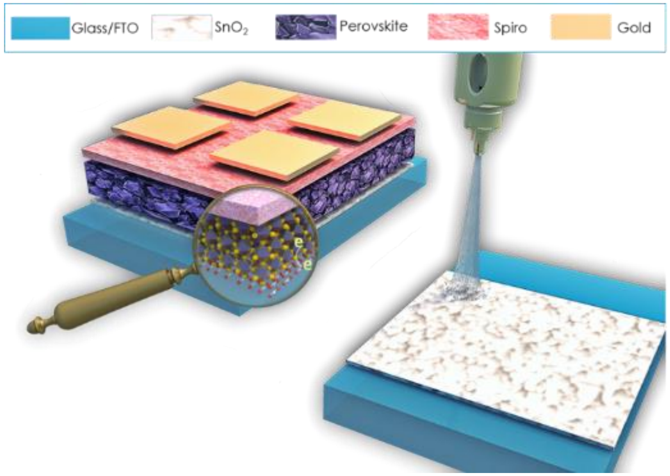
S. Sumaiya et al. Technologies 2017, 5, 53; doi:10.3390/technologies5030053

Inkjet printing

S. Sumaiya et al. Technologies 2017, 5, 53; doi:10.3390/technologies5030053

Spray-coating technique

Commercial Airbrush



ADVANTAGES

- **Solution processing → Low-cost deposition**
- **Large Area deposition** suitable also for **flexible** substrates with **different morphologies**
- **Fluid waste reduced** respect to spin-coating
- **Easy to use**

ISSUES

- **Film control →** thickness, uniformity and roughness
- **Many process-variables to be controlled**

Spray-Coating parameters

Instrument variables

Nozzle Aperture(AP): Nozzle opening radius

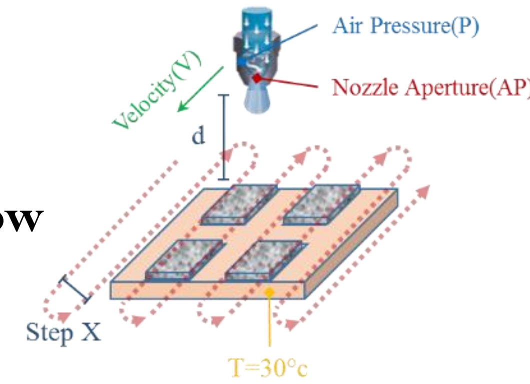
d : Distance between Spray nozzle and substrate

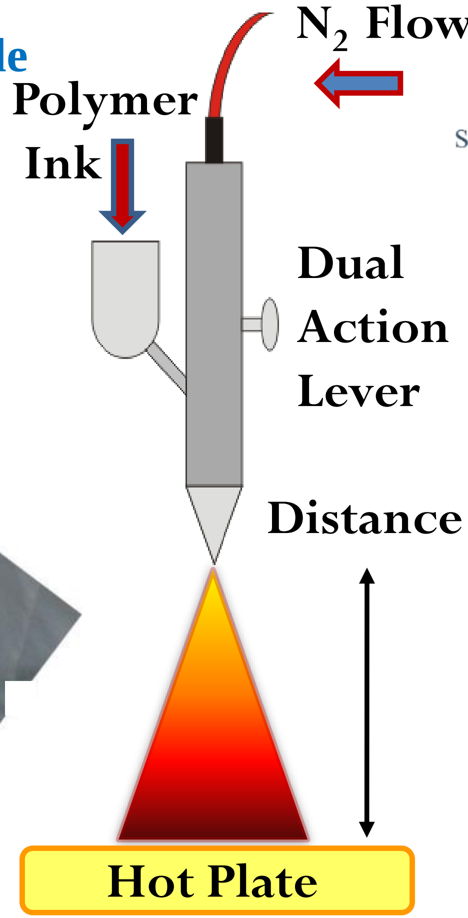
Air Pressure(P) : Air pressure inside the nozzle

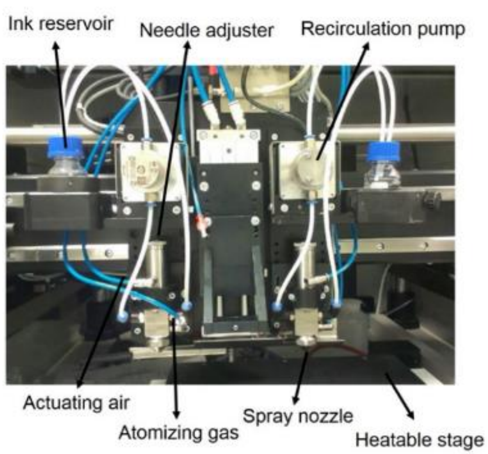
Velocity(V) : speed of nozzle X Y movements

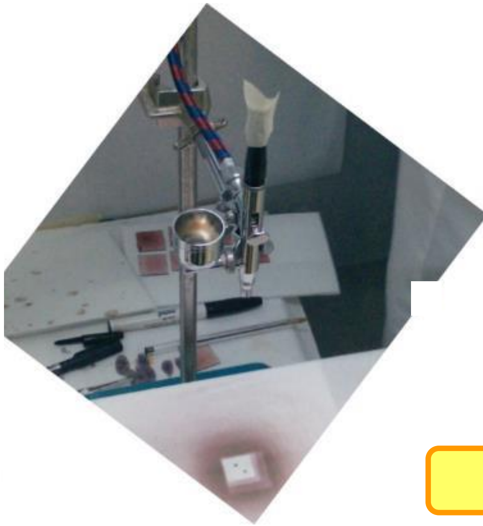
T=30°c : Substrate temperature

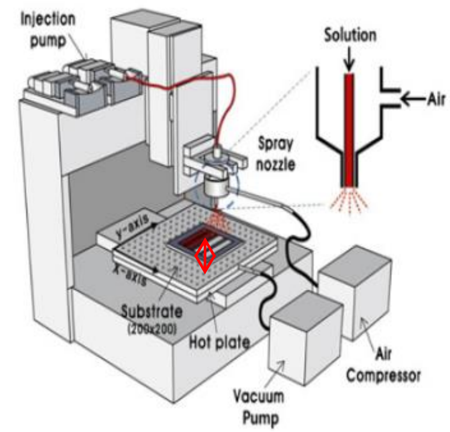
Flow rate (FR): Flow rate of solution









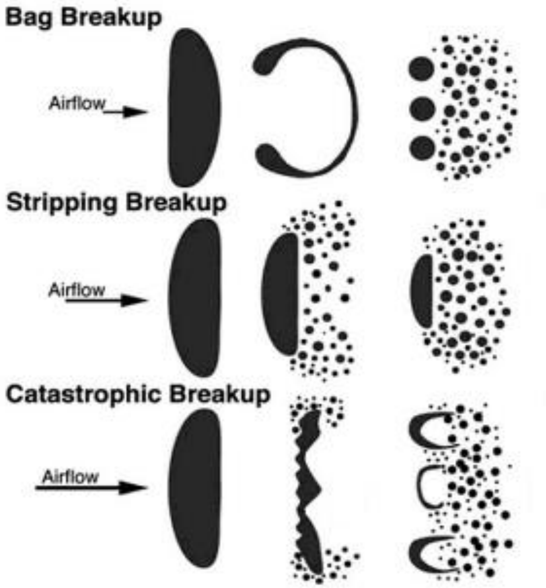


Atomization

For low-viscosity liquids, the deformation of the drop is primarily determined by the Weber number (W_e), a dimensionless parameter representing the ratio of the aerodynamic forces and the stabilizing surface tension:

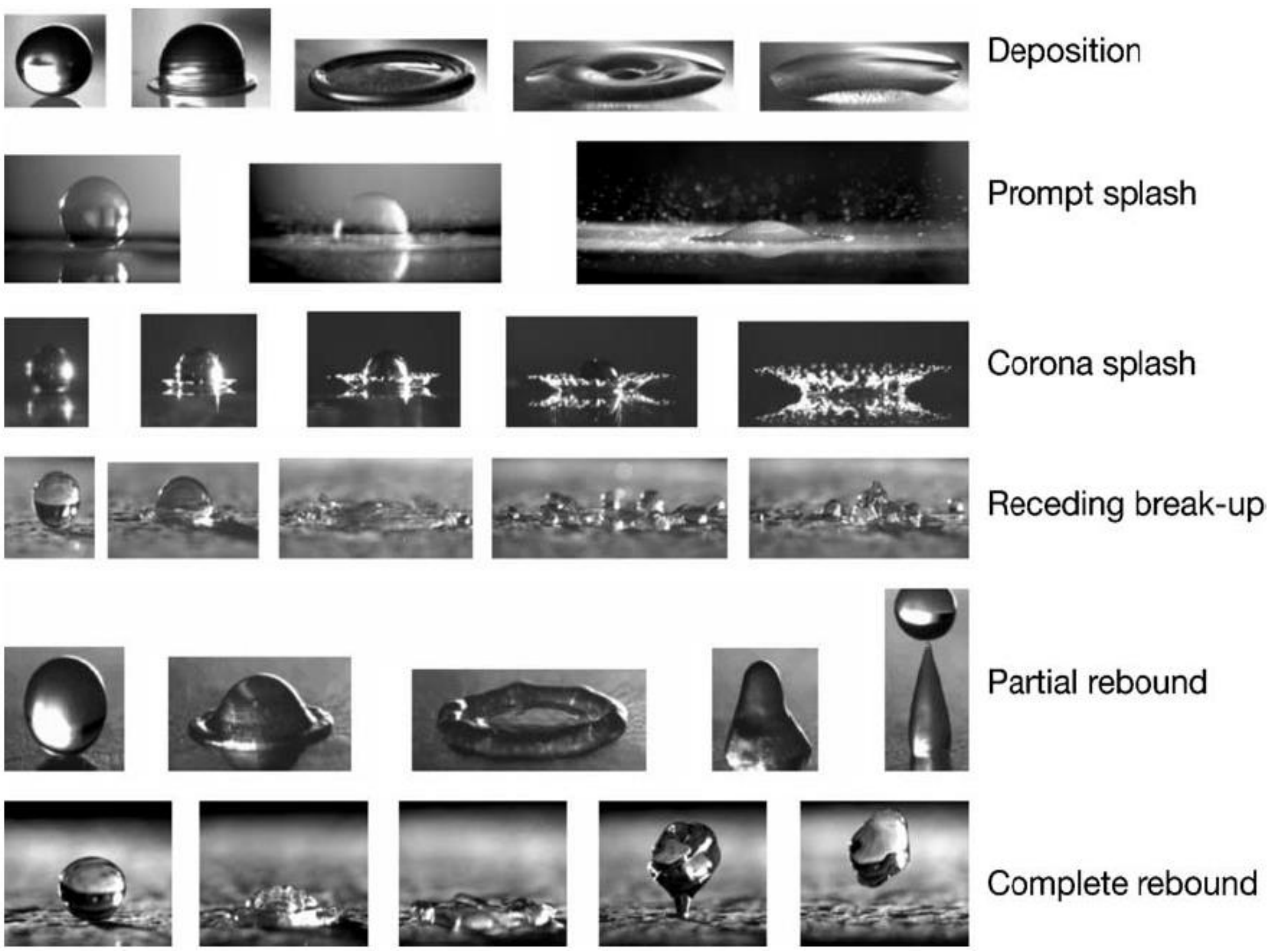
$$W_e = (\rho V^2 D)/\sigma$$

where ρ is the gas density (kg/m^3), V is the initial relative velocity between the gas and the liquid (m/s), D is the initial diameter of the drop (m) and σ is the surface tension of the drop (N/m). The higher the Weber number, the larger are the deforming external pressures forces (resulting in droplet breakup) compared with the reforming surface tension forces, aiming at droplet aggregation.



- **Bag → $12<W_e<100$**
- **Stripping (or shear) → $100<W_e<350$**
- **Catastrophic → $W_e>350$**

Drop impact


Deposition
Prompt splash
Corona splash
Receding break-up
Partial rebound
Complete rebound

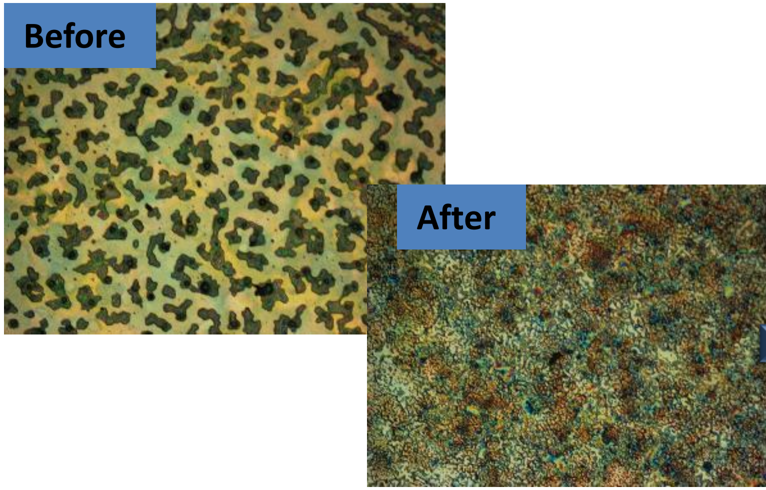
Drop impact

An increase of	Deposition	Prompt splash	Receding breakup	Complete rebound	Corona splash	Partial rebound
V	↓	↑	↑		↑	↑
D	↓	↑				
σ		↓	↑	↑	↓	↑
μ	↑	↓	↓		↓	
R_a	↓	↑			↓	
R_w		↓				
$\theta_{rec.}$			↑	↑		↑

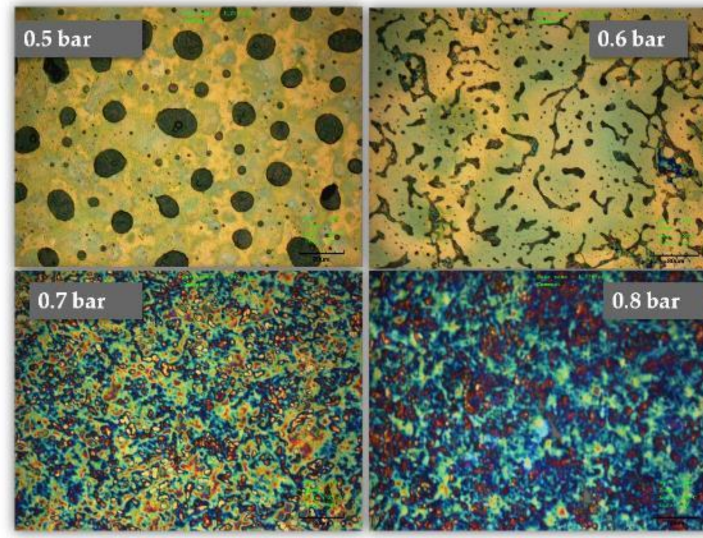
The parameters that affect the outcome of the drop are listed in Table: in addition to the impact velocity (V), the drop size (D), the surface tension (σ) and the viscosity (μ) included in Weber and Ohnesorge numbers, the surface roughness and wettability are also considered through the roughness amplitude (R_a), the roughness wavelength (R_w) and the receding contact angle (Θ_{rec}).

PEDOT:PSS Spray coating

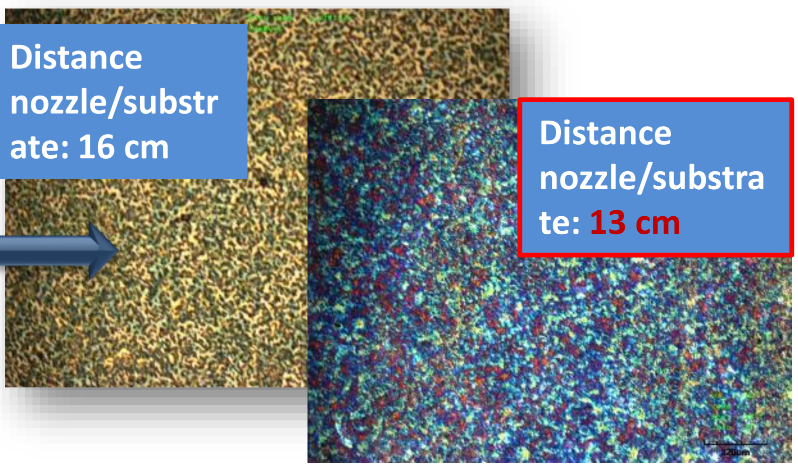
Variable Parameters: dilution, time of spray



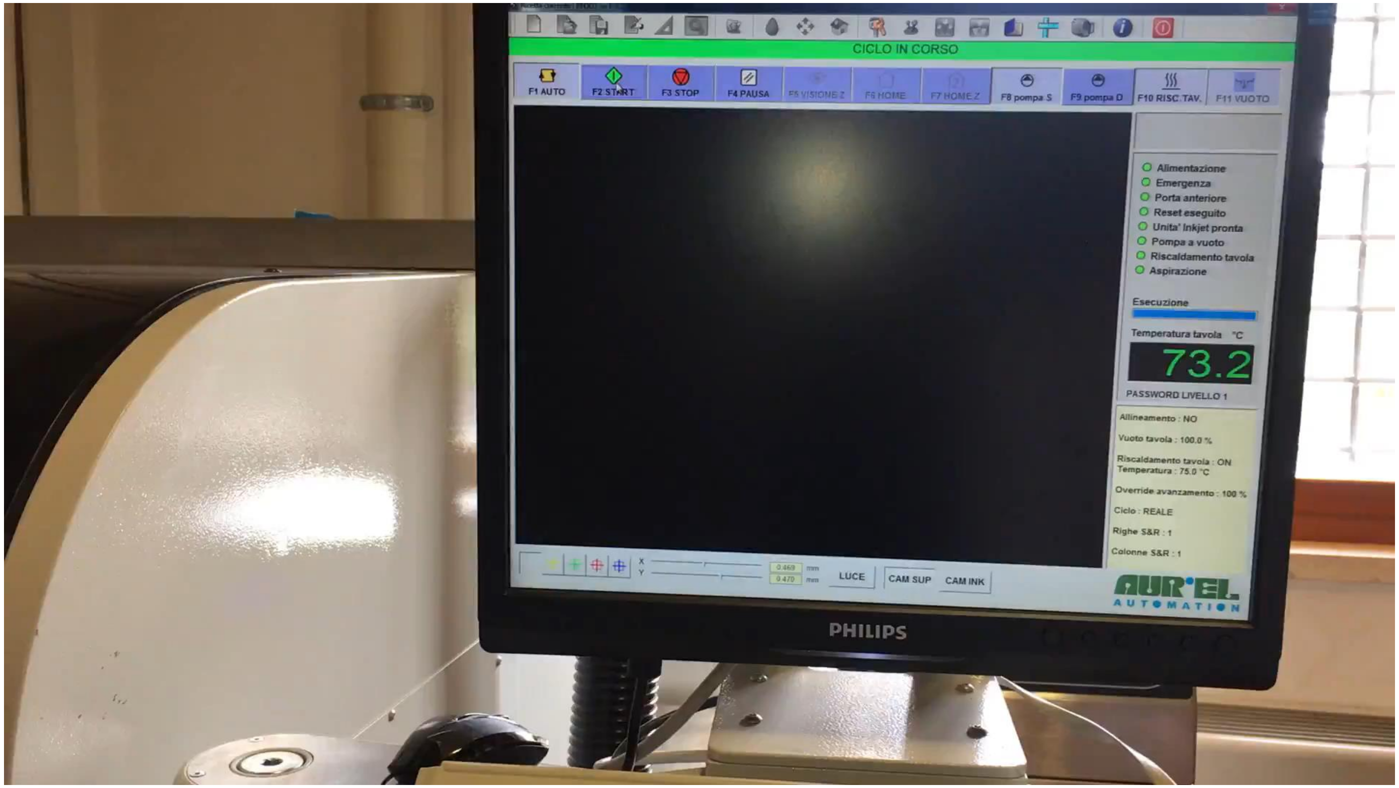
Variable Parameters: PRESSURE



Variable Parameters: distance from substrate



Large area spray coating



Comparison of the deposition techniques

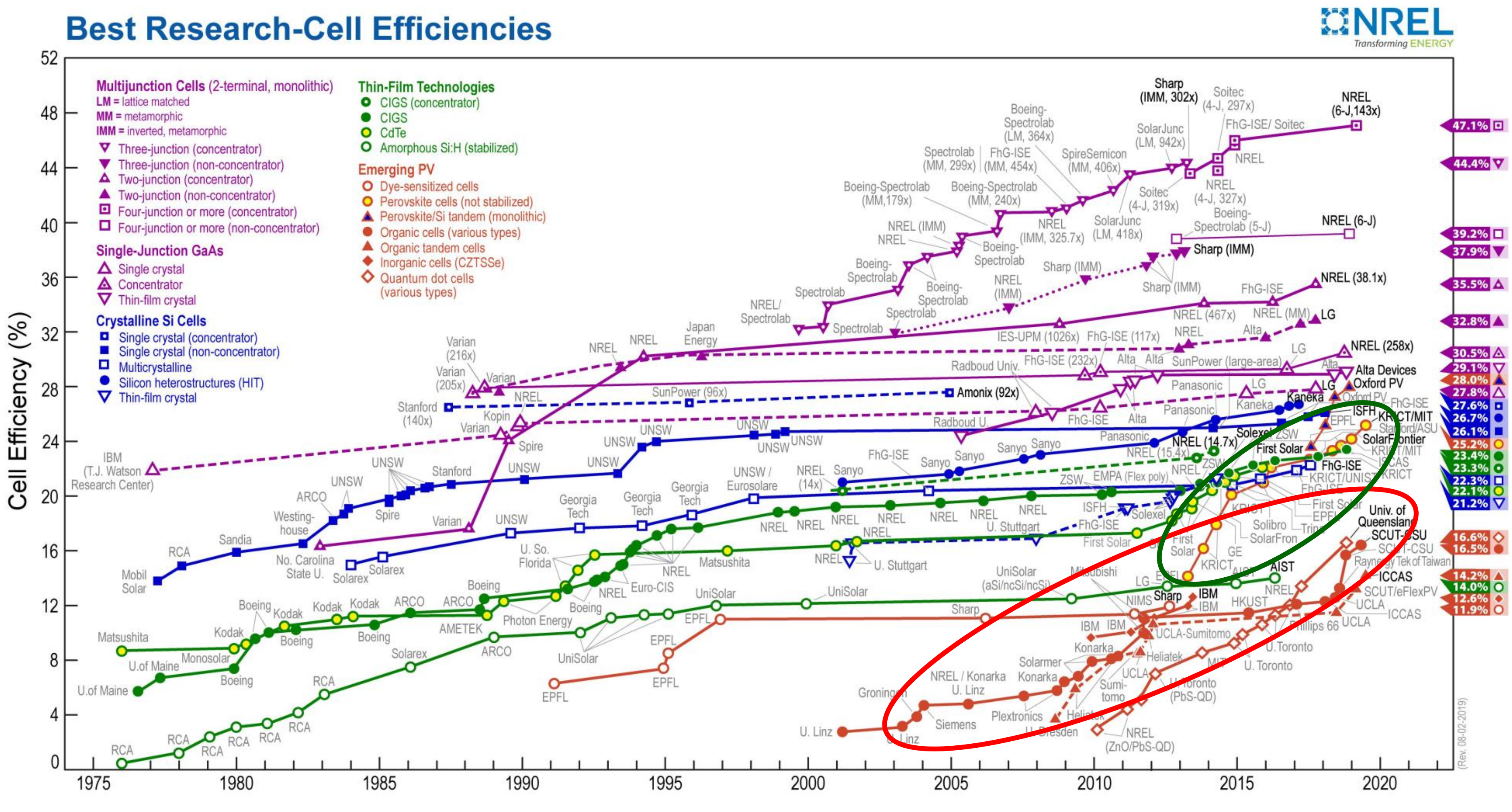
Technique	Ink waste	Pattern	Speed	Ink preparation	Ink viscosity (cP)	Wet thickness (μm)	R2R compatible
Spincoating	5	0	–	1	1	0–100	No
Doctor blade	2	0	–	1	1	0–100	Yes
Casting	1	0	–	2	1	5–500	No
Spraying	3	0	1–4	2	2–3	1–500	Yes
Knife-over-edge	1	0	2–4	2	3–5	20–700	Yes
Meniscus	1	0	3–4	1	1–3	5–500	Yes
Curtain	1	3	4–5	5	1–4	5–500	Yes
Slide	1	3	3–5	5	1–3	25–250	Yes
Slot-die	1	1	3–5	2	2–5	10–250	Yes
Screen	1	2	1–4	3	3–5	10–500	Yes
Ink jet	1	4	1–3	2	1	1–500	Yes
Gravure	1	2	3–5	4	1–3	5–80	Yes
Flexo	1	2	3–5	3	1–3	5–200	Yes
Pad	1	2	1–2	5	1	5–250	Yes

Ink waste: 1 (none), 2 (little), 3 (some), 4 (considerable), 5 (significant). Pattern: 0 (0-dimensional), 1 (1-dimensional), 2 (2-dimensional), 3 (pseudo/quasi 2/3-dimensional), 4 (digital master). Speed: 1 (very slow), 2 (slow $<1\,m\,min^{-1}$), 3 (medium $1–10\,m\,min^{-1}$), 4 (fast $10–100\,m\,min^{-1}$), 5 (very fast $100–1000\,m\,min^{-1}$). Ink preparation: 1 (simple), 2 (moderate), 3 (demanding), 4 (difficult), 5 (critical). Ink viscosity: 1 (very low <10 cP) 2 (low 10–100 cP), 3 (medium 100–1000 cP), 4 (high 1000–10,000 cP), 5 (very high 10,000–100,000 cP).

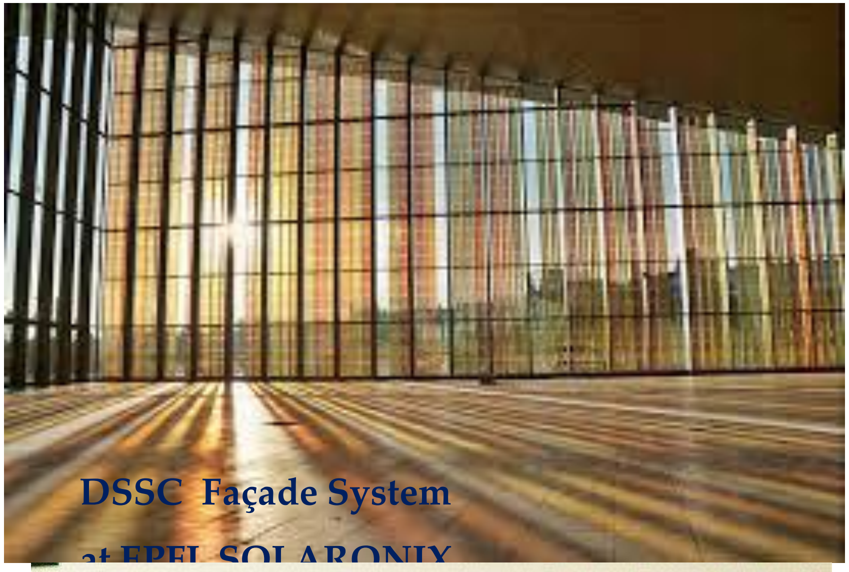
F.C. Krebs / Solar Energy Materials & Solar Cells 93 (2009) 394–412

Example 1: Printable solar cells and modules

Application: Solar cell realization

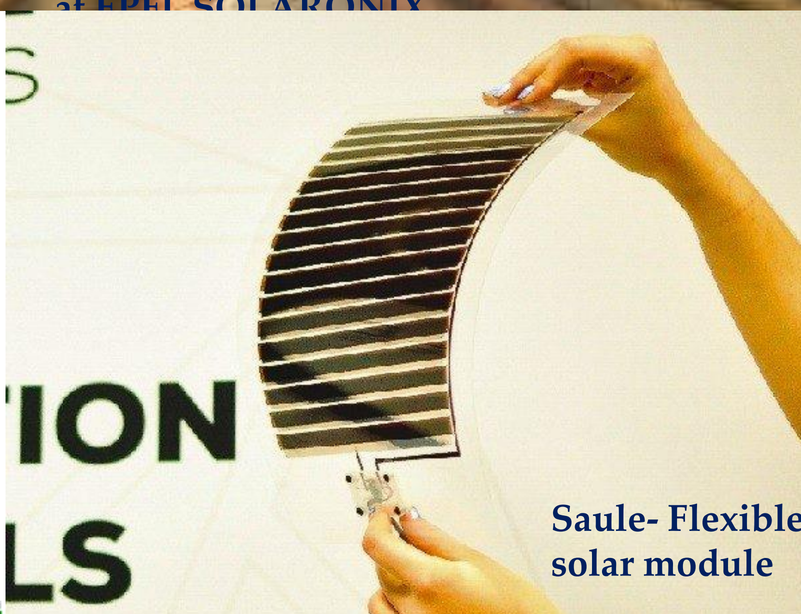


Solution processed Photovoltaic

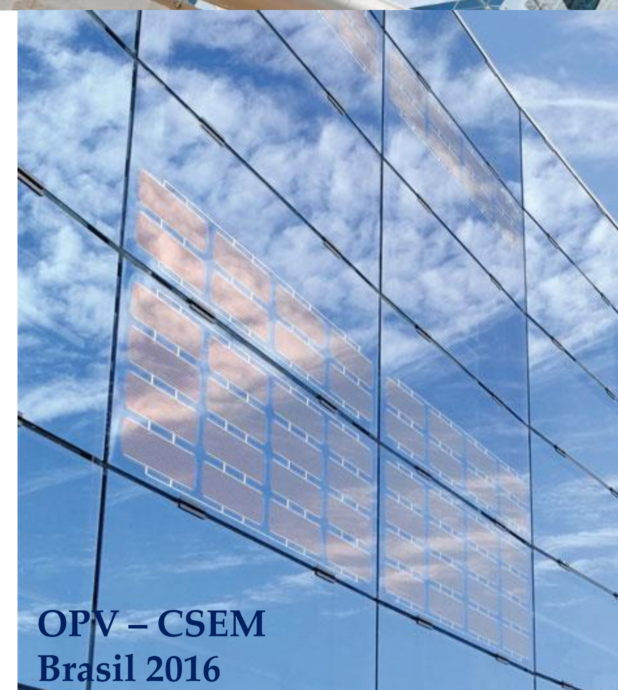


DSSC Façade System
at EPFL SOLARONIX

OPV -OPVius Expo
Milan 2015



Saule- Flexible Perovskite
solar module

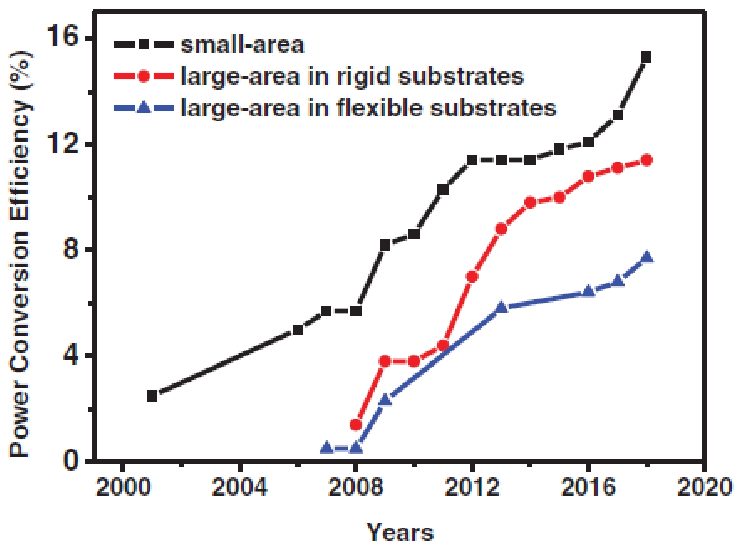


OPV – CSEM
Brasil 2016

State of the art OPV

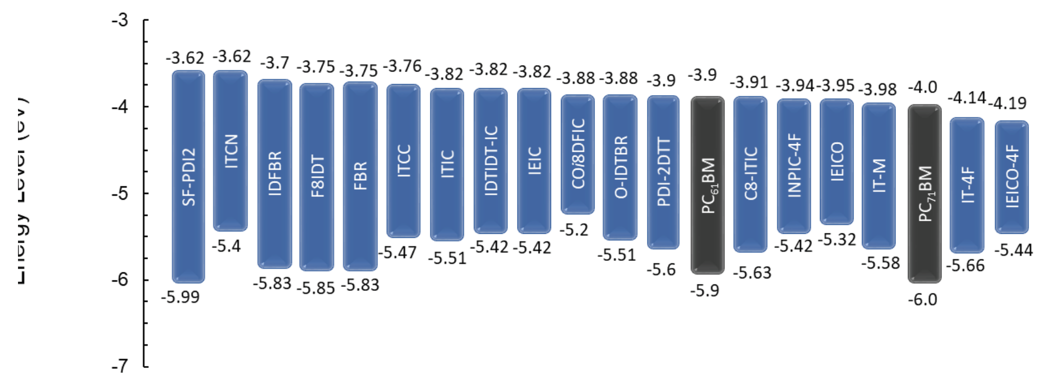
OPV has see in the last years a new rise in performances thanks to the introduction of plethora of new materials (nonfullerene acceptors and thick low bandgap donors)

In general for scalablity of the process, material requirements have been fulfilled both in terms of processability (thick active layer films for large-area printing) and safety (non hazardous solvents)

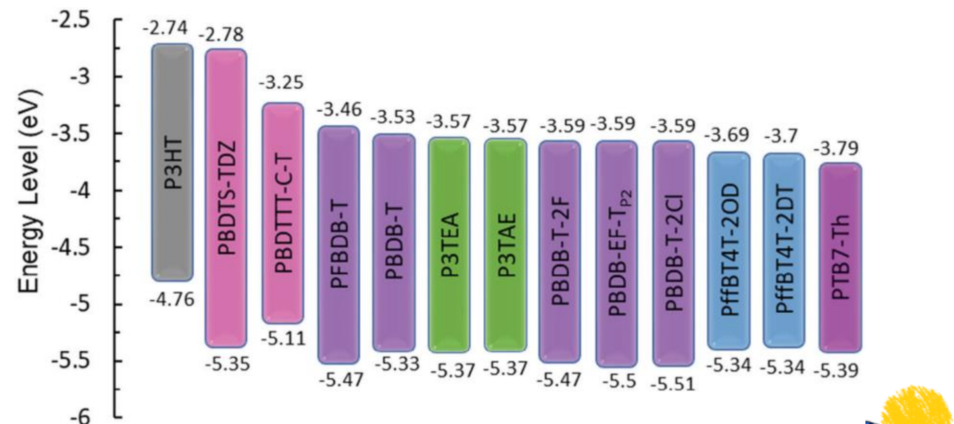


Wang et al. Adv. Mater. **2018**, 1805089

Record Efficiency with CB:DCB solvent mixture

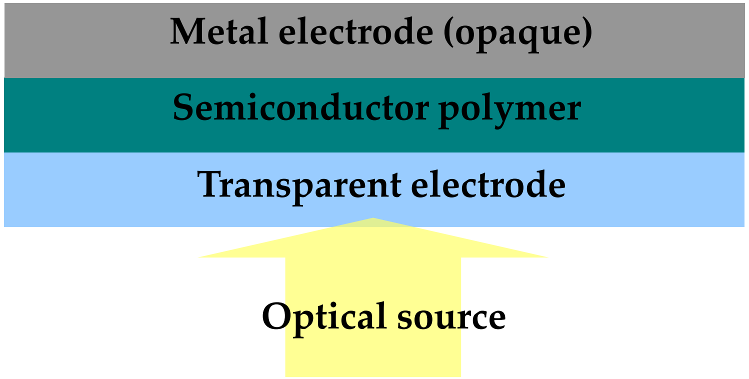


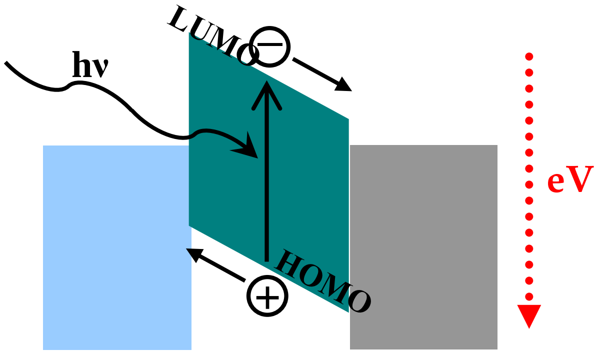
R. S Gurney *et al* 2019 *Rep. Prog. Phys.* **82** 036601



Single-layer

Single-layer device





Problem: insufficient photon-current conversion (efficiency ~ 0,1%)

a) polymers are amorphous

- "hopping" transport
- low mobility

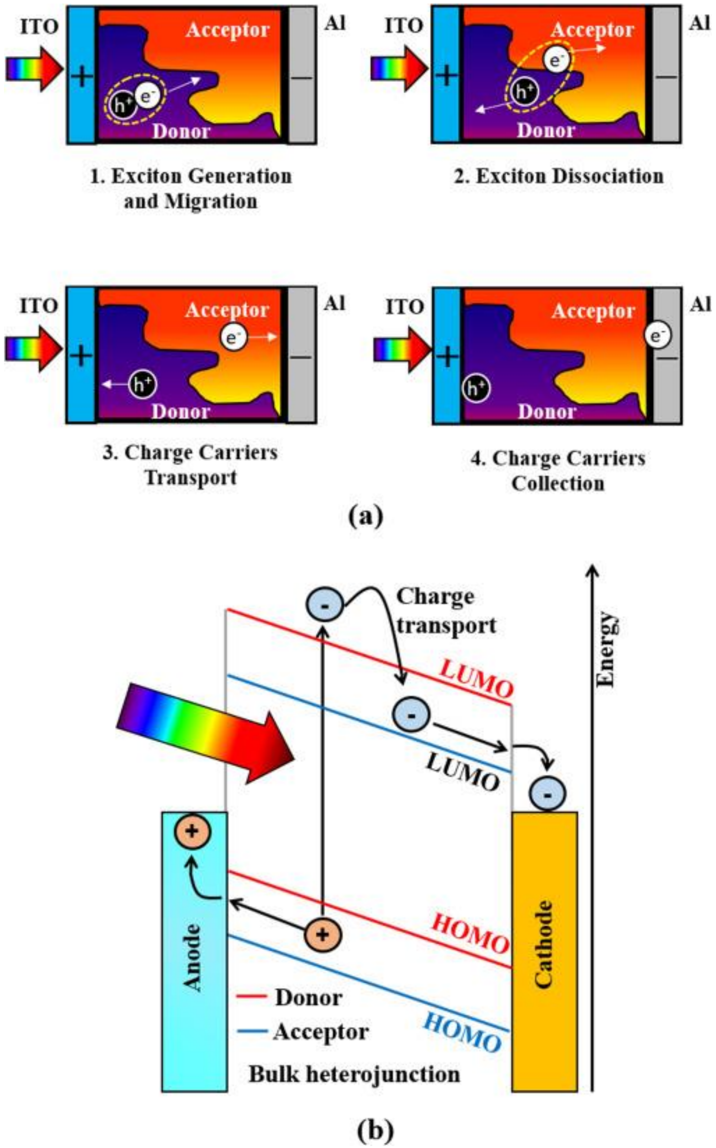
b) strong electrostatic interactions

- strong exciton bound
- high dissociation energies

c) exciton diffusion length ~10nm, but dissociation occurs at the interfaces (too far!)

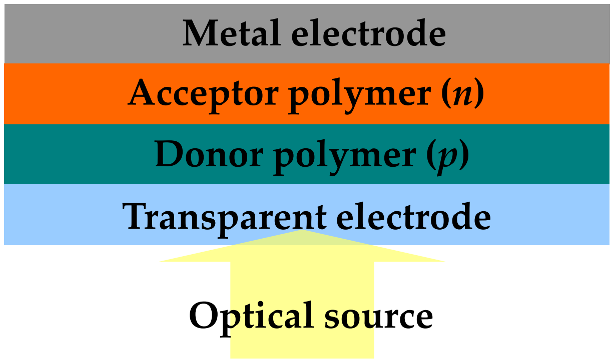
Single layer organic devices

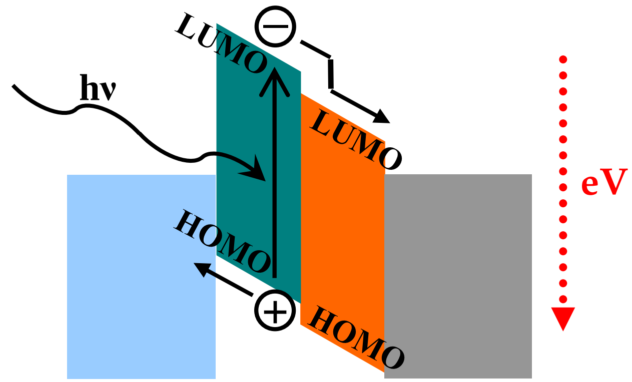
- Organic films between asymmetric contacts
- Light generates excitons, charge separation by exciton dissociation at interfaces
- Exciton diffusion length 1-10 nm, absorption depth >100 nm
- Photocurrent limited by exciton diffusion length
- Power efficiency η< 0.1%



Double-layer

Bi-layer device (heterojunction)





Use of two polymers, donor and acceptor (***p*** and ***n*** type) → better conversion efficiency (~1%)

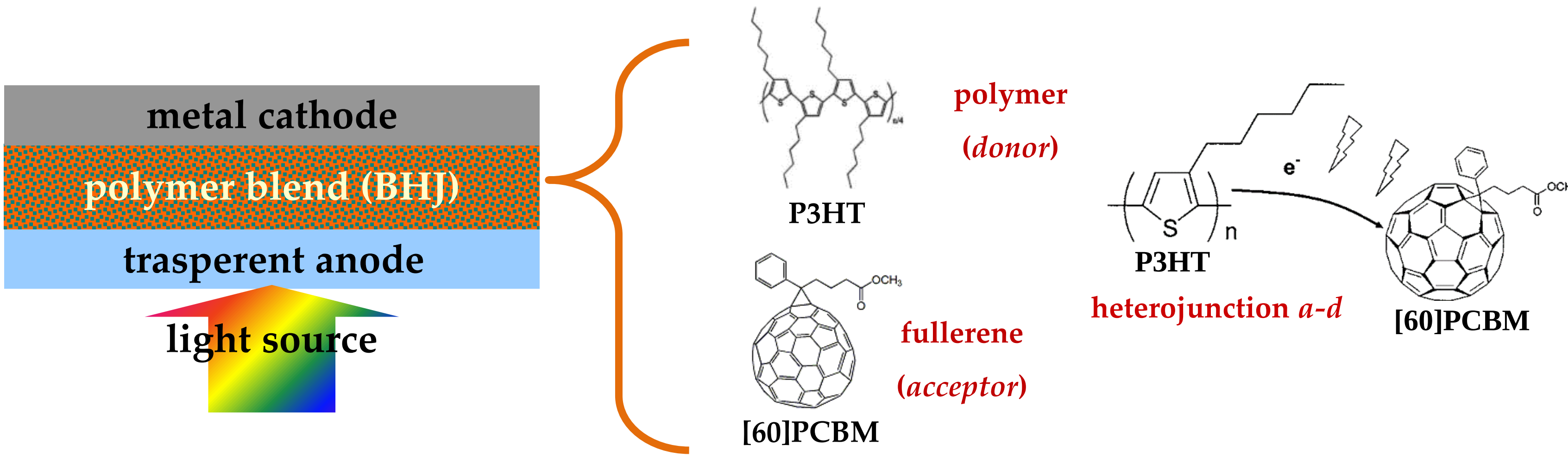
- photon absorption and exciton formation next to interface
- exciton dissociation favored by energetic levels

Remaining problems:

? higher series resistance

? solvent-crossing

Bulk-Heterojunction (BHJ) Device



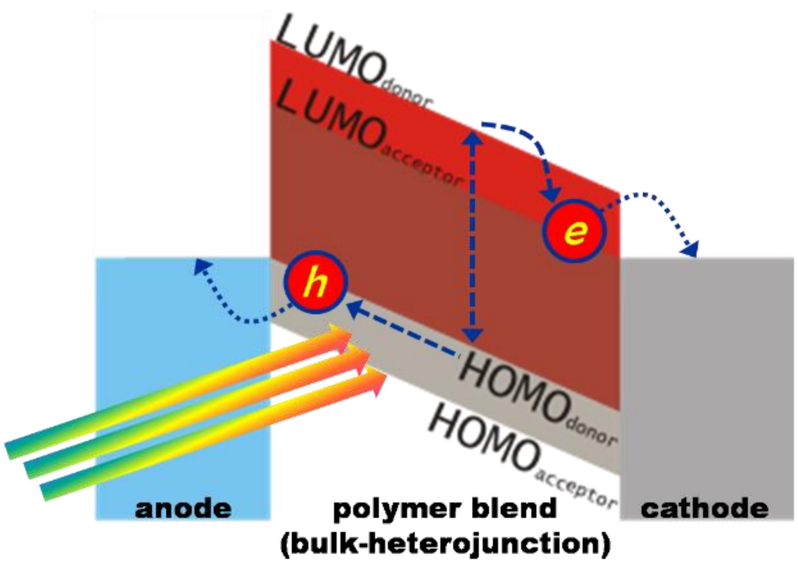
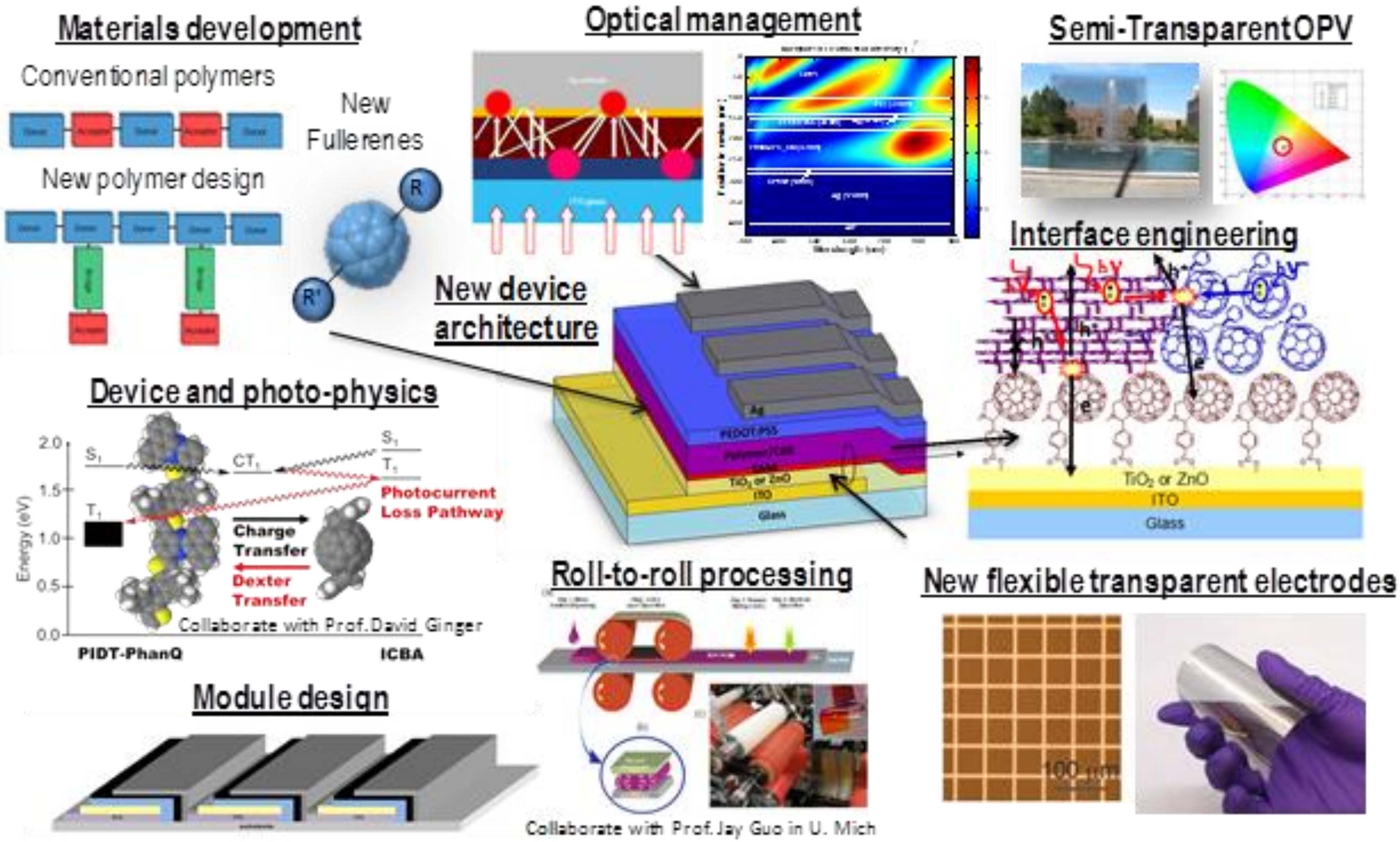


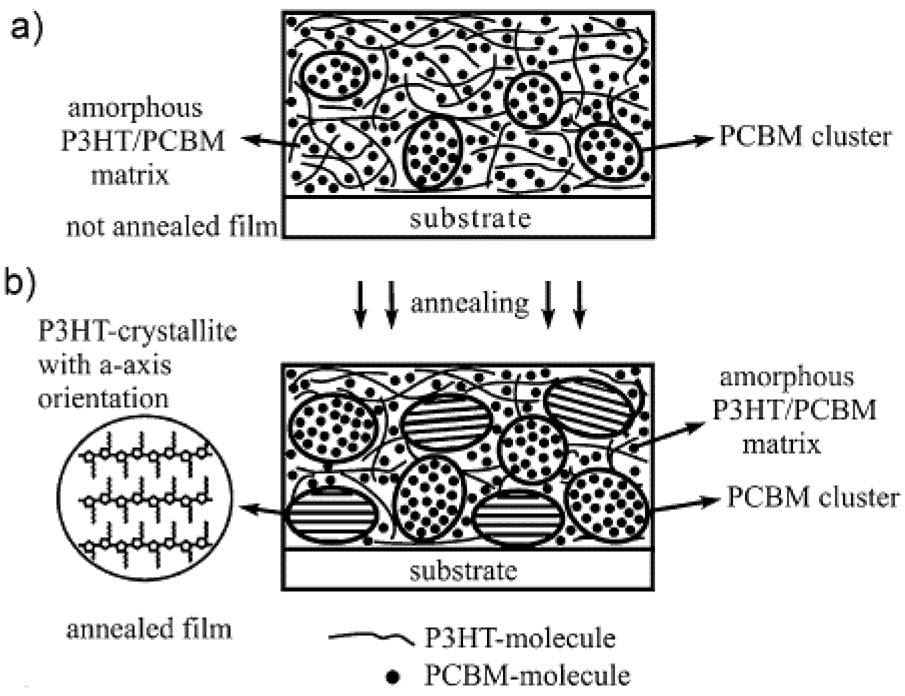
Photo-Voltaic effect in organic heterojunction:

1) Photon absorption
2) Exciton formation
3) Exciton diffusion to heterojunction *a-d* (acceptor-donor)
4) Exciton dissociation (electrons *"hop"* from $LUMO_{donor}$ to $LUMO_{acceptor}$)
5) Carriers transport towards electrodes
6) Harvesting of carriers at electrodes

How get OPV with good preformances?



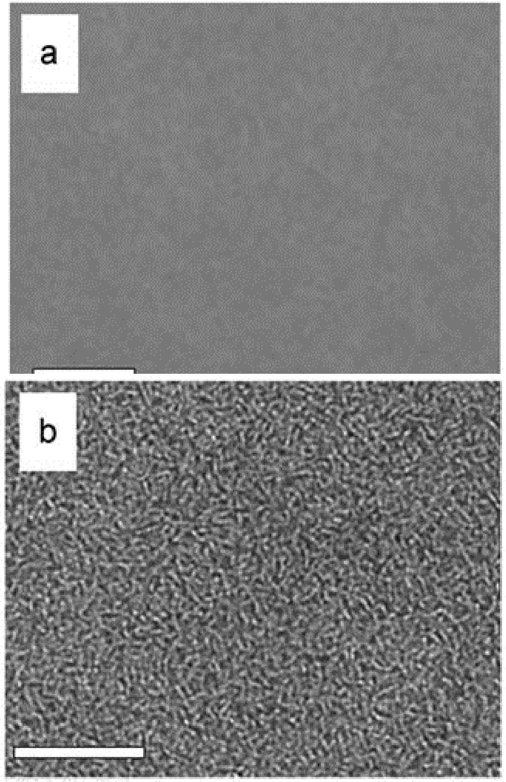
Morphology



a,b) Schematic pictures showing the microscopic process during annealing. c) Grazing incidence X-ray spectrum on a blend before and after annealing, showing the evolution of the a-axis oriented P3HT crystals.

Dennler et al., *Adv. Mater.*, 2009, 21, 1–16

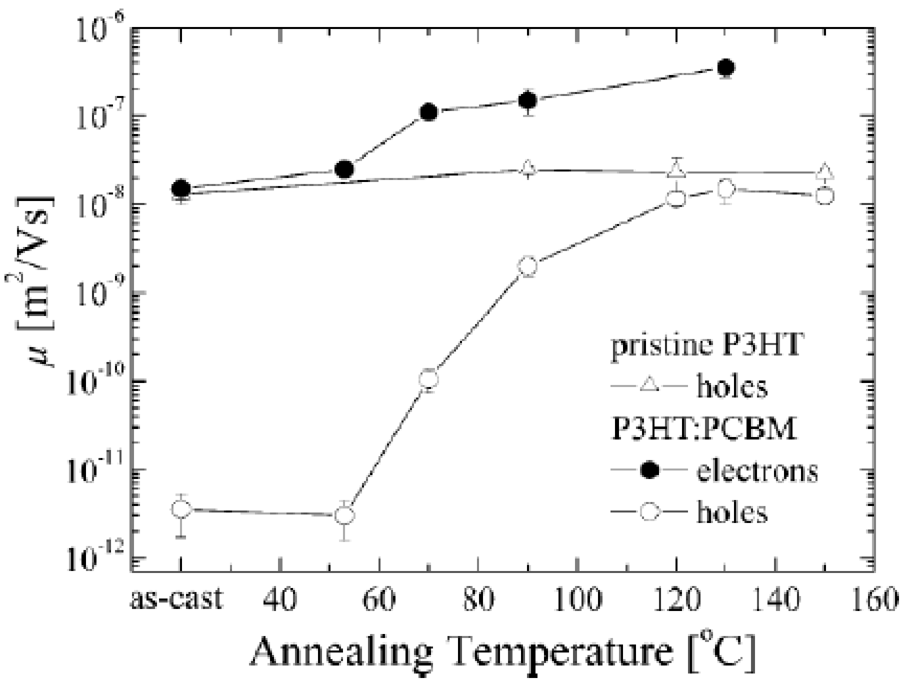
Effect of the thermal annealing on the phase separation



TEM images of 1:1 blend of P3HT and PCBM prior (a) and after (b) thermal annealing at 150°C for 30 minutes (scale bar 0.5 mm).

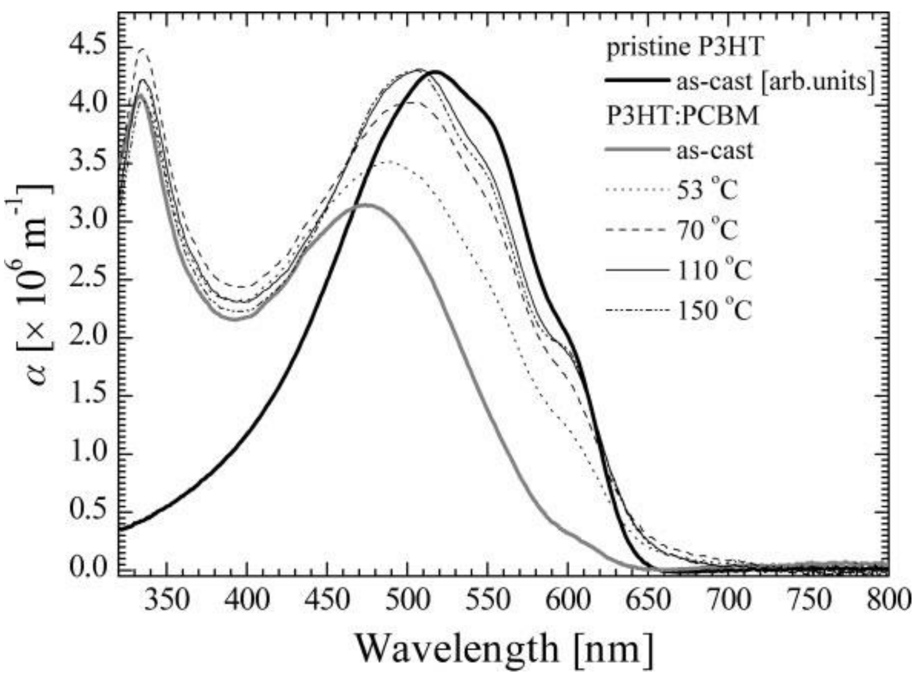
Thomson et al., *Angew. Chem. Int. Ed.*, 2008, 47, 58–77

Effects of morphology



Room-temperature electron (•) and hole (o) zero-field mobilities in (1:1) blends of P3HT:PCBM as a function of postproduction annealing temperature of the completed devices. For comparison, the hole mobility measured in pristine P3HT devices (Δ) is also shown.

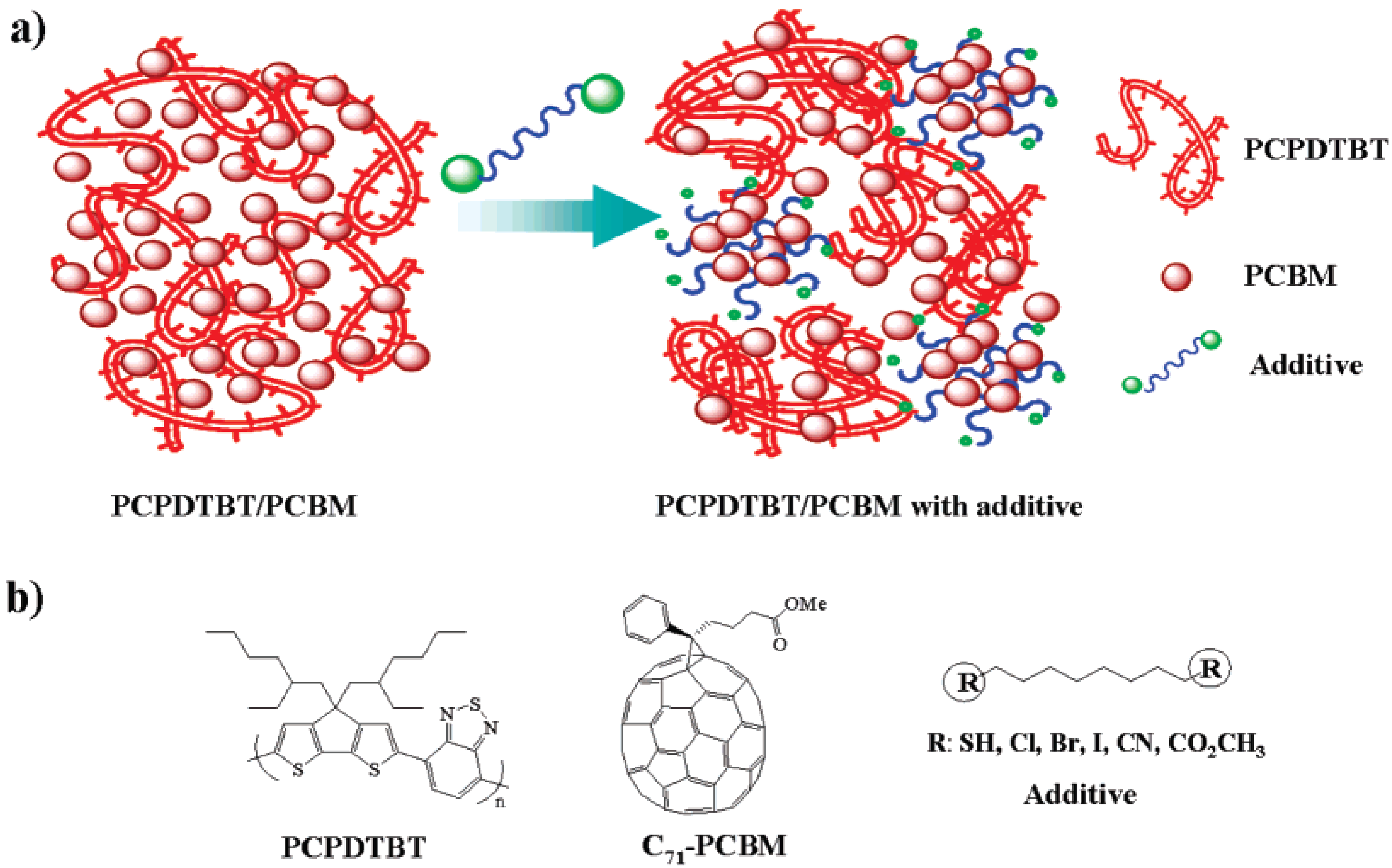
Mihailetchi et al., *Adv. Funct. Mater.*, 2006, 16, 699



Absorption spectra of P3HT:PCBM blend films for different annealing temperatures.

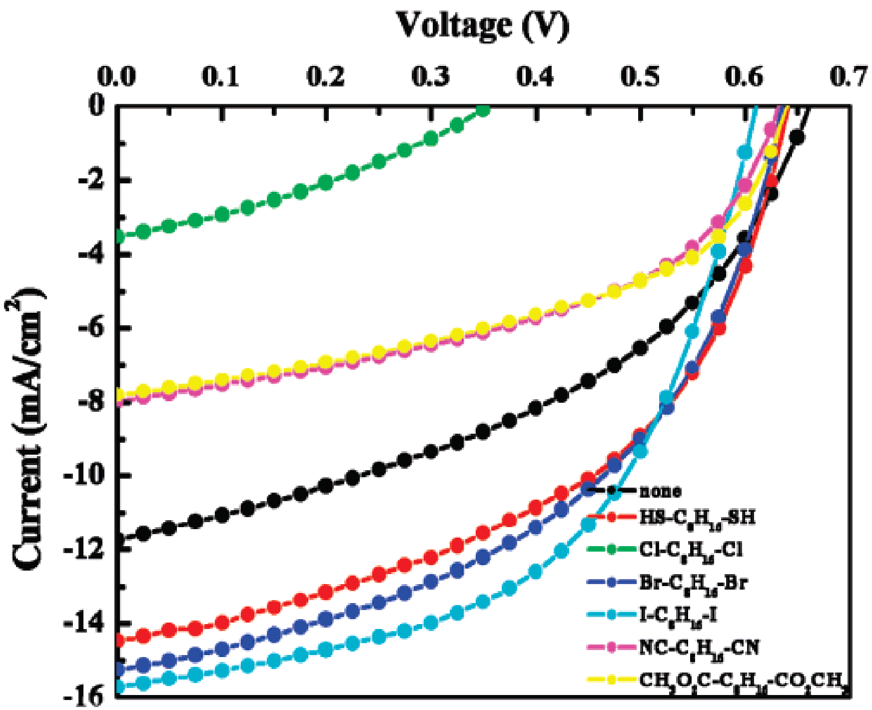
Mihailetchi et al., *Adv. Funct. Mater.*, 2006, 16, 699

Additives



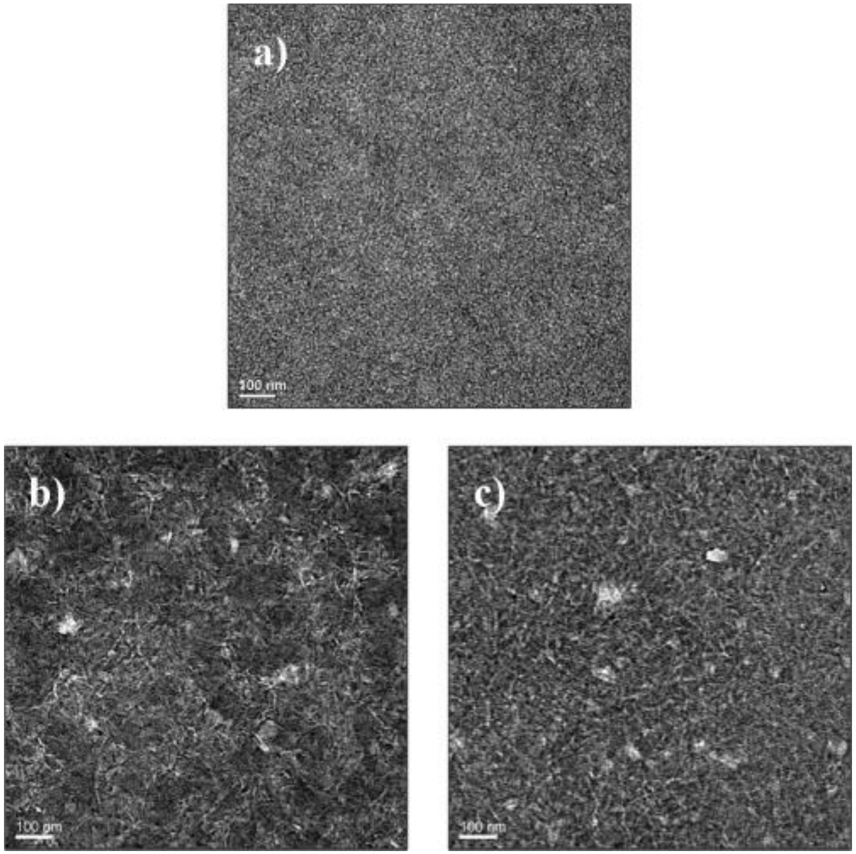
Lee et al., *J. Am. Chem. Soc.*, 2008, 130, 3619-3623

Additives



J-V characteristics of PCPDTBT/C71-PCBM composite films with various additives: (a) none (black), (b) 1,8-octanedithiol (red), (c) 1,8-dicholorooctane (green), (d) 1,8-dibromooctane (blue), (e) 1,8-diiodooctane (cyan), (f) 1,8-dicyanooctane (magenta), and (g) 1,8-octanediacetate (yellow)

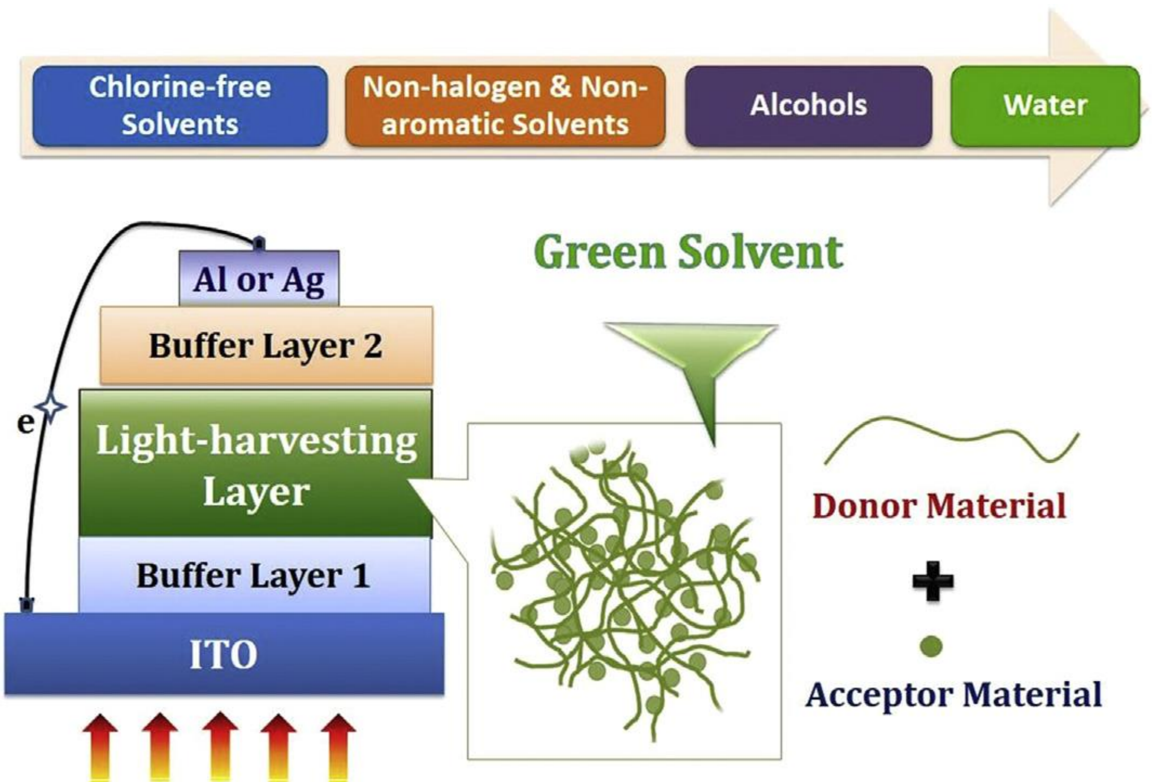
Lee et al., *J. Am. Chem. Soc.*, 2008, 130, 3619-3623



TEM image of films cast from PCPCTBT/C71-PCBM with additives: (a) none, (b) 1,8-octanedithiol, and (c) 1,8-diiodooctane

Ink preparation for AN INDUSTRY COMPATIBLE PROCESS

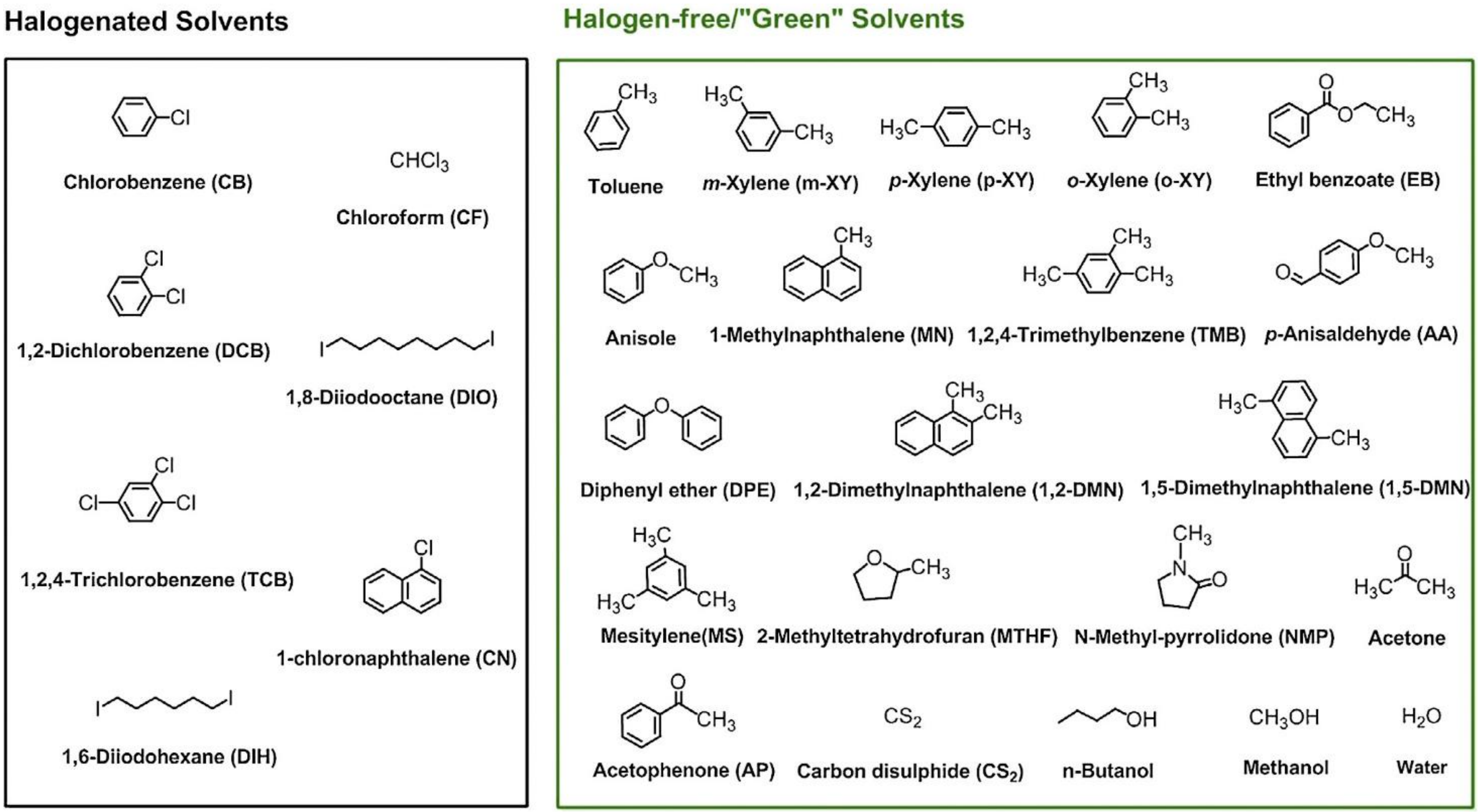
GREEN MATERIALS & SUSTAINABILITY



- Non halogenated solvents
- Non-toxic and with low volatile organic compounds (VOC)
- Boiling point ≤ 200°C
- Reduced environmental impact

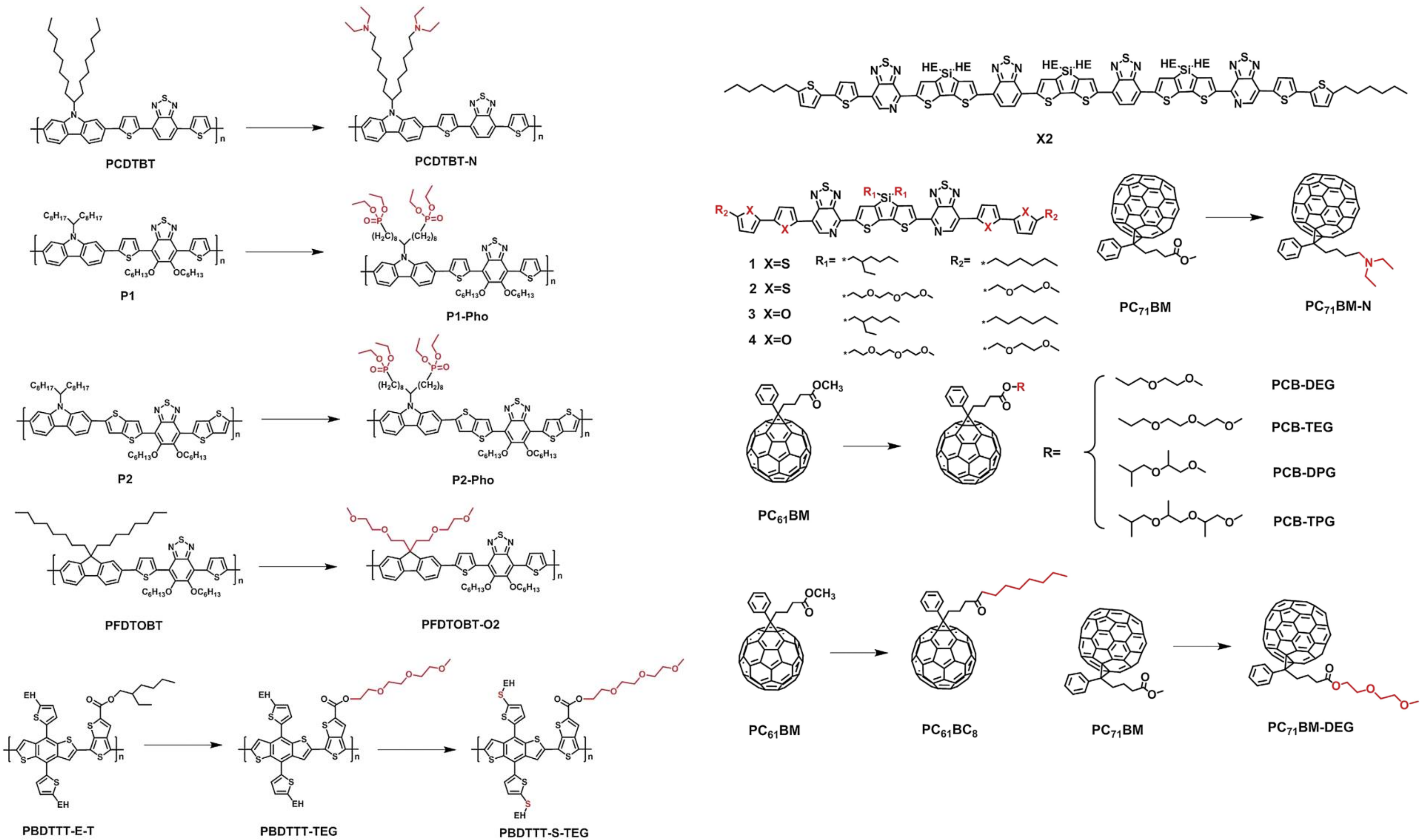
S. Zhang et al. Materials Today Volume 19, Number 9 November 2016

Solvent typically used for OPV solution preparation



S. Zhang et al. Materials Today Volume 19, Number 9 November 2016

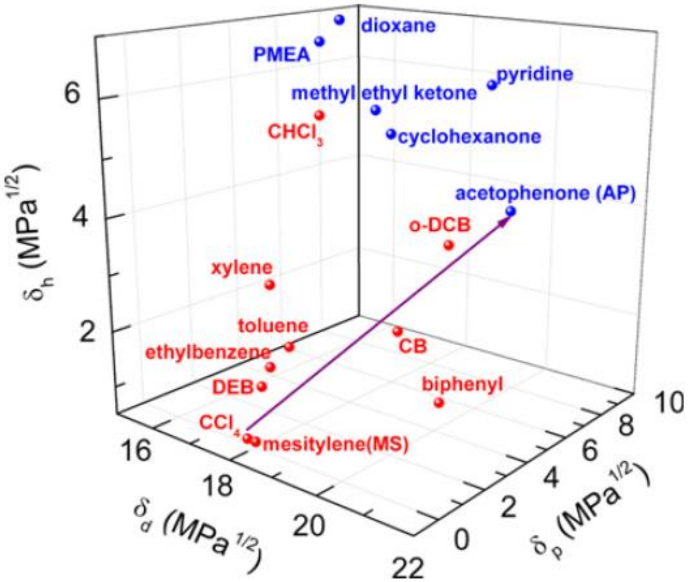
How to change materials towards the use of green solvents?

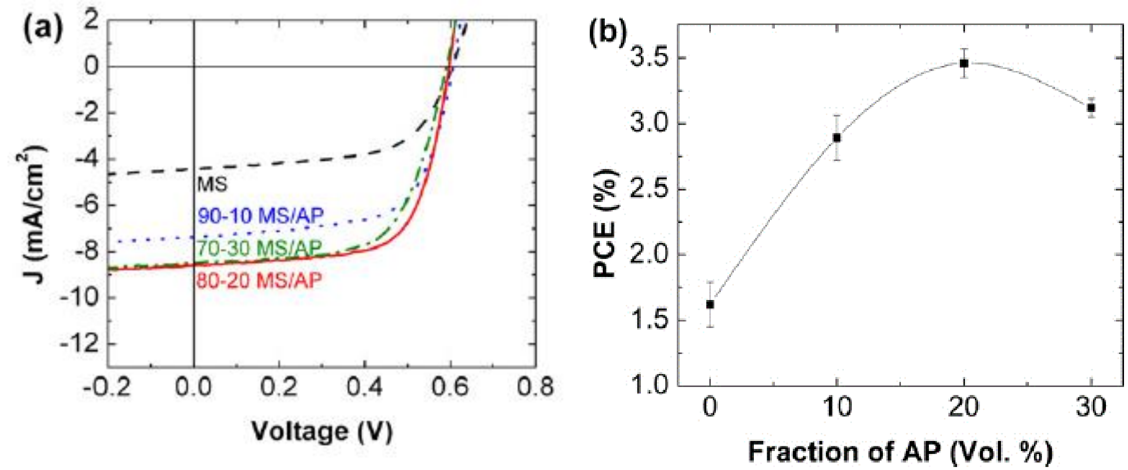


S. Zhang et al. Materials Today Volume 19, Number 9 November 2016

Ink preparation: role of solvent

The choiche of the proper solvent can be done using the Hansen solubility parameters (HSP), which describe the total cohesion energy, E by three contributions: the dispersion interactions, Ed, permanent dipolepermanent dipole molecular interactions, Ep, and the hydrogen bonding molecular interactions, Eh.





$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

$$\delta=(E/V)^{1/2}$$

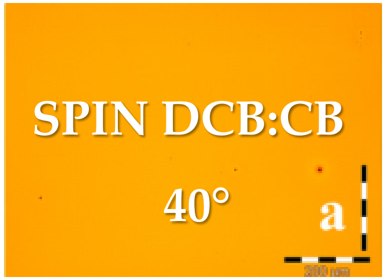
- δ_D Dispersive interaction
- δ_p Intermolecular dipole interaction
- δ_H Hydrogen bond interaction

Boiling points: MS = 165°C / AP = 202°C

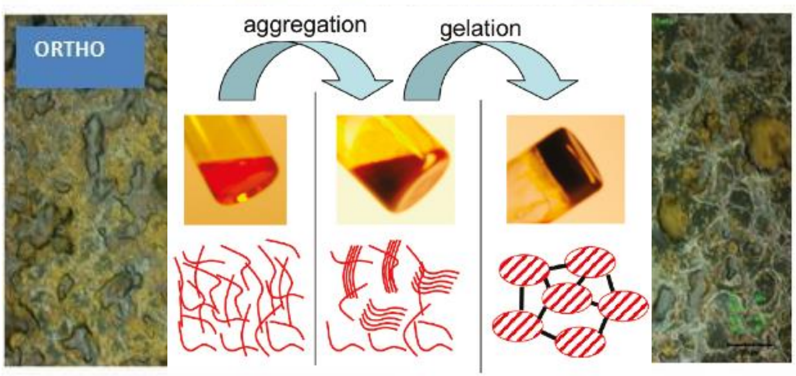
Ink preparation: The role of molecular weight

P3HT(Poly(3-hexylthiophene-2,5-diyl): PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) with non- halogenated solvent (Xylenes)

P3HT:PCB$_{60}$M → **P3HT high molecular weight (60-75k) in o-DCB:CB**



P3HT:PCB$_{60}$M → **P3HT high molecular weight (60-75k)**



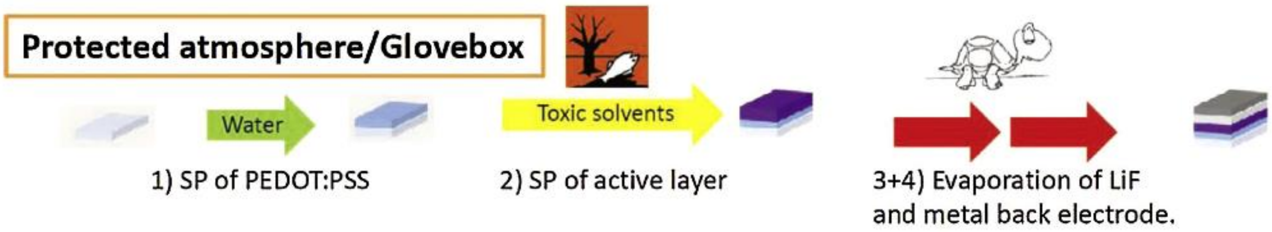
P3HT:PCB$_{60}$M → **P3HT low molecular weight (21k)**

	Voc (mV)	Jsc (mA/cm²)	FF (%)	Eff (%)
Inverted structure	510	7.8	45	1.8
Direct structure	546	9.4	49	2.5

M-Koppe et al ,Macromolecules, 2009, *42* (13), pp 4661–4666
G. Susanna et al., Solar Energy Materials & Solar Cells 95 (2011) 1775–1778

Water based OPV

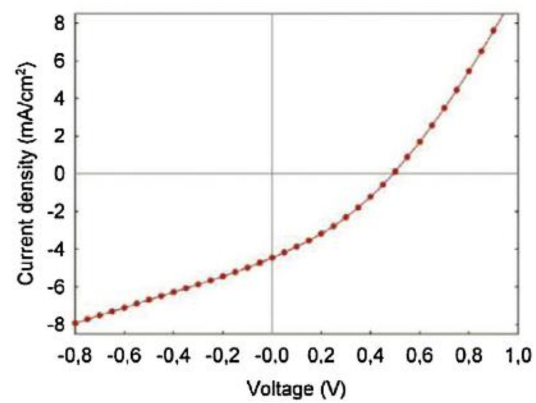
Processing steps of a ‘Normal’ structure solar cell:

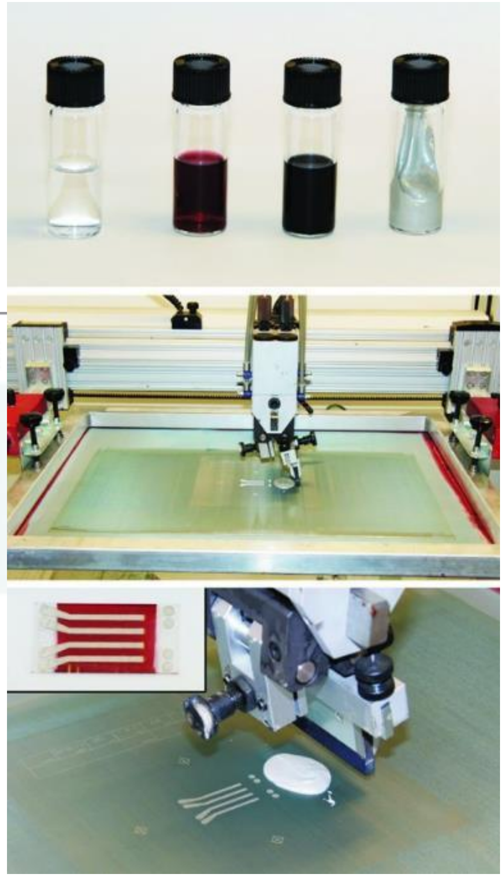


Processing steps of all-water-processable solar cell with ‘Inverted’ structure:

SP: Solution processing

- Green arrow: Compatible with high throughput production and is environmentally friendly
- Yellow arrow: Compatible with high throughput production but NOT environmentally friendly
- Red arrow: NOT compatible with high throughput production.





Low efficiency → η= 0.7 %

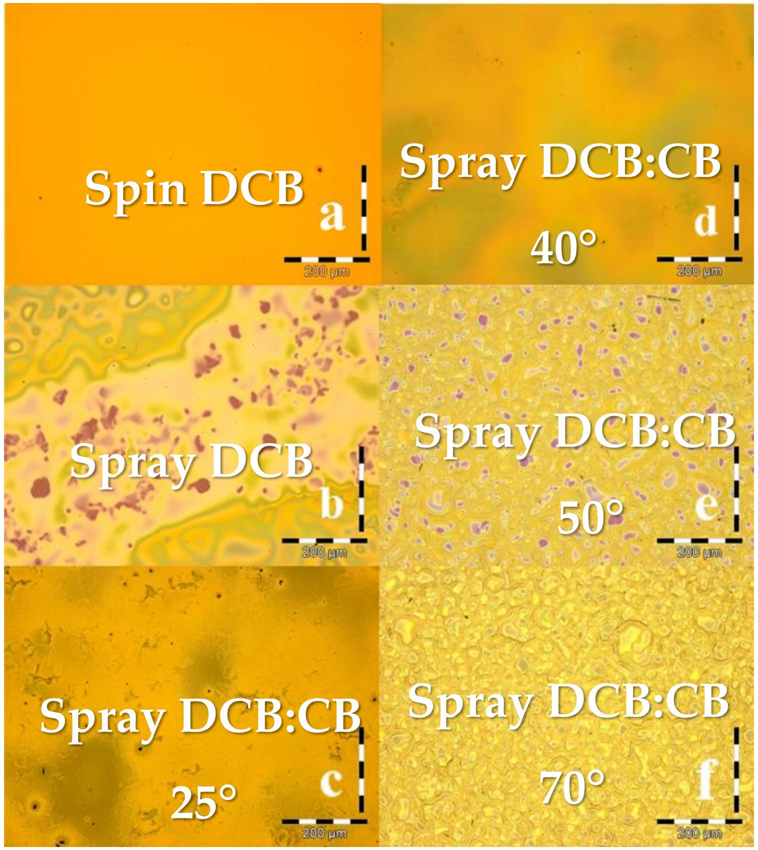
Example of printing techniques applied to OPV: spray coating

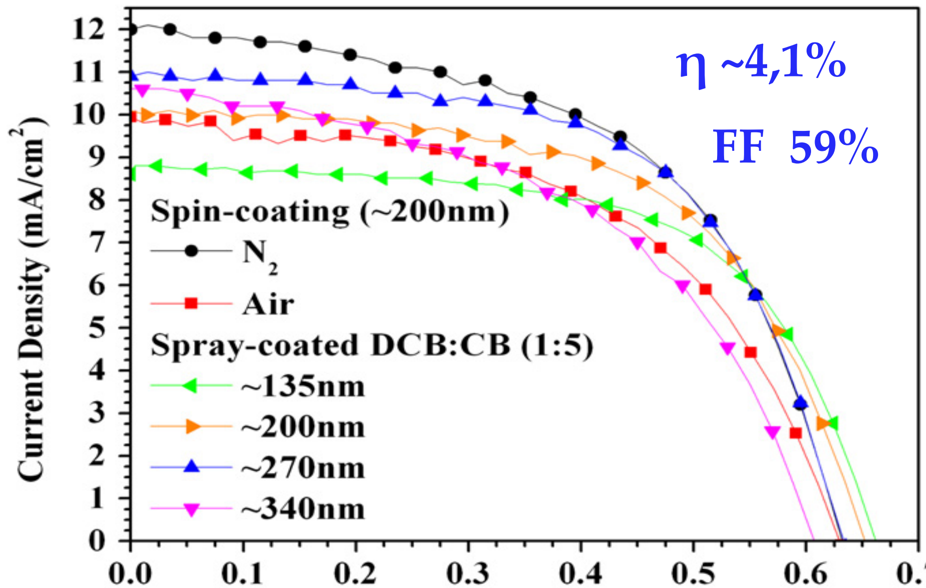
Co-Solvent optimization: morphology tuning

Co-solvent mixture: **DCB:CB (1:5)**

DCB: improves the phase separation

CB: allows better spray deposition





Dep	Amb	Tk (nm)	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	η [%]
Spin	N_2	200	0.63	11.96	55	5.1
	Air			9.97	53	3.3
Spray		135	0.66	8.89	60	3.6
		200	0.64	10.34	57	3.8
		270		10.98	59	4.1
		340	0.61	10.62	50	3.2

G. Susanna et al., Solar Energy Materials & Solar Cells 95 (2011) 1775–1778

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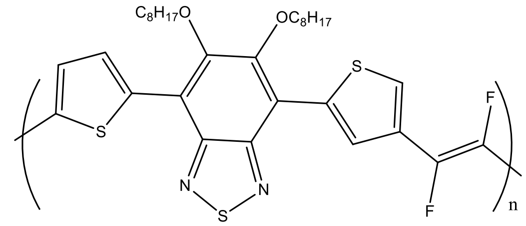
BHJ-SC with non-Chlorinated solvents

The introduction of non-chlorinated solvents plays a fundamental role in the direction of large area device realization

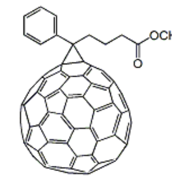
polymer (*donor*)

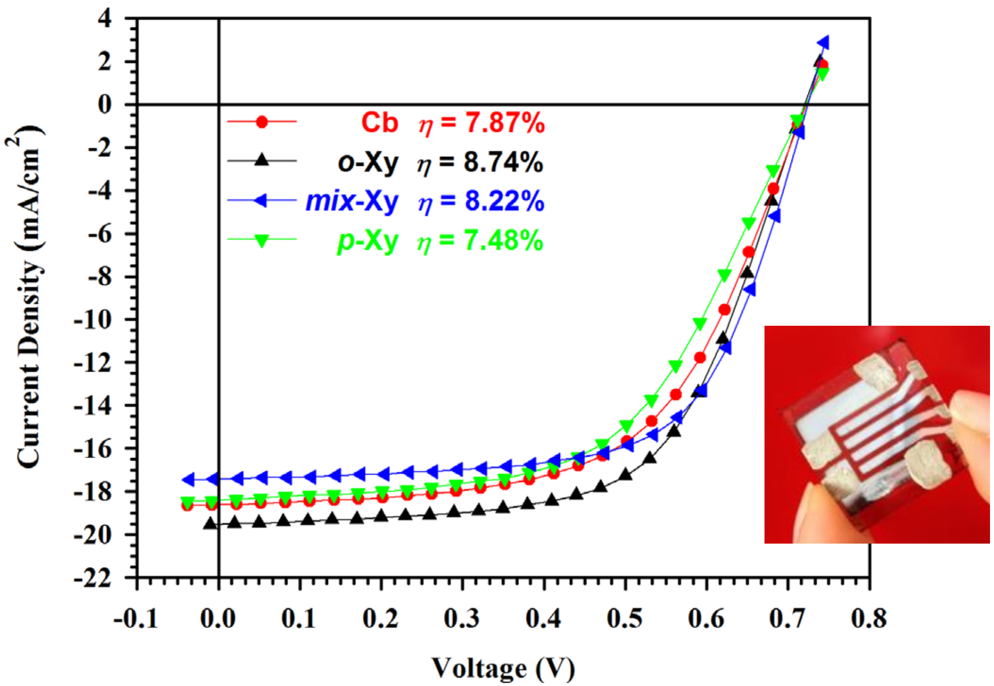


PTB7

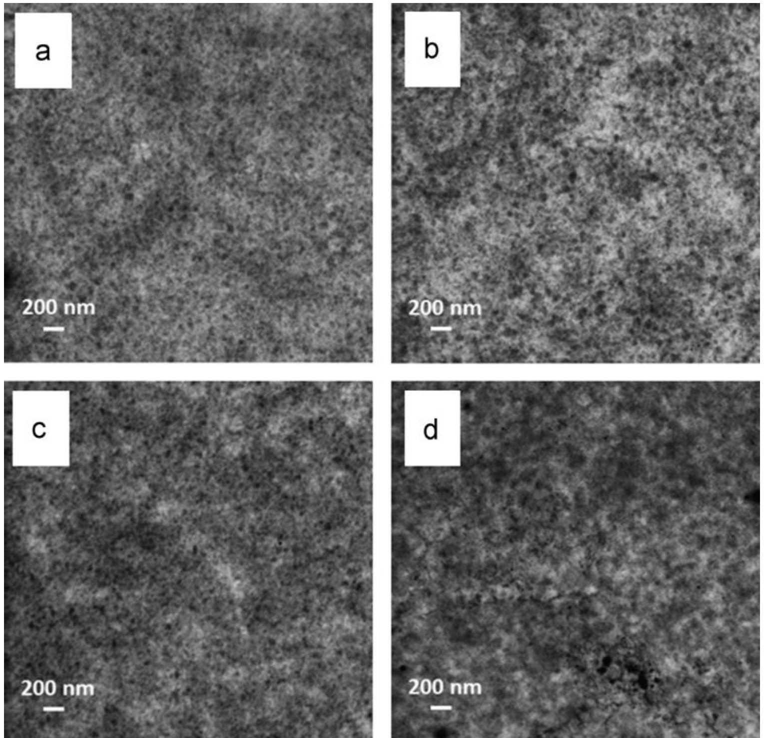
fullerene derivative (*acceptor*)

PCBM



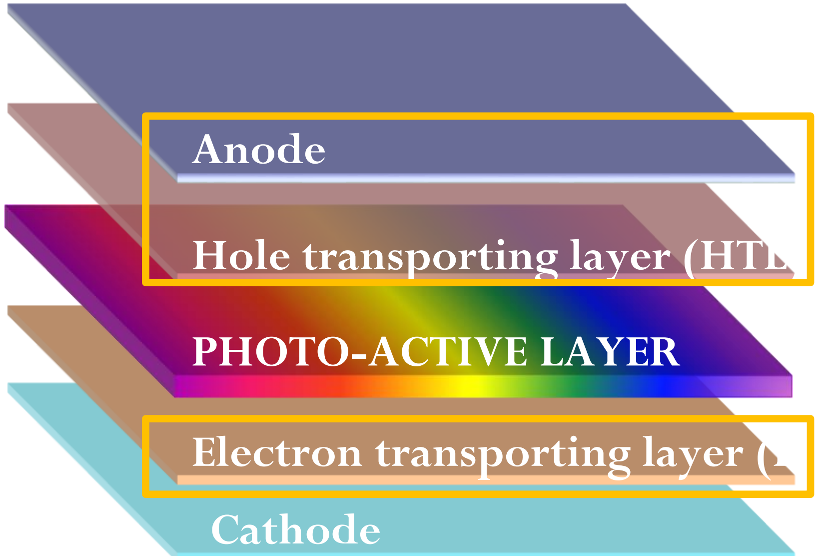


Solvents	Thickness [nm]	Voc [V]	Jsc [mA/cm²]	FF [%]	PCE [%]	Max PCE [%]
Cb	~100	0.716 ± 0.006	17.72 ± 0.55	58.5 ± 1.9	7.43 ± 0.27	7.87
o-Xy	~80	0.719 ± 0.005	18.58 ± 0.69	61.9 ± 1.9	8.22 ± 0.41	8.74
mix-Xy	~80	0.725 ± 0.005	17.34 ± 0.22	63.6 ± 1.5	8.00 ± 0.19	8.22
p-Xy	~80	0.715 ± 0.010	17.54 ± 1.53	56.1 ± 2.62	6.73 ± 0.70	7.48

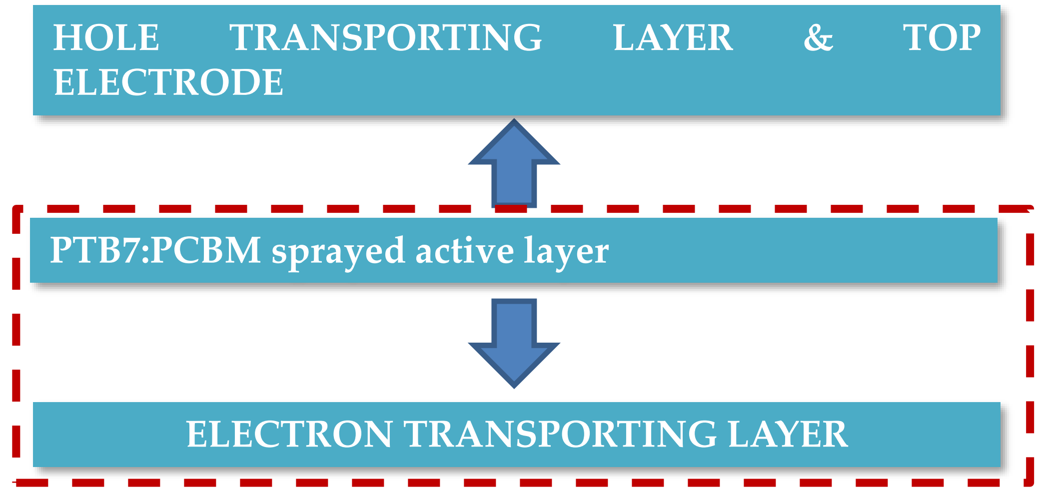


Susanna et al. Solar EnergyMaterials&SolarCells134(2015)194–198

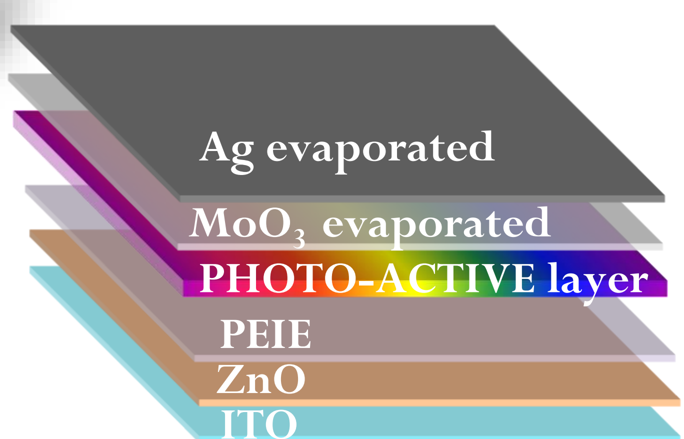
Fully spray coated module



SMALL AREA DEVICE 0.1 cm^2

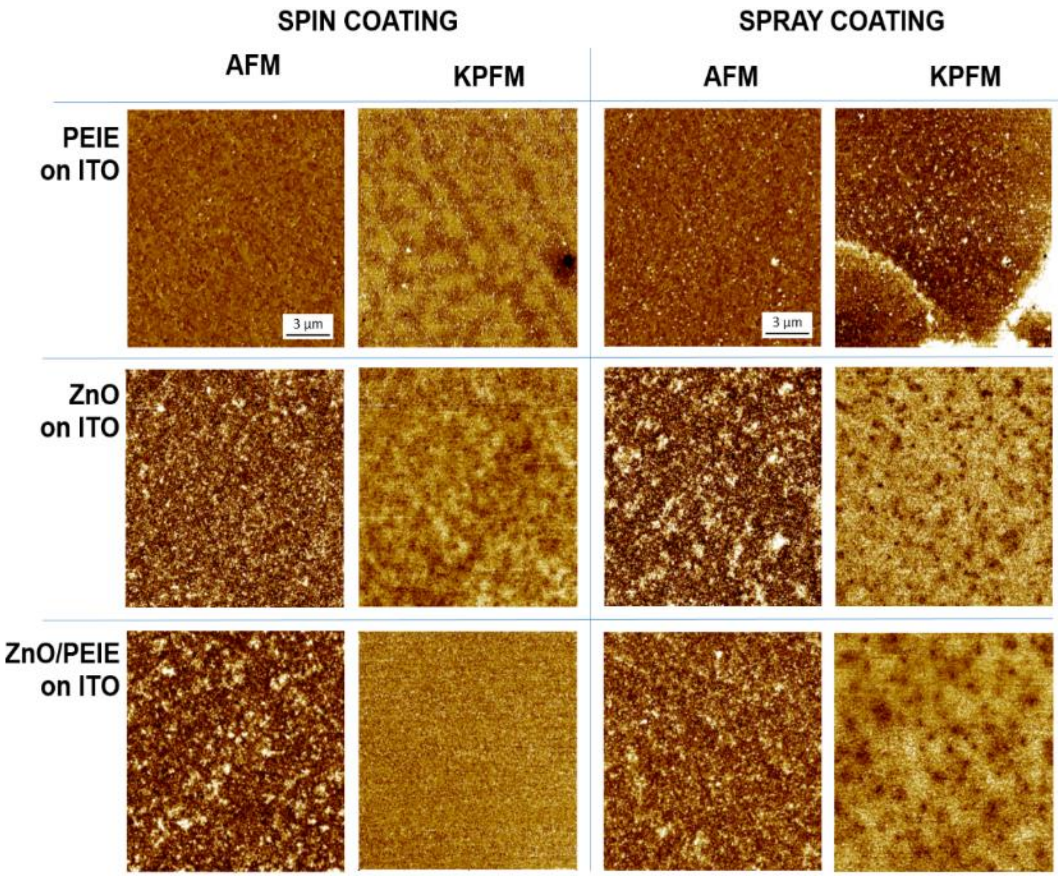


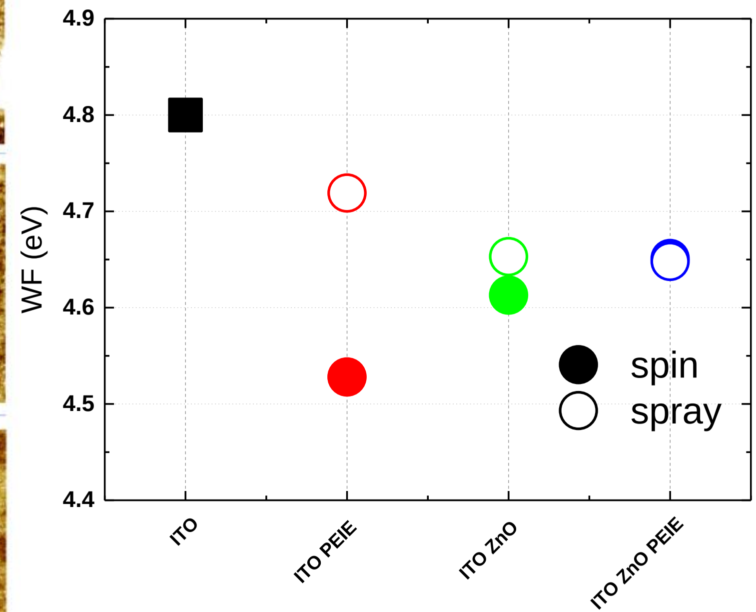
1° INTERFACE: ELECTRON TRANSPORTING LAYER



- Work Function reduction
- Lower energy barrier for charge transport PAL/ETL
- Avoid electron trapping and high series resistance
- Charge acceleration transfer
- Reduction of recombination at interface

SPRAY COATED ETL/PAL INTERFACE





	Spin Coating		Spray coating	
	AFM	KPFM	AFM	KPFM
PEIE	2.4±0.3 nm	9±1 mV	3.8±0.4 nm	15±3 mV
ZnO	11±3 nm	7±1 mV	12±3 nm	10±1 mV
PEIE+ZnO	12±2 nm	7±1 mV	9±2 nm	9±1 mV

The use of different deposition techniques does not affect the surface roughness of single ETL

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Polino et al, Energy Technol. 2019 doi.org/10.1002/ente.201800627

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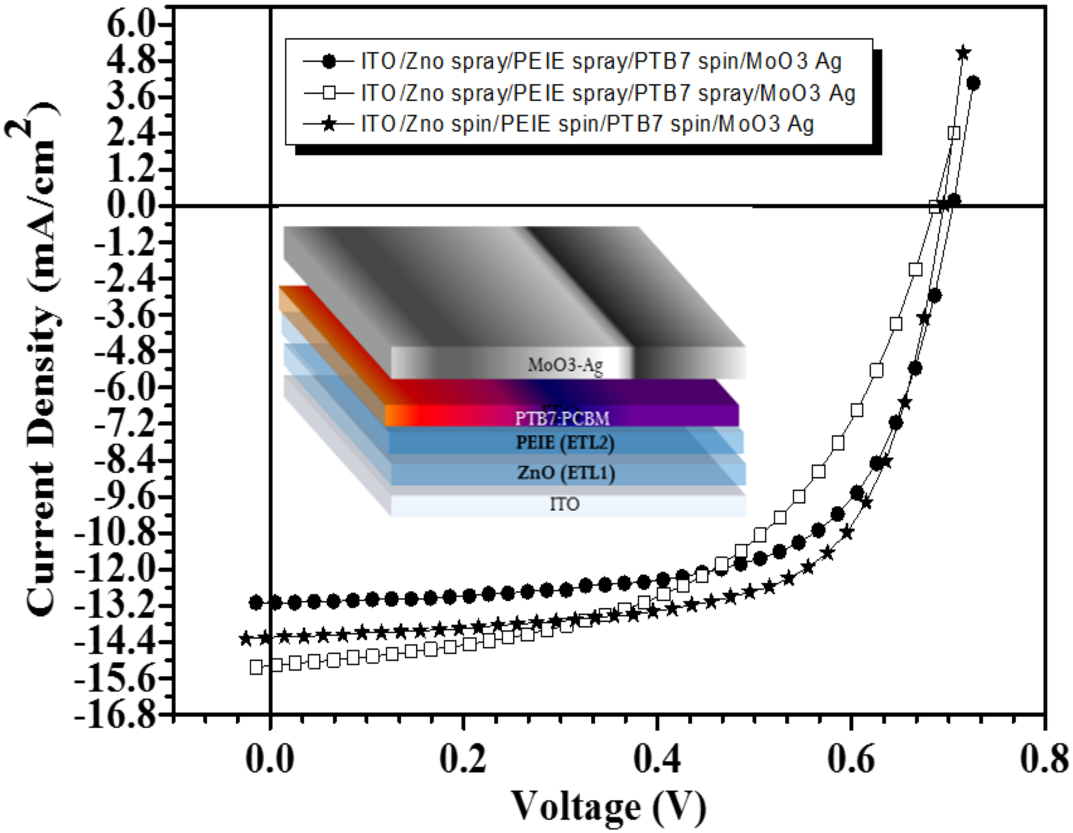
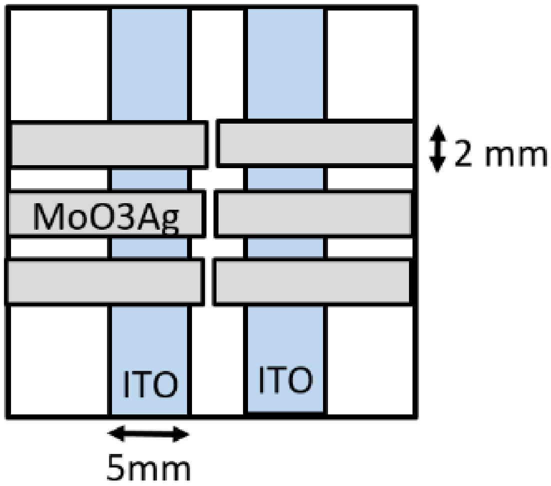
SPRAY COATED ETL/PAL INTERFACE





ZnO/PEIE	PAL	V_{oc} (mV)	J_{sc} (mA/cm²)	FF(%)	Eff(%)
Spray	Spray	0.68±0.30	13.7±0.20	54±0.07	5.5±0.01
Spin	Spin	0.70±0.01	14±0.08	67±0.08	6.6±0.40
spray	Spin	0.70±0.02	13±0.07	65±0.08	6.0±0.06

Polino et al, Energy Technol. 2019 doi.org/10.1002/ente.201800627

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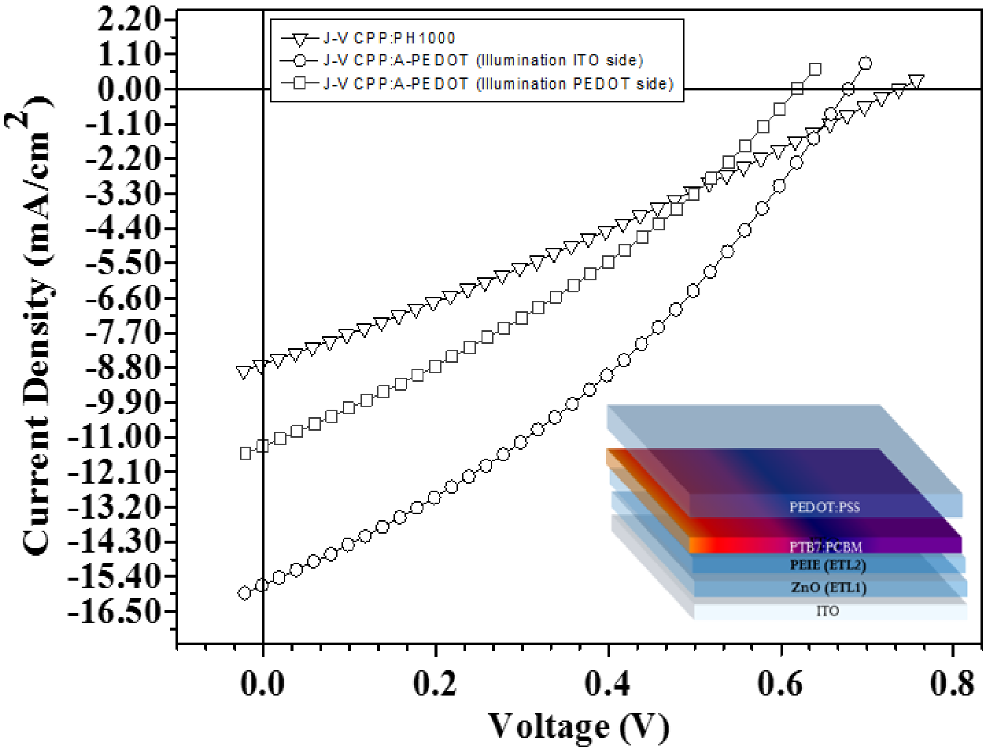
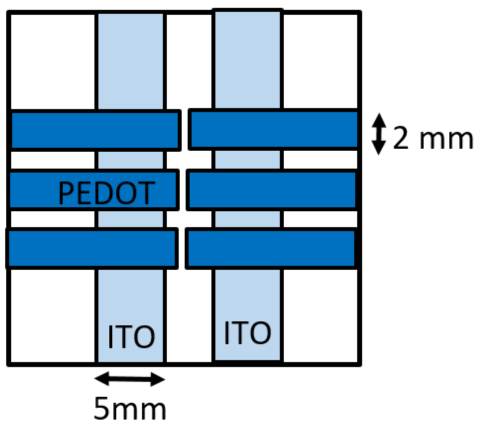
SPRAY COATED HTL/PAL INTERFACE



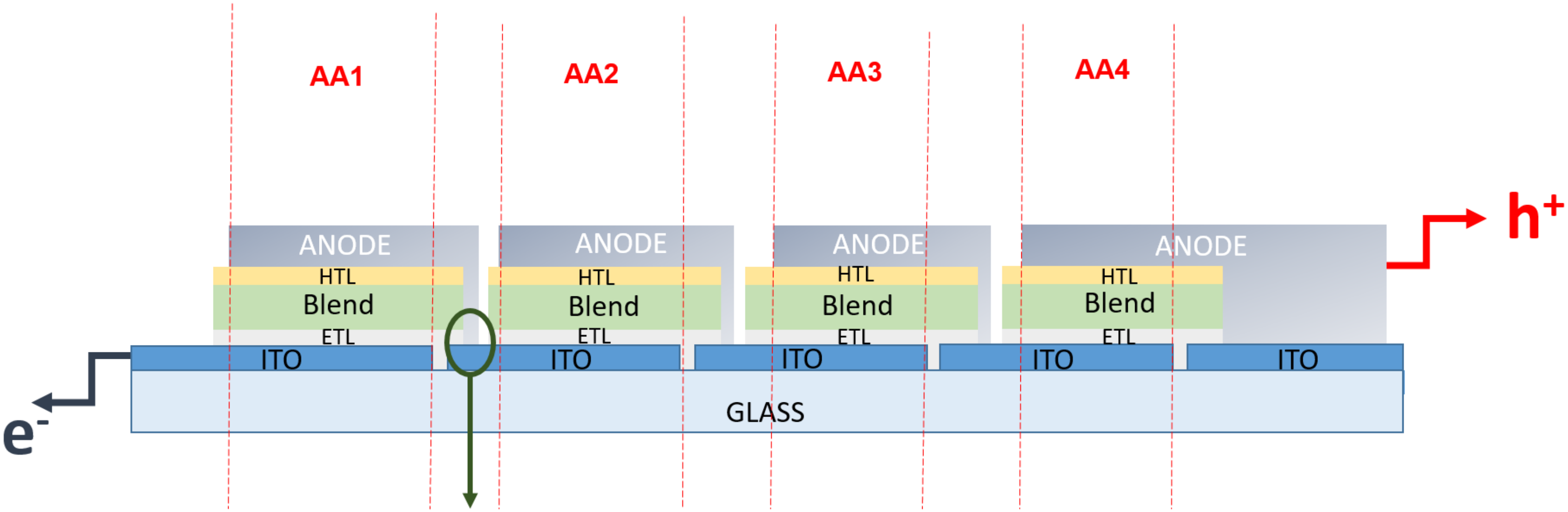


	Voc (mV)	Jsc (mA/cm^2)	FF (%)	Eff (%)
CPP:PH1000	0.69	8.60	28.2	1.7
CPP:A-PEDOT	0.68	15.6	33.8	3.6
CPP:A-PEDOT (ILL. PEDOT)	0.64	9.55	33.2	2.0

Polino et al, Energy Technol. 2019 doi.org/10.1002/ente.201800627

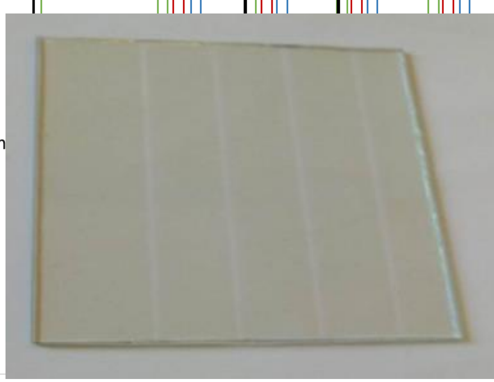
FROM SMALL TO LARGE AREA

The module is composed of 4 series-connected solar cells



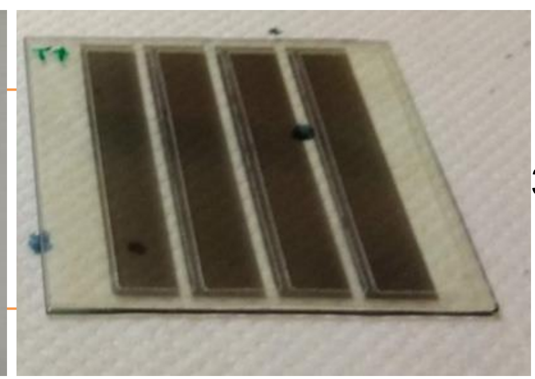
Contact between top eletrode of a cell with the bottom one of the adjacent cell

Laser patterned ITO substrate
P1



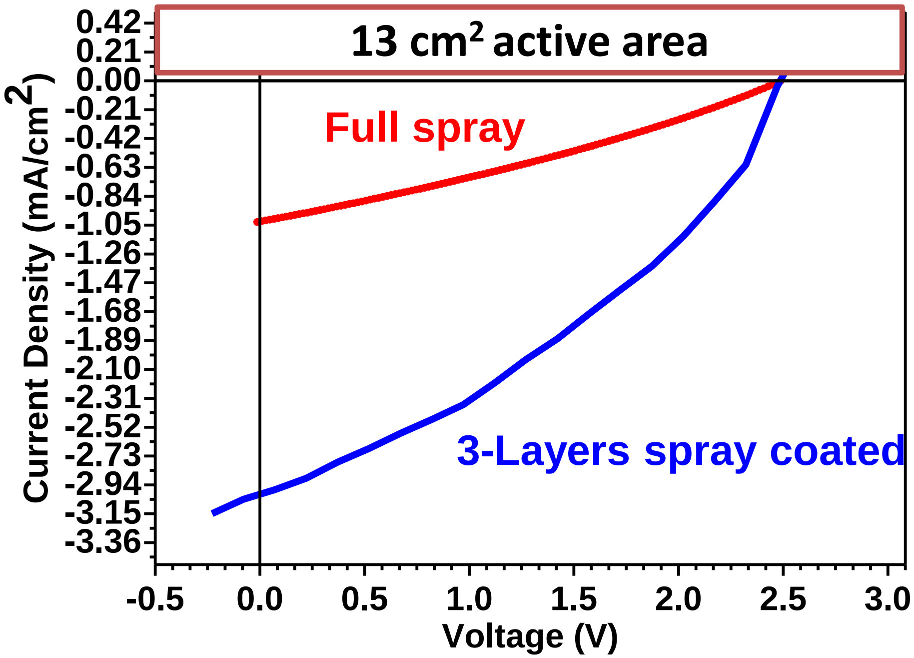
Mask to deposit ETL/BLEND/HTL
P2

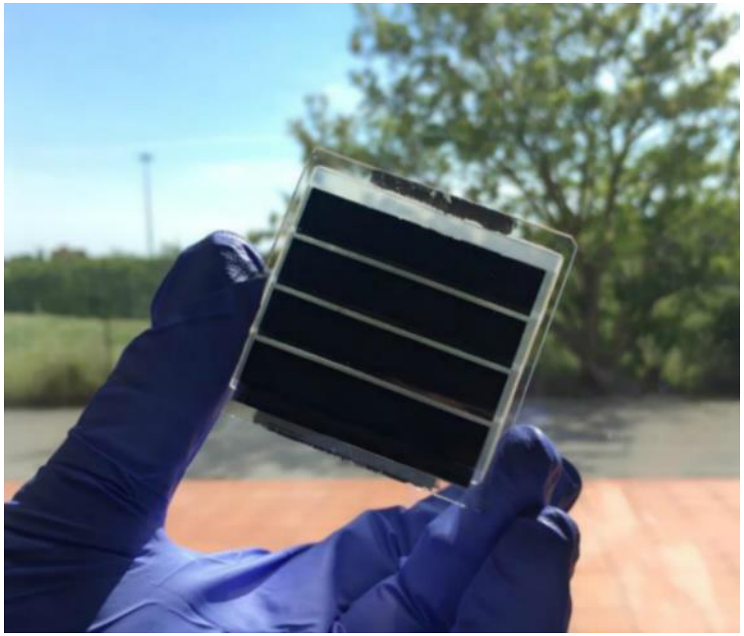
Mask to deposit HTL/ANODE
P3



3.7cm^2

FULL SPRAY MODULES





	Voc (V)	Jsc (mA/cm²)	FF (%)	Eff (%)
MoO3 Ag evap	2.8	3.0	37.2	3.0
V2O5/ A-PEDOT	2.5	1.1	30.6	0.8

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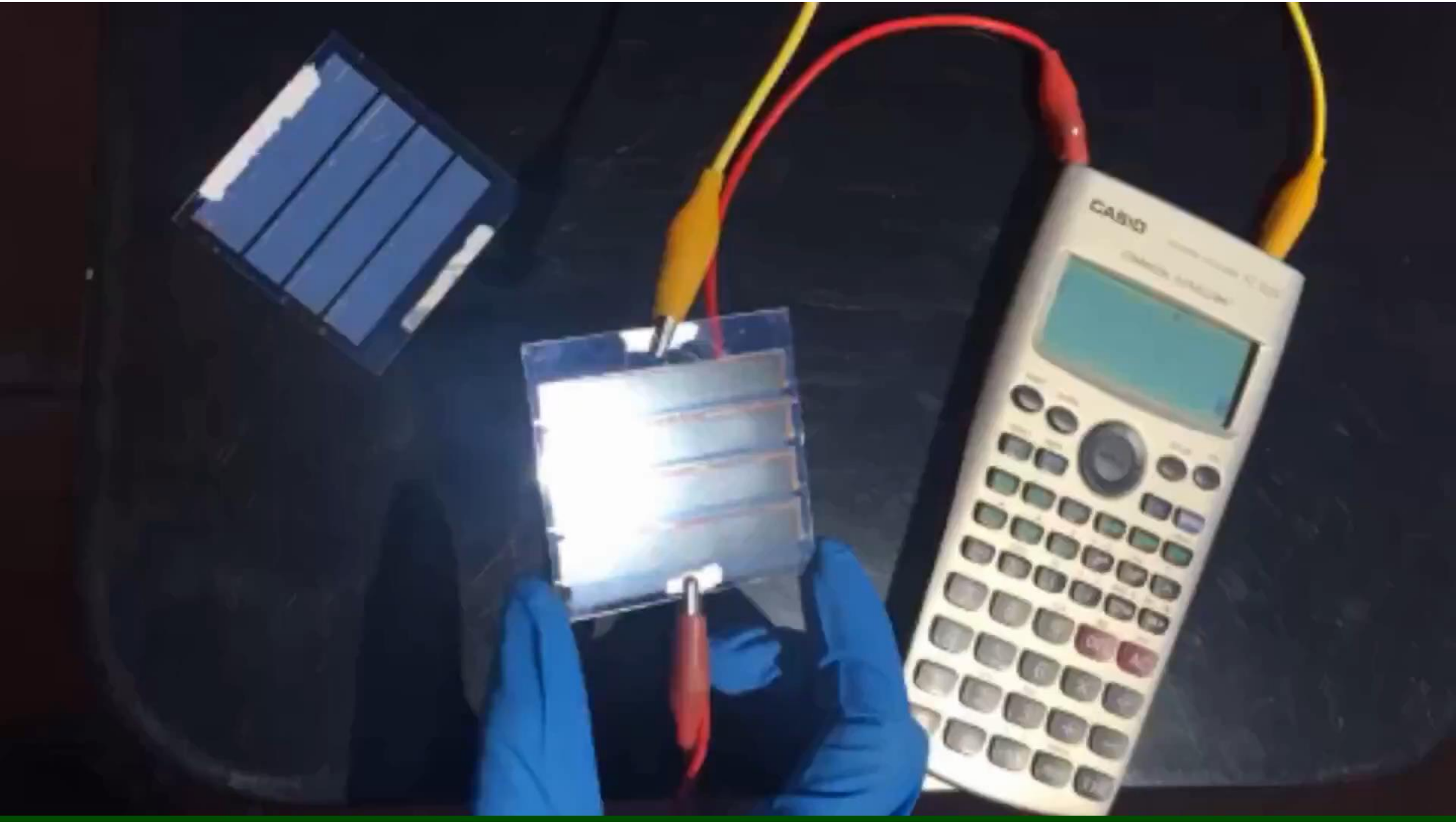
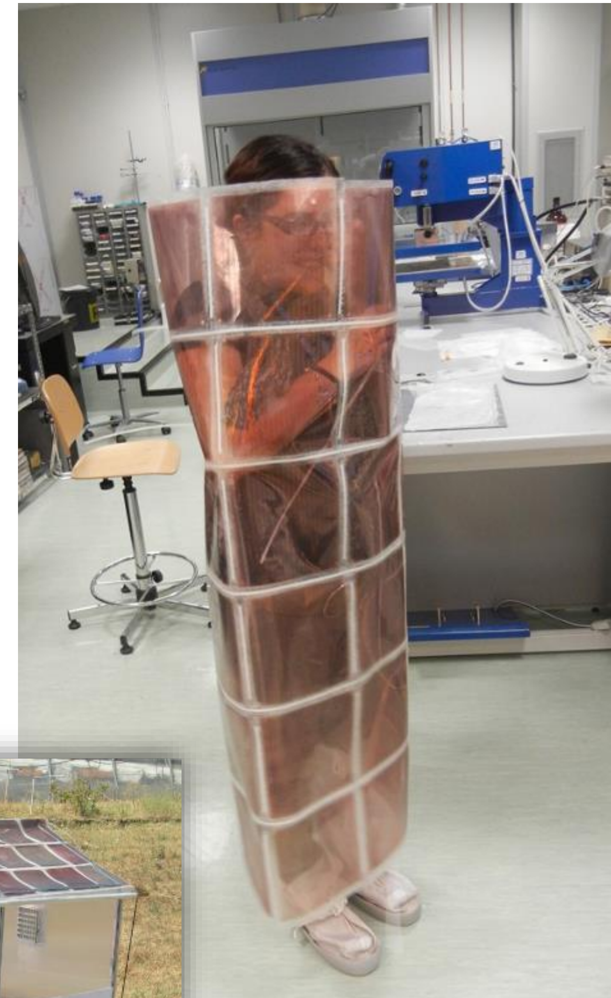
FULL SPRAY MODULES AT WORK!



Devices on flexible substrates

Semi-trasparent

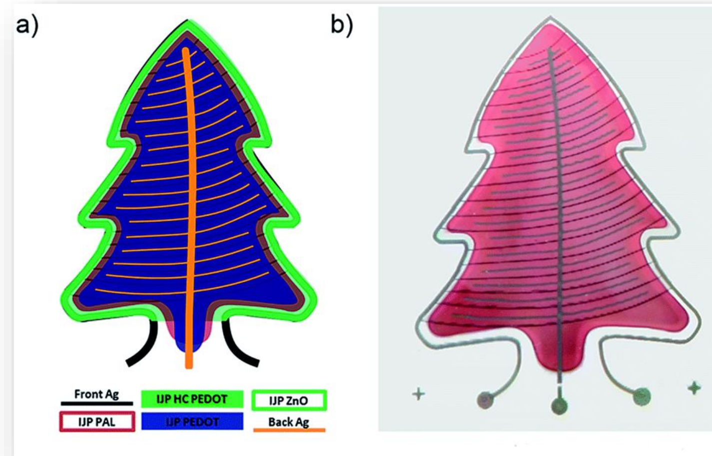


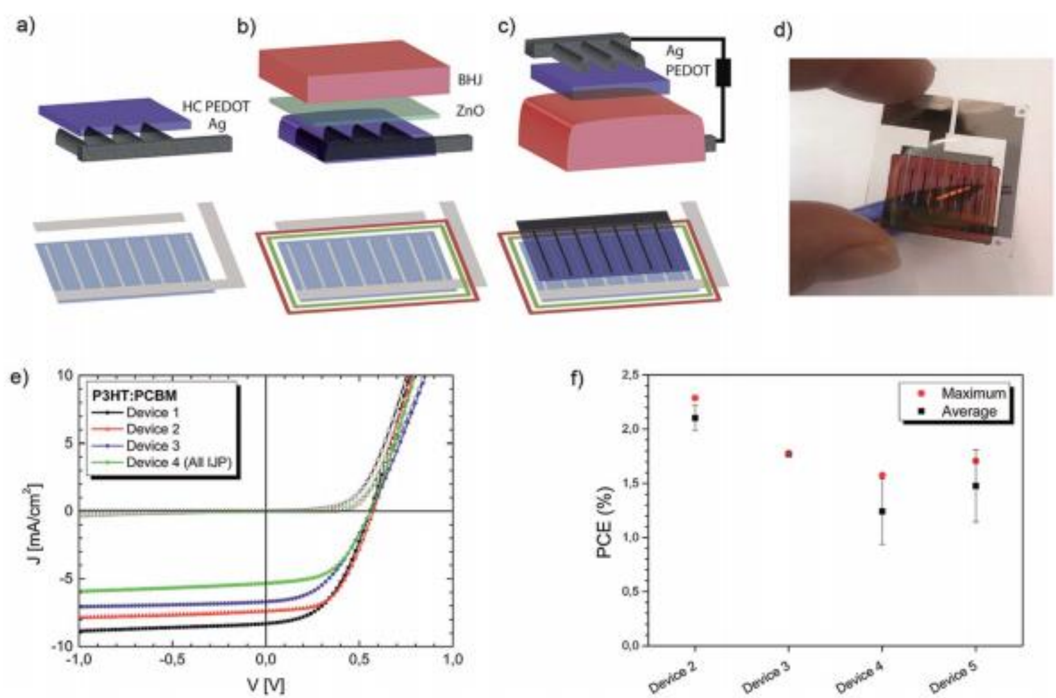
Flexible

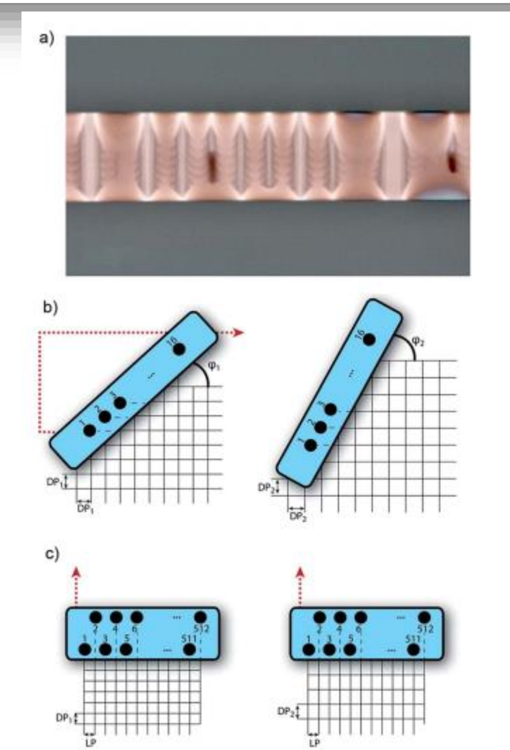
Completely inkjet printed OSC

All-inkjet printed large area (>1 cm^2) organic solar cells with power conversion efficiency of 4.1% deposited from environmentally friendly solvents in an air atmosphere.

The semitransparent front and back electrodes consist of PEDOT:PSS and conductive Ag fingers, avoiding the use of ITO.

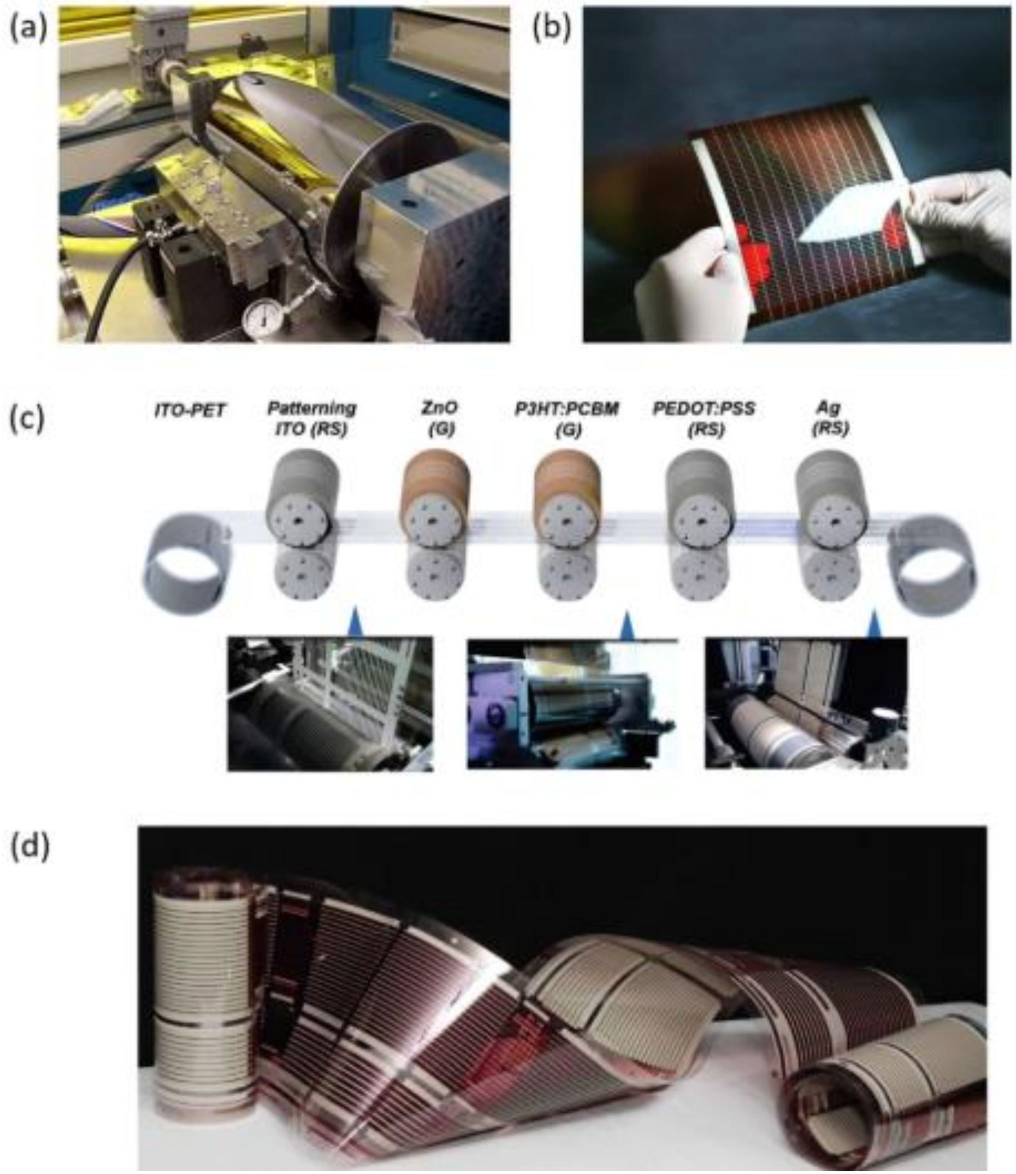






T.M Eggenhuisen et al, J. Mater. Chem. A, 3, (2015)

Fully printed OPV



Y. Galagan et al. Adv. Eng. Mater. 2018, 1701190

Large area Modules

Techniques used:

→ Screen printing

→ Blade coating

→ Slot-die coating

Maximum efficiency on the module with low bandgap polymers: 5%

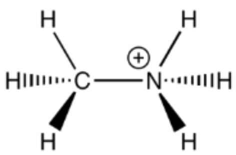
csem brasil

Perovskite Solar cells
PSC

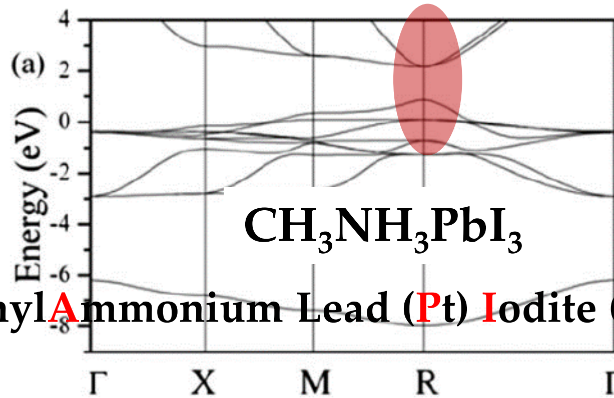
Organometal trihalide Perovskite

Methylammonium lead halide perovskite

A=$CH_3NH_3^{(+)}$; B= $Pb^{(+)}$; Sn X= $I^{(-)}$, $Cl^{(-)}$, $Br^{(-)}$



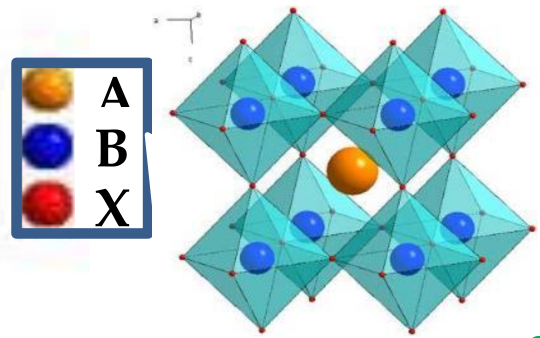
methylammonium ion



$CH_3NH_3PbI_3$

MethylAmmonium Lead (Pt) Iodite (MAPI)

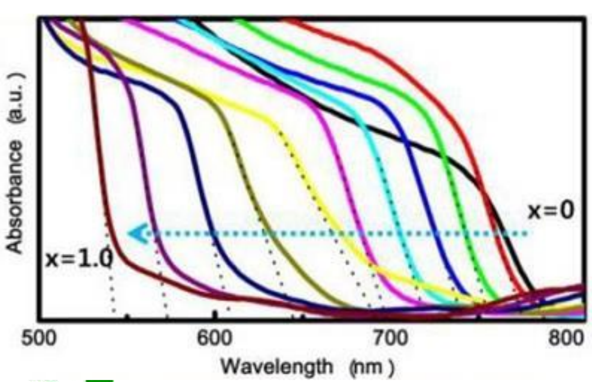
Direct band gap of 1.51 eV for $CH_3NH_3PbI_3$

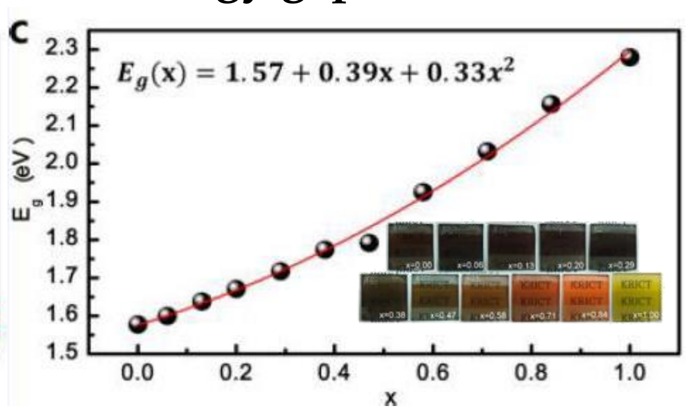


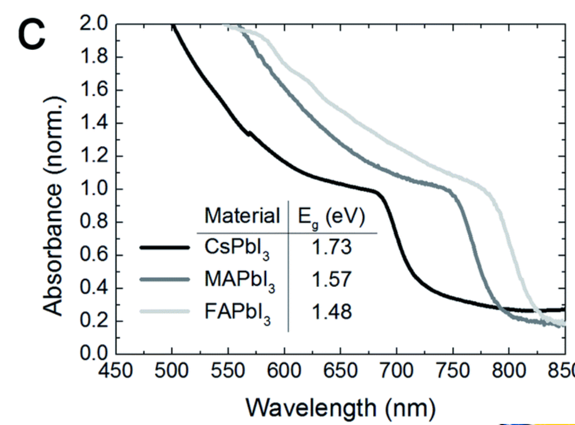
Solution process

Good hole and electron conductor, Diffusion length from 100 nm to 1 μm

By the insertion of Br atoms (x) on the perovskite crystalline structure, or using a different organic molecule the energy gap can be varied.







Baikie et al. J. Mater. Chem. A, 2013, 1, 5628, *G. Eperon et al Energy Environ. Sci., 2014,7, 982-988, P. Gau et al, Energy Environ. Sci., 2014,7, 2448-2463*

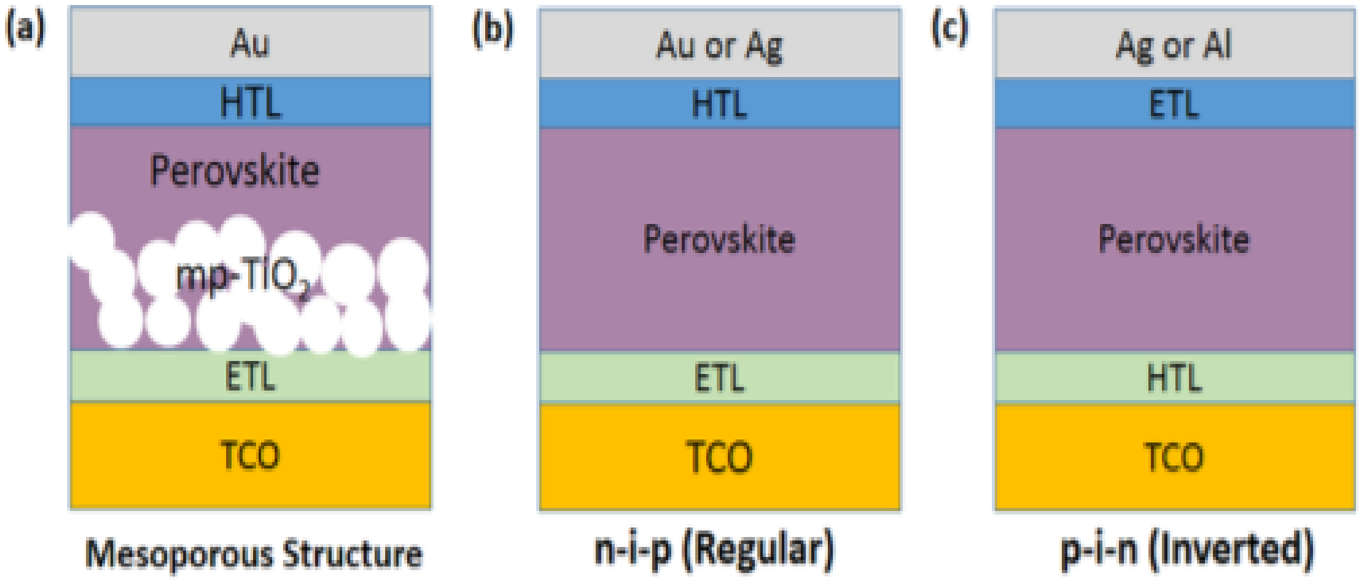
Mesostructured vs Planar Perovskite Solar cells

Mesostructured

(DSC like)

Planar

(OPV like)



- **Easier perovskite grown**
- **Better charge transport**

- **Less production step**
- **No sintering step**

Y. Zhang, et al. *Materials Horizons*, 2015, **2**, 315-322

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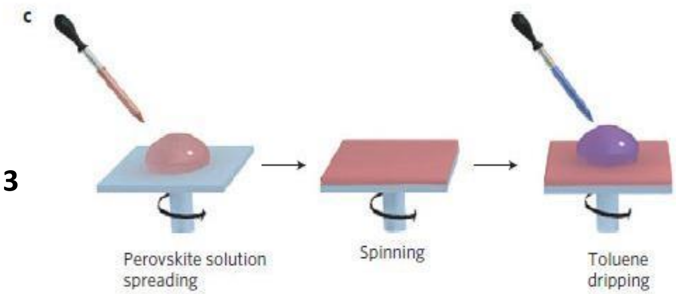
Several deposition methods

1) One-step procedure

Spin coating perovskite → Drying RT → Annealing 90-130°C

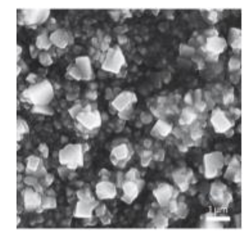
1a) $3\ CH_3NH_3I + PbCl_2 \rightarrow CH_3NH_3PbI_{3-x}Cl_x + \ldots$



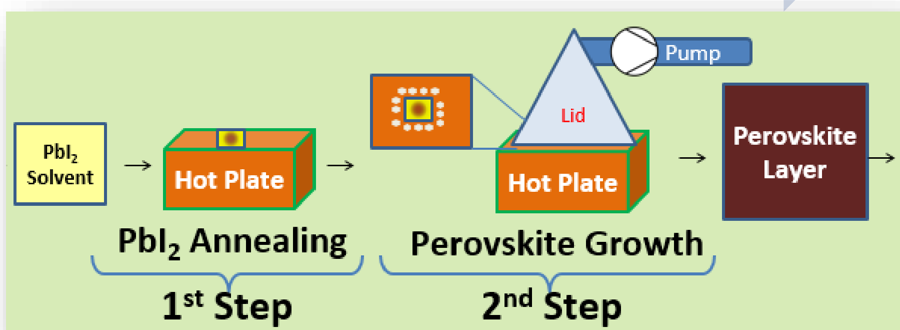
1b) Solvent engineering $CH_3NH_3I + PbI_2 \rightarrow CH_3NH_3PbI_3$

2) Two-step procedure

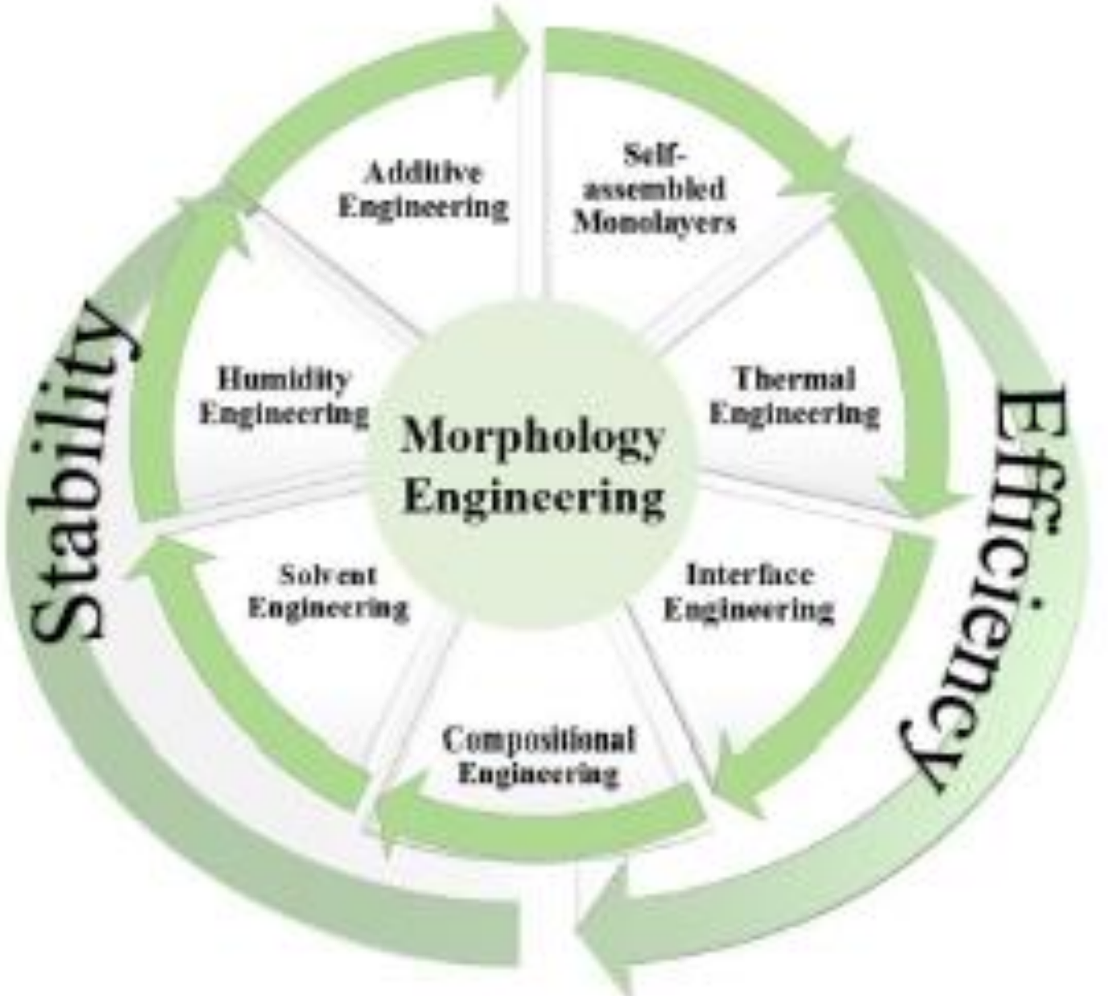
PbI_2 deposition → CH_3NH_3I addition → Perovskite layer



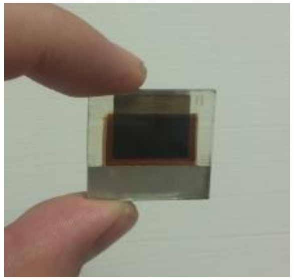
3) Vapor deposition



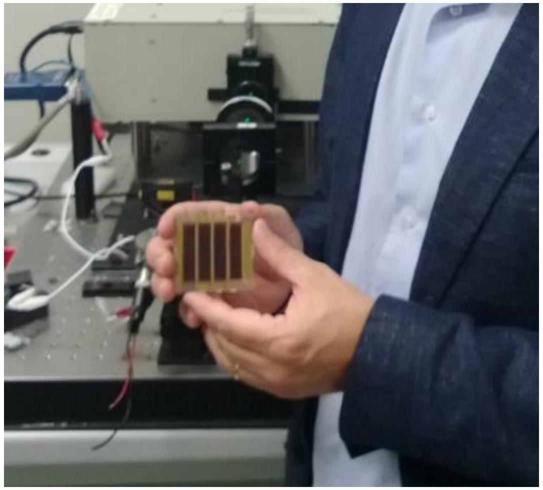
Key issue for PSK ink formulation



From cells to Modules

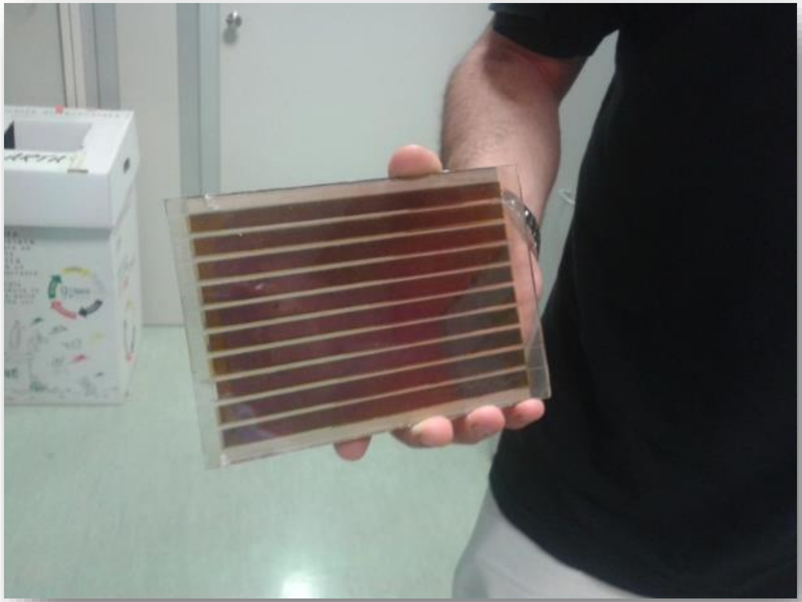


1 cm^2



10 cm^2

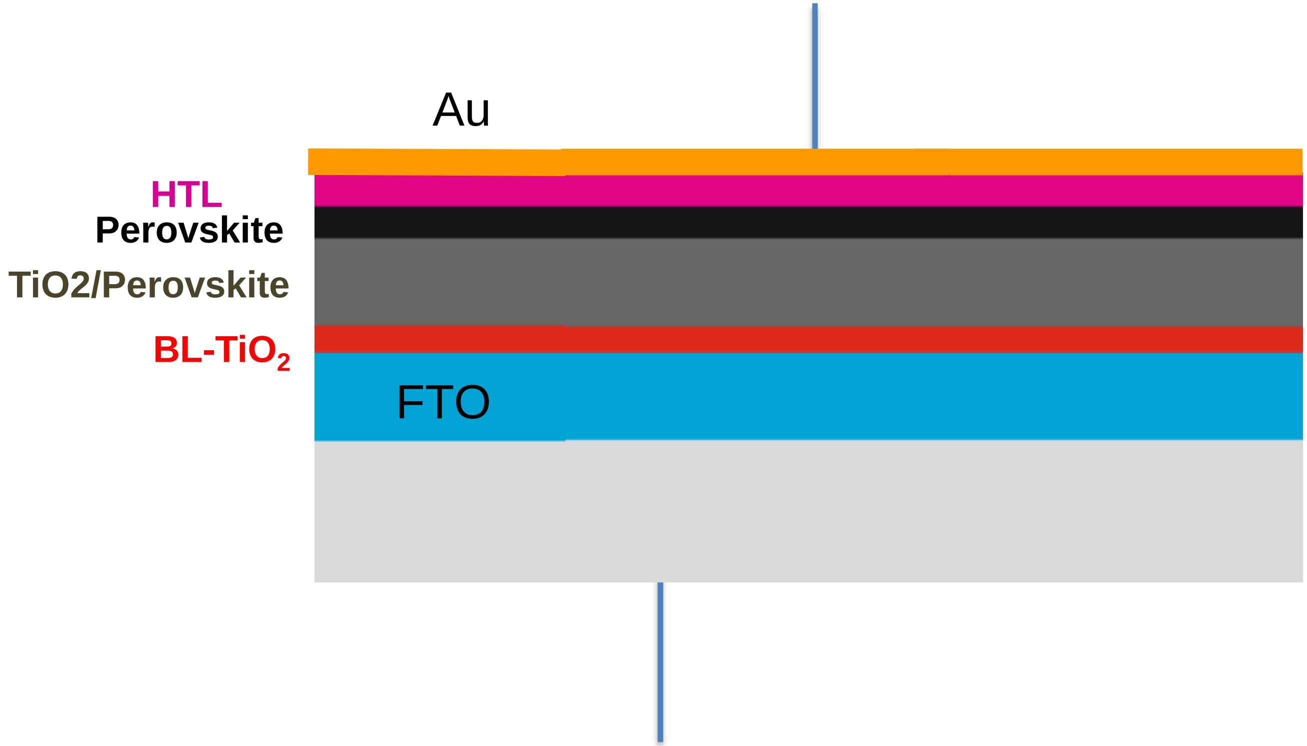
100 cm^2



?

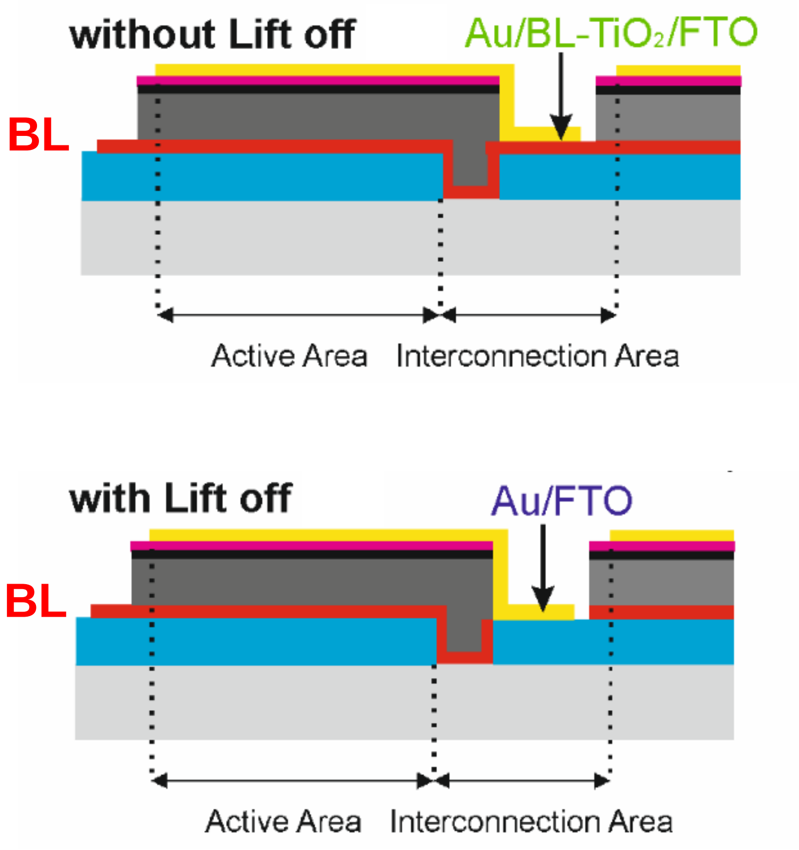
Perovskite module: Monolithic integration

Patterning of C-TiO_2, Perovskite and HTM. **Very critical**

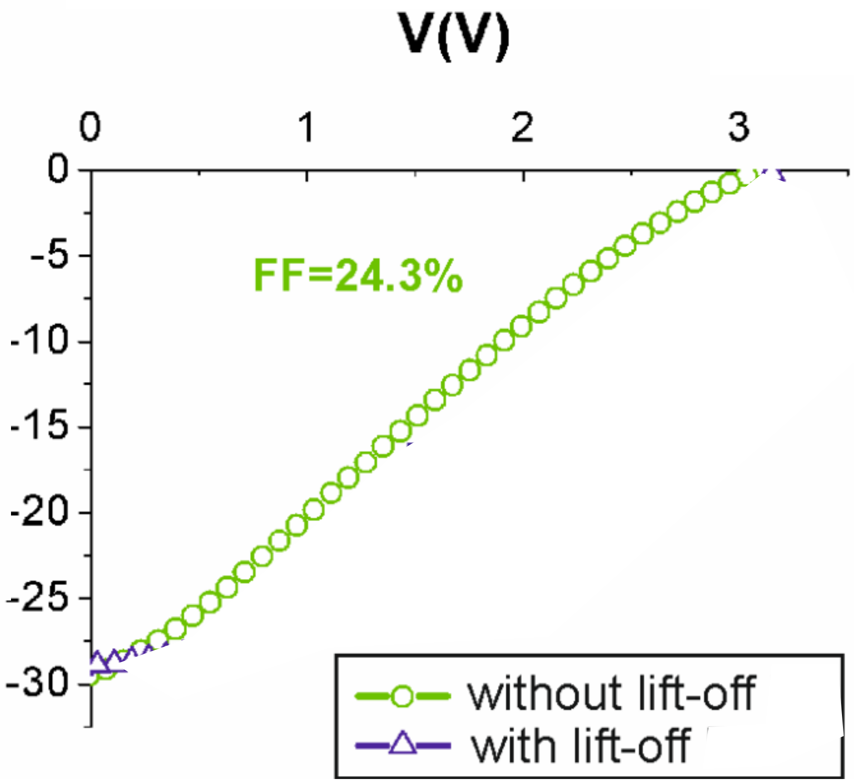


Scribing of the FTO.
Easy: laser (CO_2 etc.)

Au/FTO: Influence on the I-V characteristics



TLM meas.	L_t [mm]	R_C [Ω]
Au/BL-TiO_2/FTO	3.6	2.607



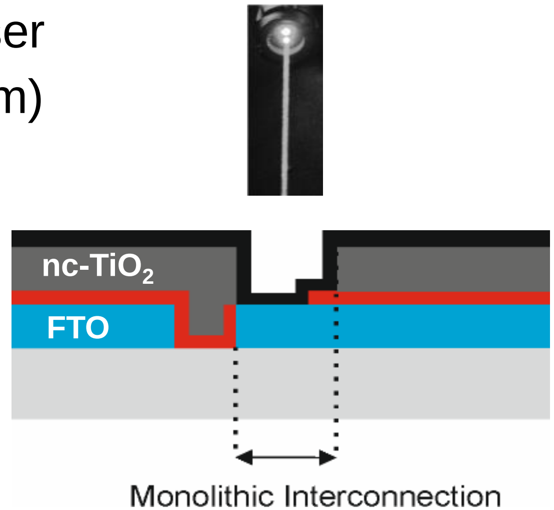
F. Matteocci et al. Prog. Photovoltaics 24, (2016) 436

Laser Patterning Procedures (LPP)

$LPP_{PEROVSKITE}$

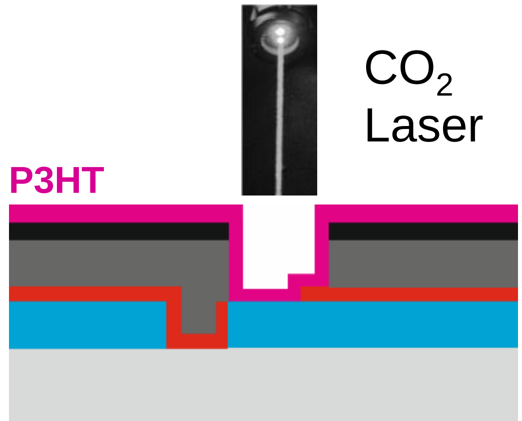
CO_2 Laser
(λ=10µm)

Perovskite
BL-TiO_2



LPP_{P3HT}

P3HT



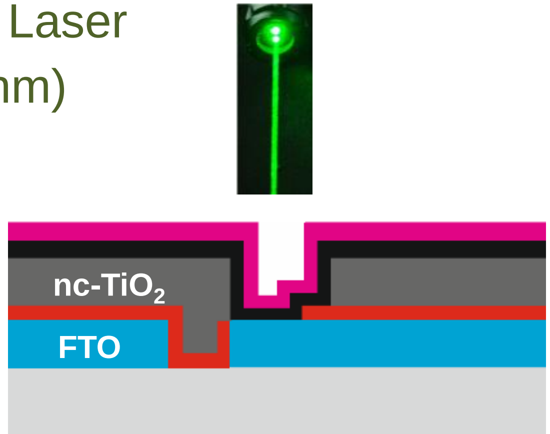
CO_2
Laser

Au deposition

$LPP_{PEROVSKITE/P3HT}$

Nd:YVO_4 Laser
(λ=532nm)

P3HT
Perovskite
BL-TiO_2



Au deposition

F. Matteocci et al. Prog. Photovoltaics 24, (2016) 436

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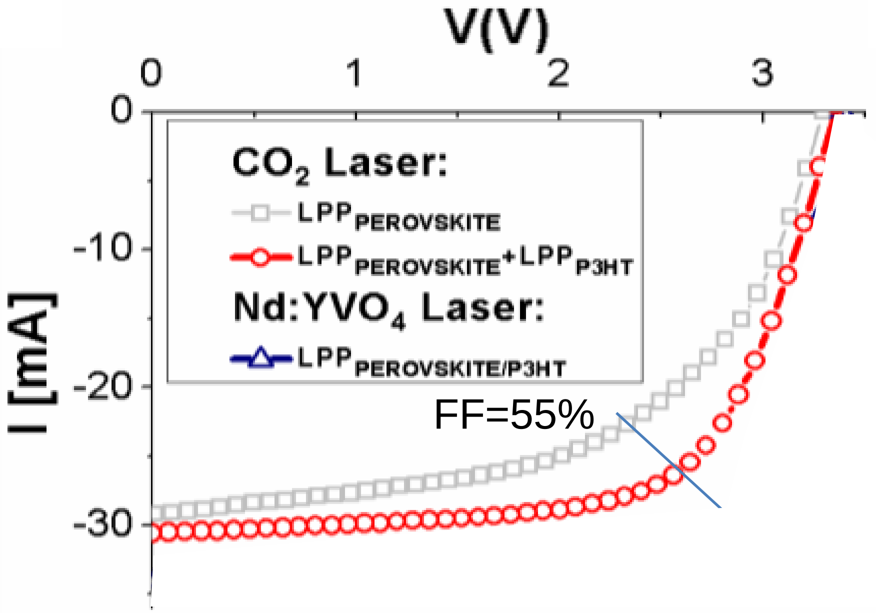
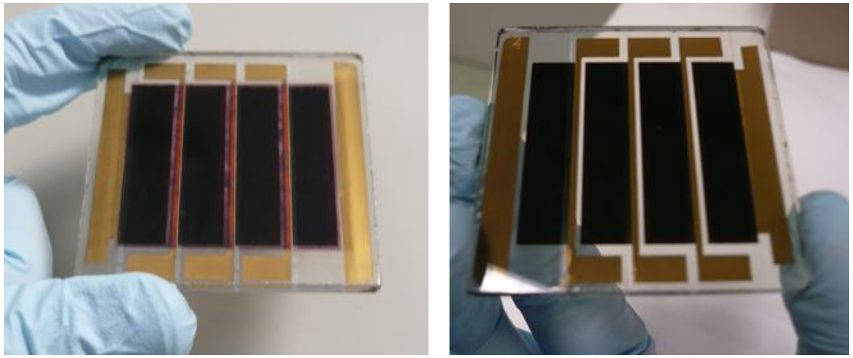
Optimization of the laser patterning



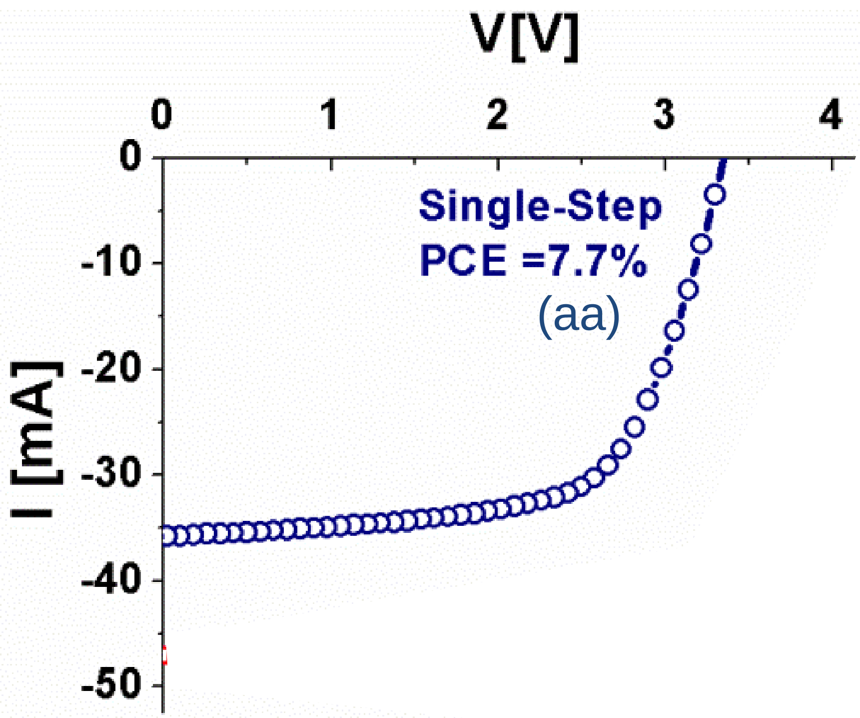


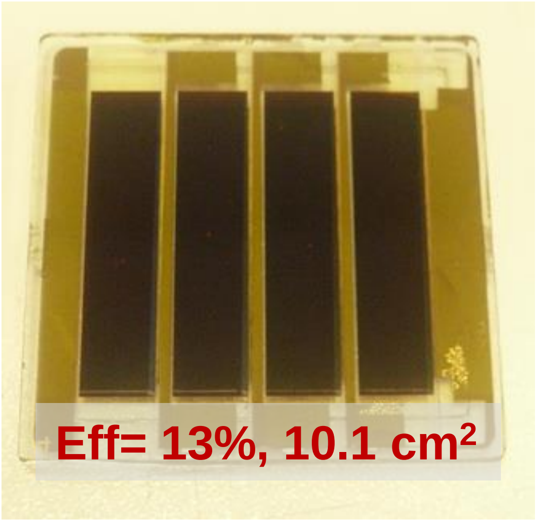
10.1 cm^2 active area

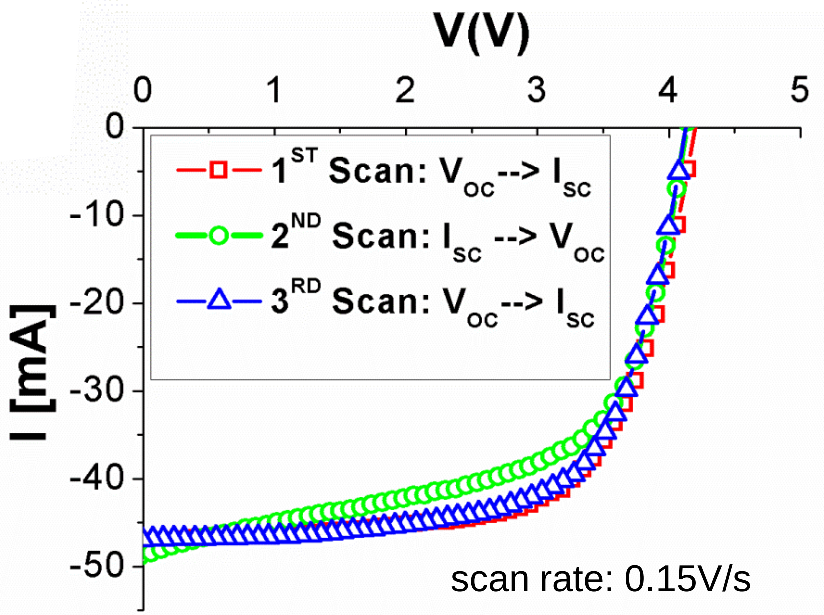
Module number	Layer	Patterning	V_{OC} [V]	J_{SC} [mA/cm^2]	FF (%)	PCE (%)
Modules 1-2	PEROVSKITE	CO_2 LASER	**3.27**	**-11.6**	**55.4**	**5.3**
	P3HT	Chemical Etch				
Modules 3-4	PEROVSKITE	CO_2 LASER	**3.34**	**-12.1**	**66.1**	**6.7**
	P3HT	CO_2 LASER				

F. Matteocci et al. Prog. Photovoltaics 24, (2016) 436

Spiro-OMeTAD Modules: one vs two step







Very limited hysteresis effect

$$\frac{J_{RS}(\tilde{V}) - J_{FS}(\tilde{V})}{J_{RS}(\tilde{V})} = 0.065$$

$$\tilde{V} = 0.8V_{OC}$$

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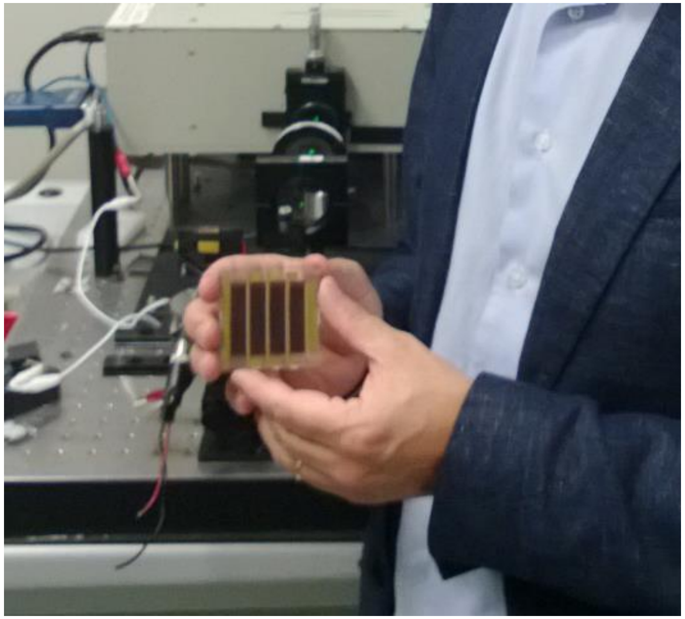
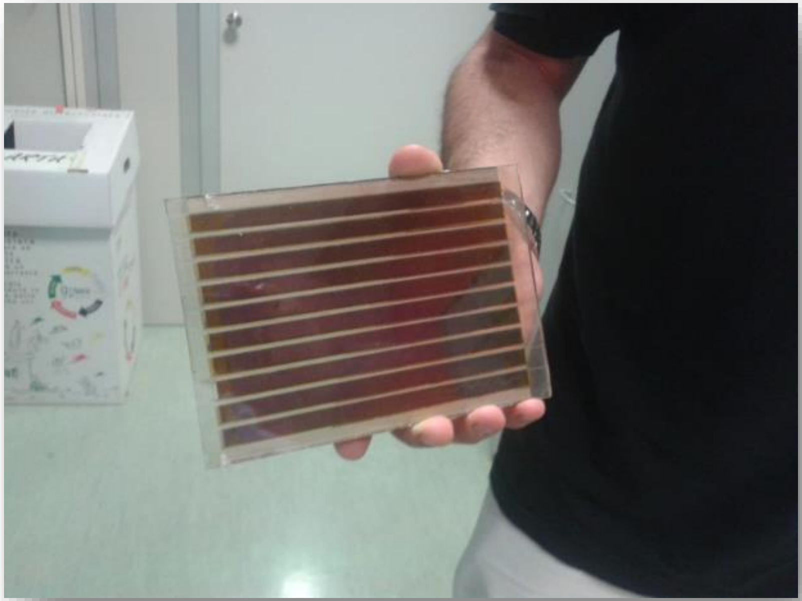
From modules to MODULES

10 cm^2



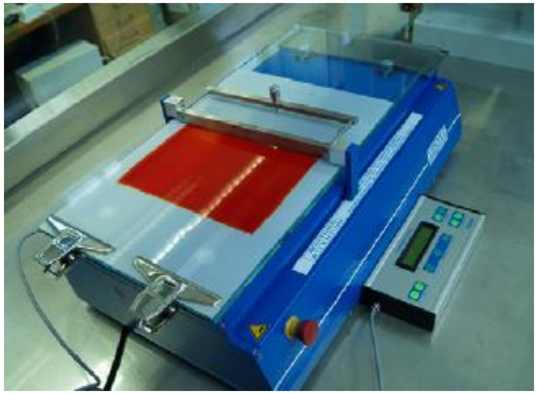
100 cm^2

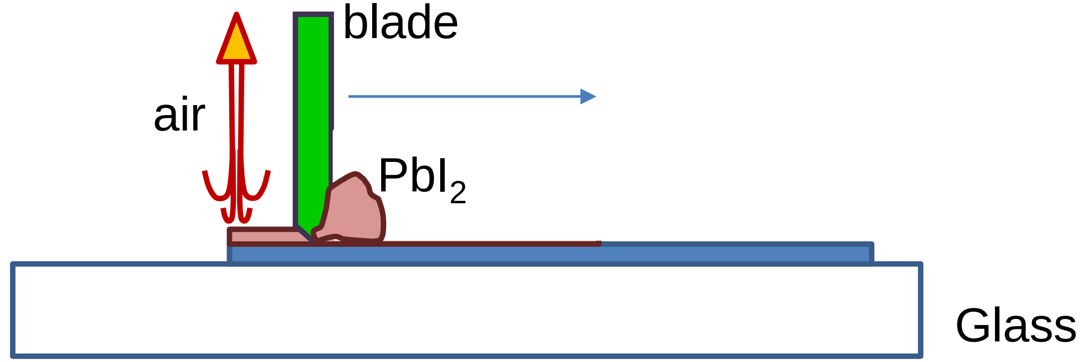


?

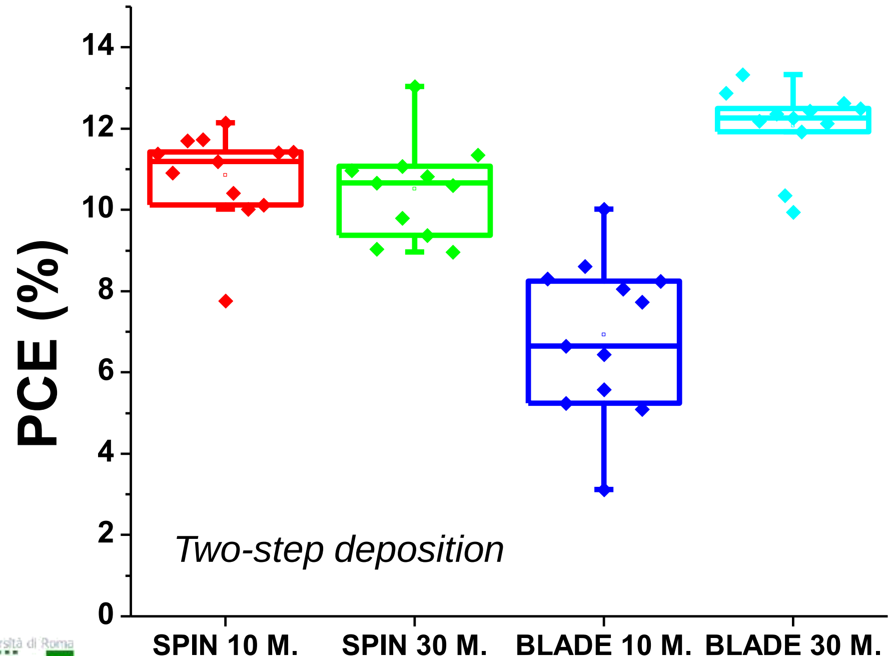
10 x

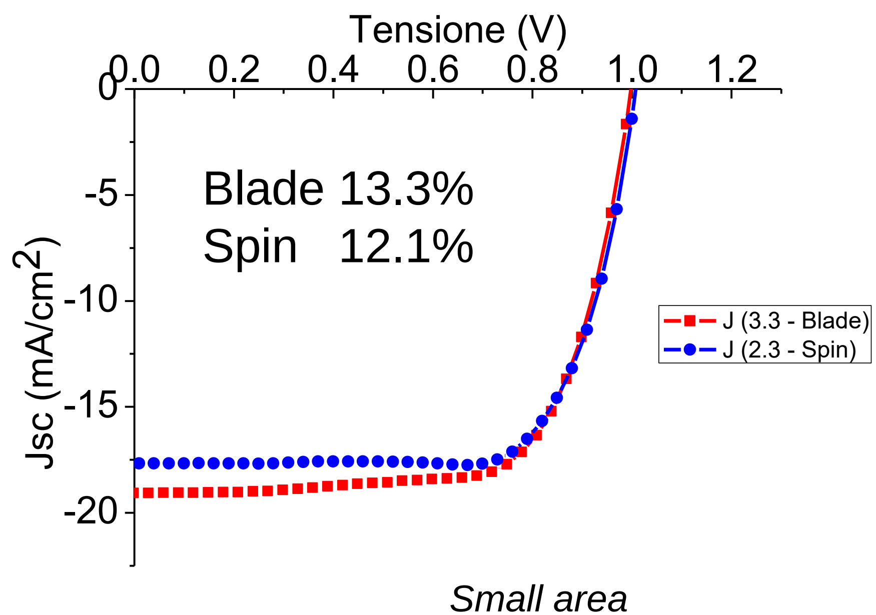
From spin coating to air-assited blade coating





A new high performing air-assisted blade coating technique for perovskite printing





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S. Razza et al. J. Power sources 277, 286 (2015)

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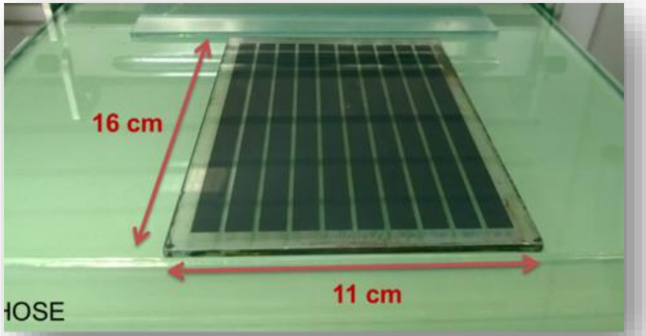
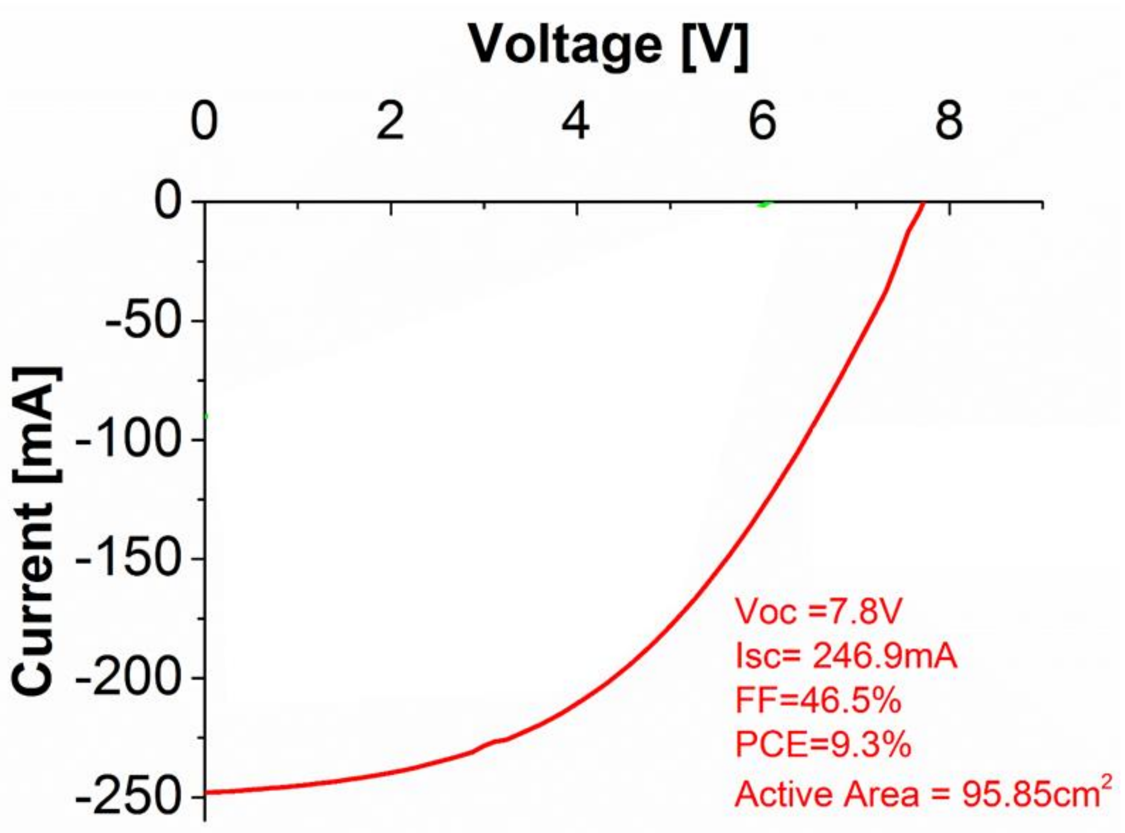
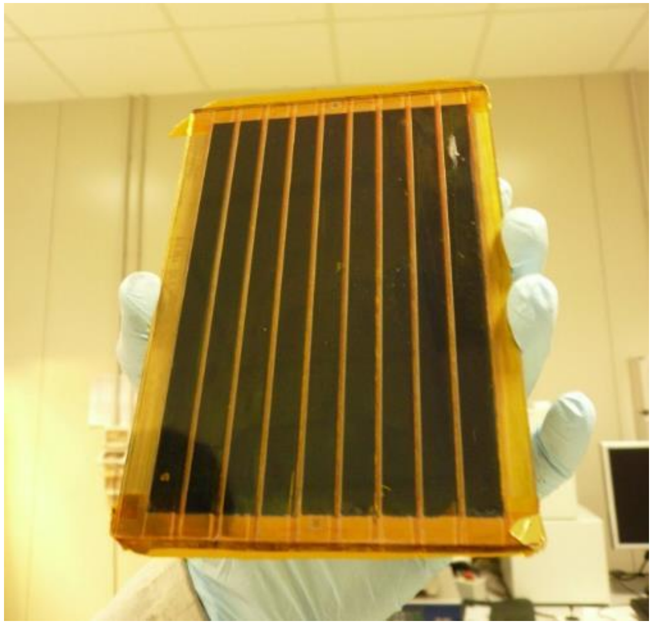
Scaling-up of perovskite modules (100 cm2)

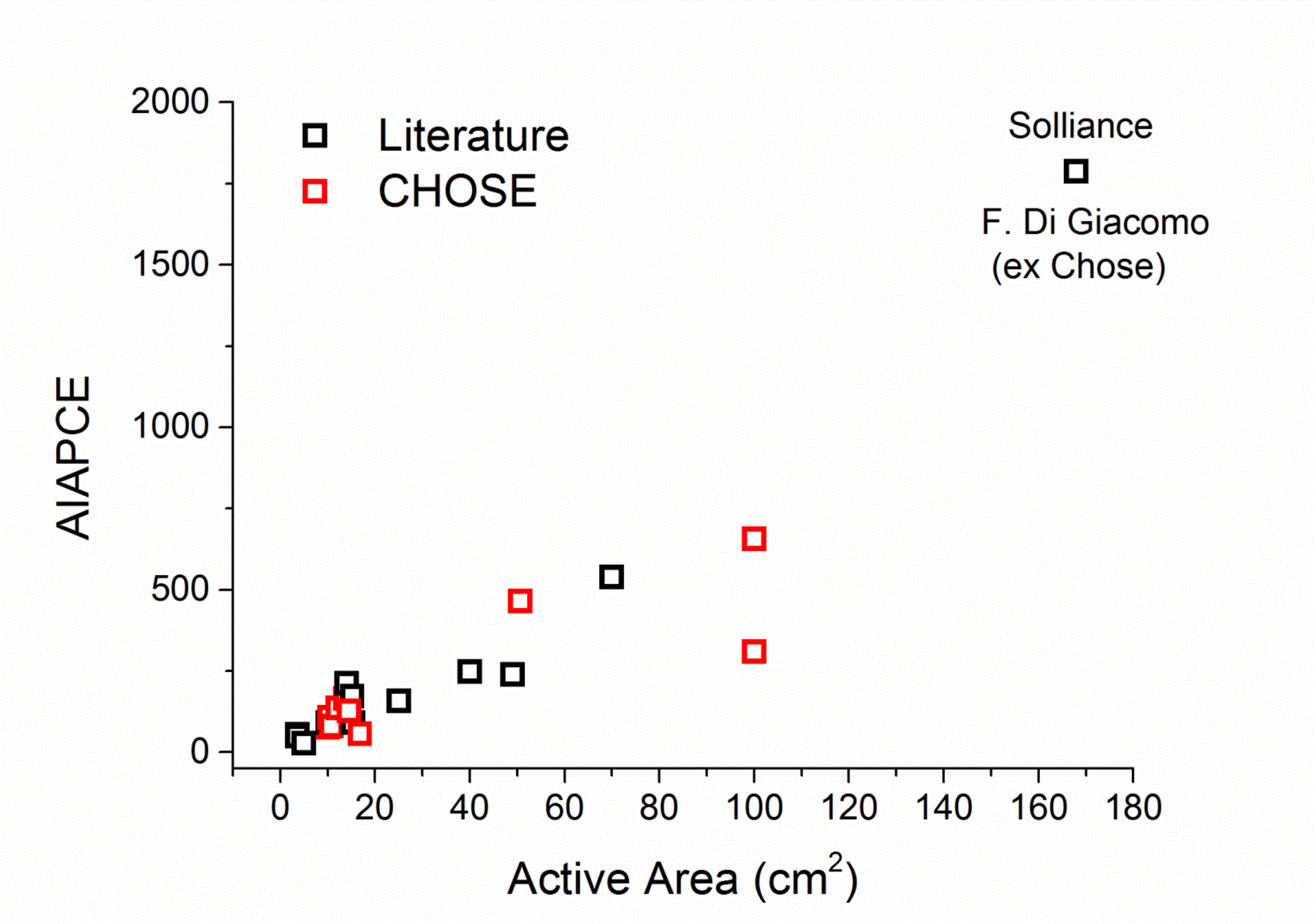


Optimized blade coating deposition



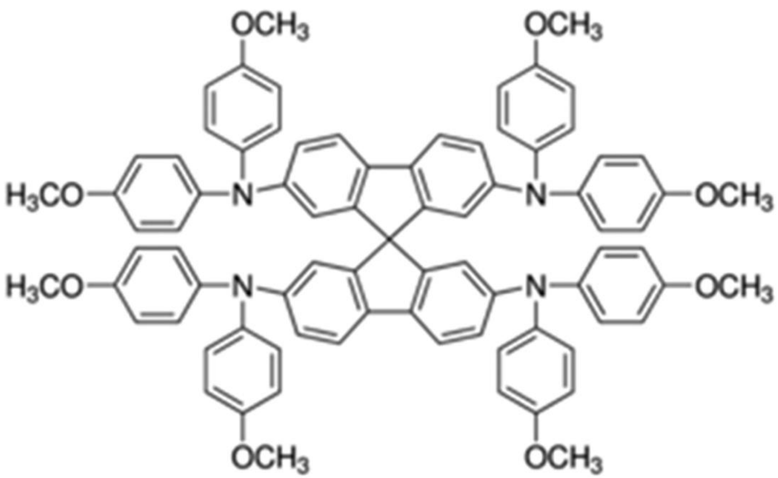


Large area PSK modules



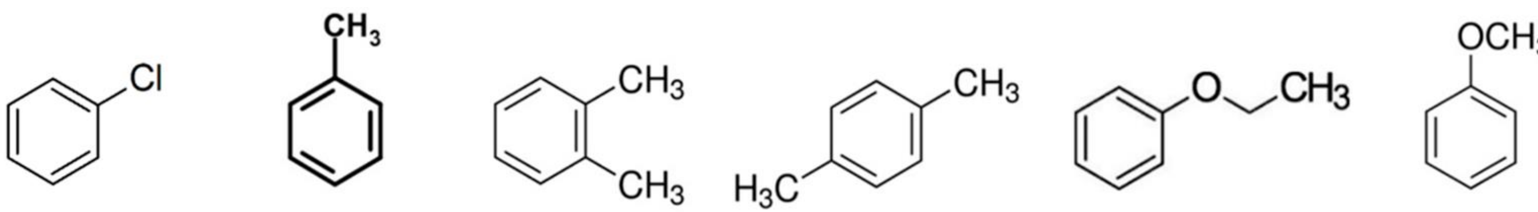
Palma et al., *IEEE Journal of Photovoltaics*, 2017, 10.1109/JPHOTOV.2017.2732223

Non Chlorinated solvent for HTM



Spiro-OMeTAD

Commonly used as HTM for PSC, diluited in Chlorobenzene which is not suitable for scalable process



	Chlorobenzene	Toluene	o-Xylene	p-Xylene	Phenetole	Anisole
Boiling Point:	132°C	110°C	143°C	138°C	170°C	154°C
Surface Energy:	33.5 mN/m @ 20 °C	27.73 mN/m @ 25 °C	29.76 mN/m @ 20 °C	28.01 mN/m @ 25 °C	38.77 mN/m @ mel.point	35 mN/m @ 20 °C
OSHA limits 8 hours total weight average:	75 ppm	100 ppm	100 ppm	100 ppm	---	---

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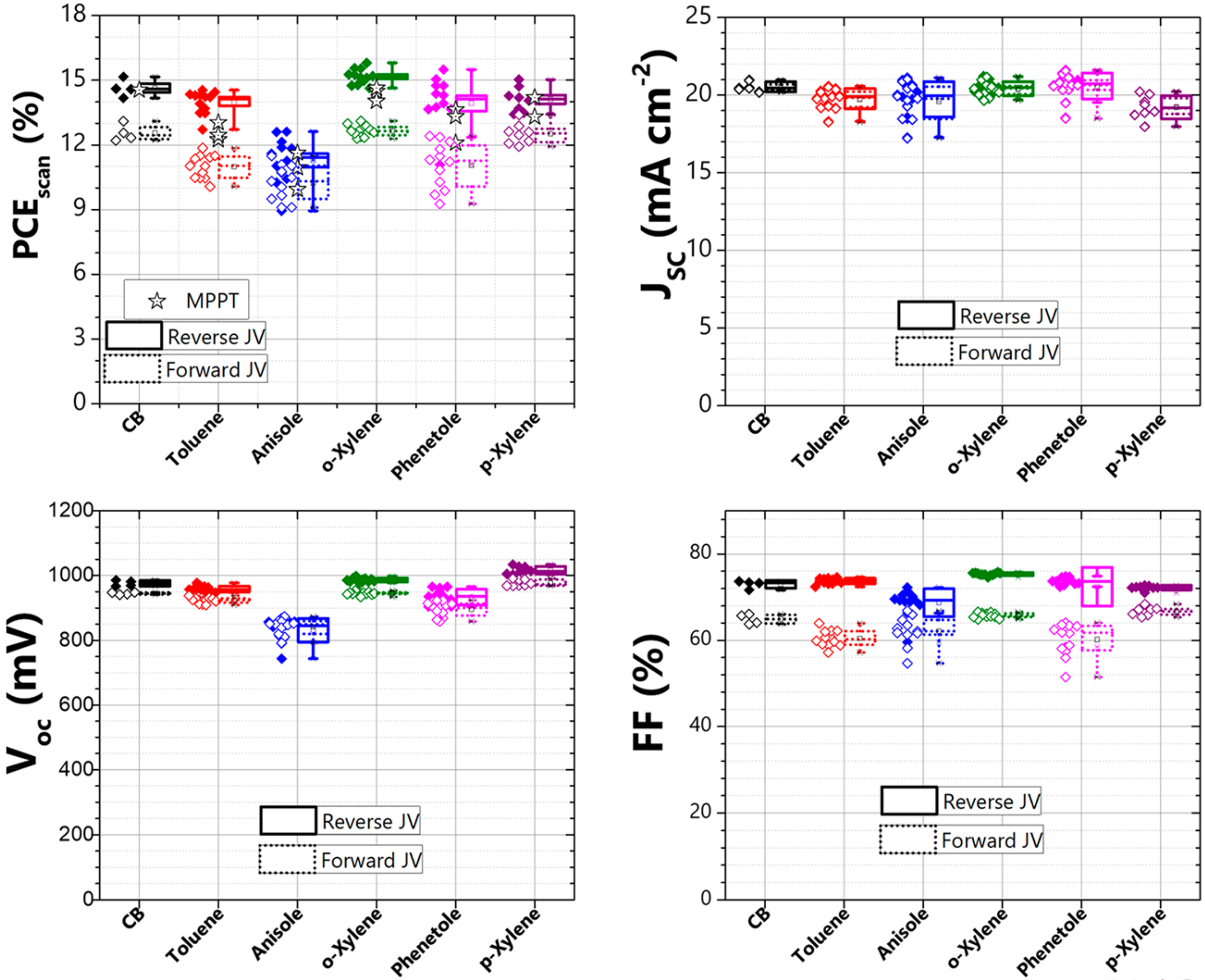
F.Isabelli et al. ACS applied energy Materials, 10.1021/acsaem.8b01122

Non Chlorinated solvent for HTM



F.Isabelli et al. ACS applied energy Materials, 10.1021/acsaem.8b01122

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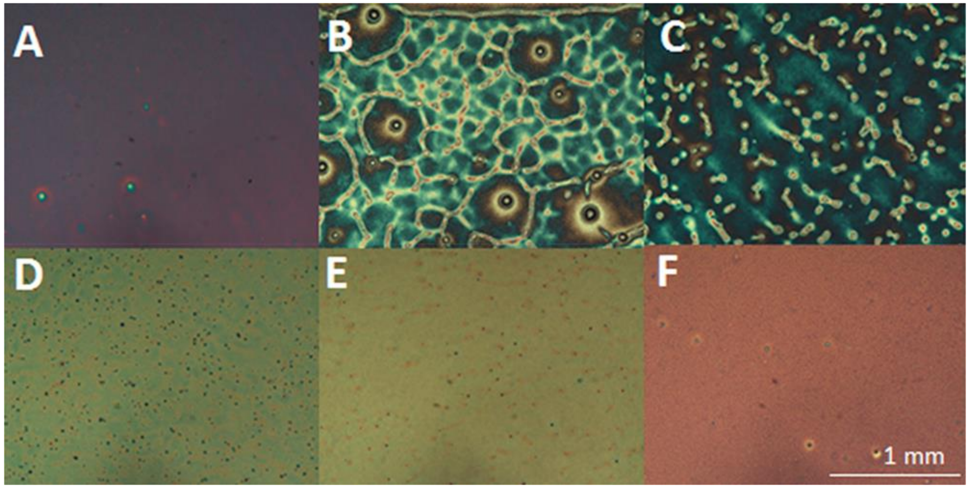
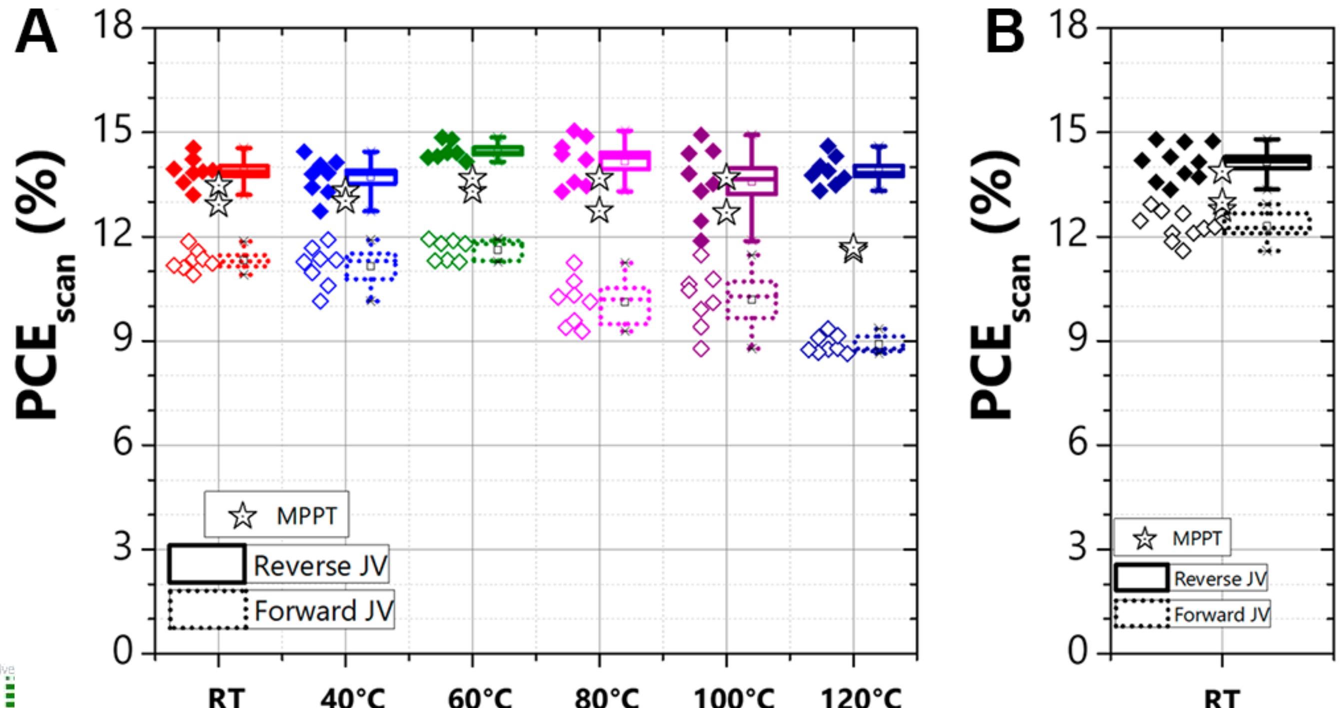
Non Chlorinated solvent for HTM



Optical microscope images of spiro-OMeTAD layer deposited from different solvents: (A) chlorobenzene, (B) anisole, (C) phenetole, (D) o-xylene, (E) p-xylene, and (F) toluene



A) Spin coating with different postannealing temperatures after the deposition of spiro-OMeTAD and

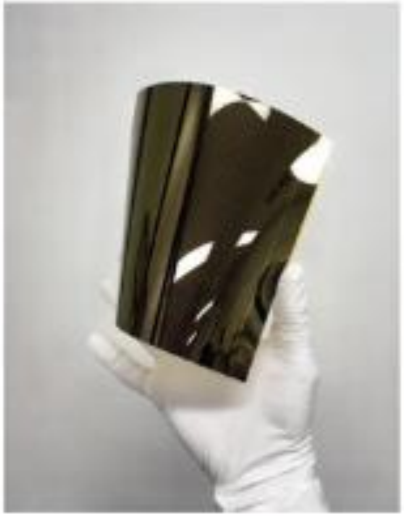
B) Doctor blading

F.Isabelli et al. ACS applied energy Materials, 10.1021/acsaem.8b01122

Perovskite on flexible substrate

(a)

(b)



Perovskite layer slot die coated on Solliance's R2R line @ Solliance.

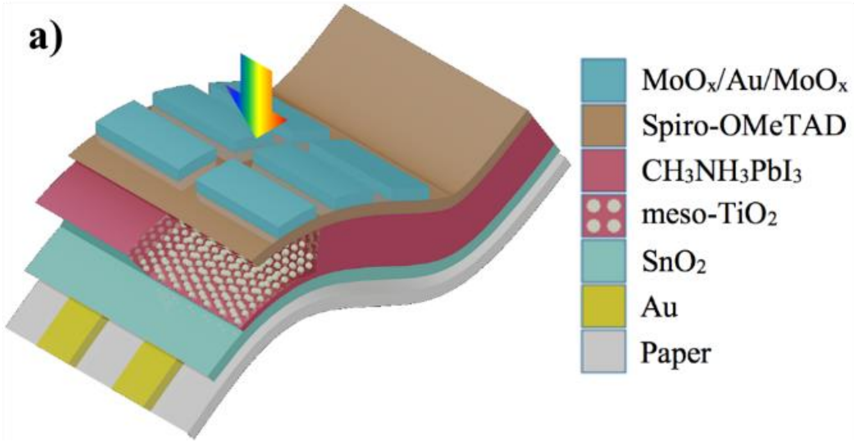
b) R2R produced flexible perovskite PV module with aperture area of 160 cm2 and PCE of 10.1%.

https://www.solliance.eu/2017/solliance-sets-world-record-for-roll-to-roll-produced-perovskite-based-solar-cells-with-a-stabilized-efficiency-of-126/

https://www.solliance.eu/2017/solliance-sets-more-world-records-for-r2r-perovskite-solar-cells-and-modules/

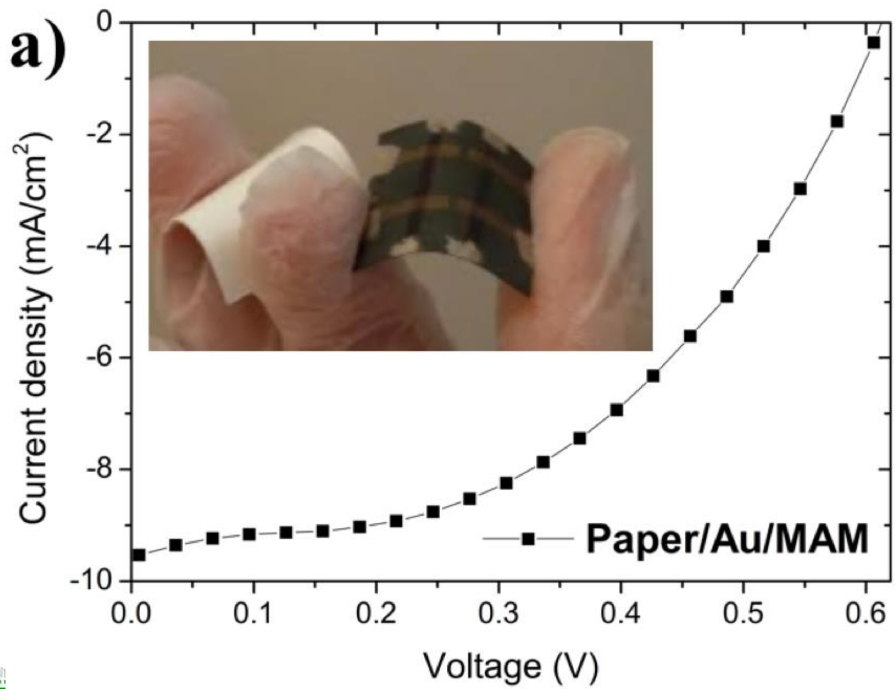
Y. Galagan et al. Adv. Eng. Mater. 2018, 1701190

PSC on unconventional substrates: Paper



First perovskite solar cell on paper

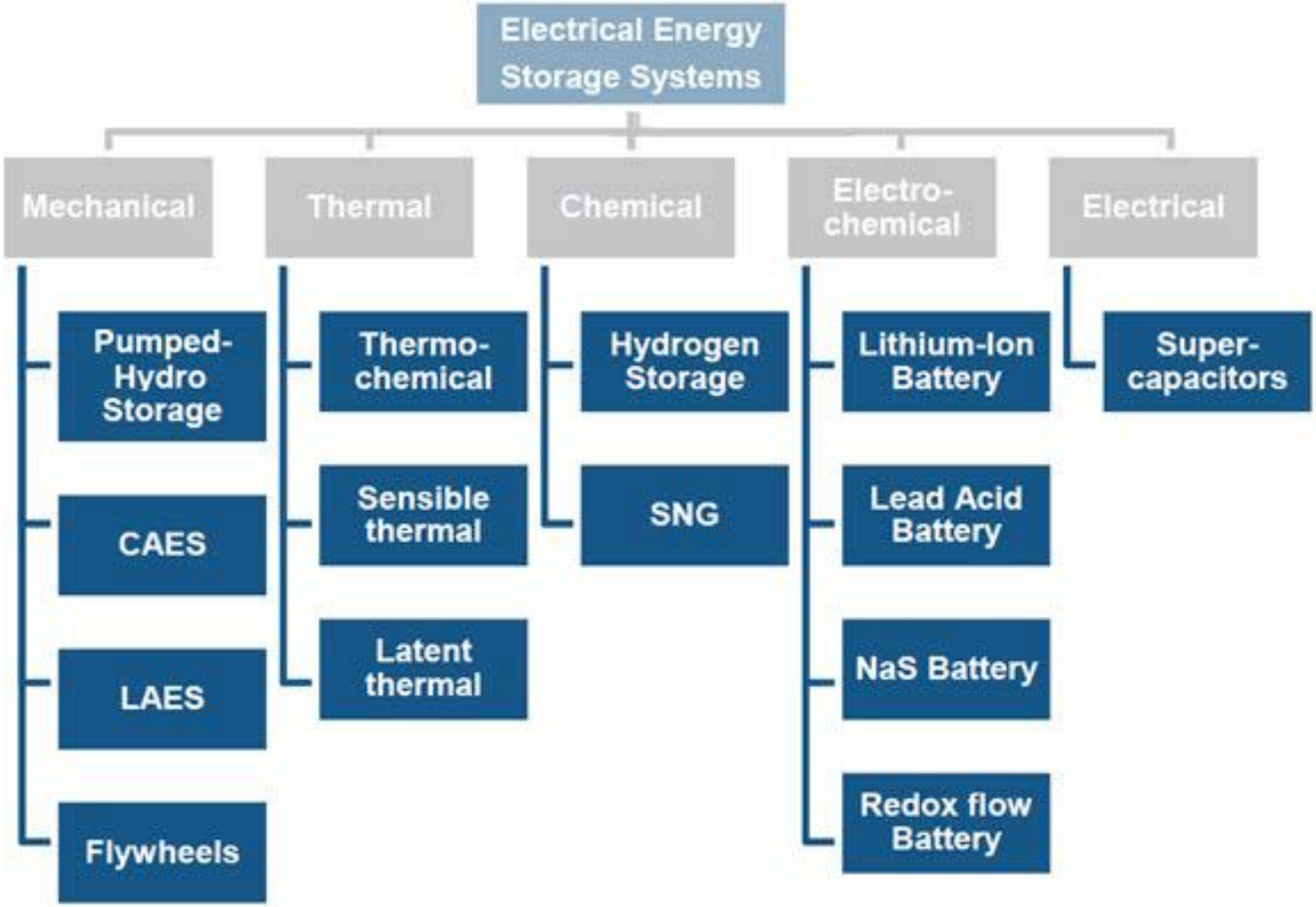
State of the art efficiency (2.7%) for cell on paper



S. Castro et al, IEEE EDL, 2017

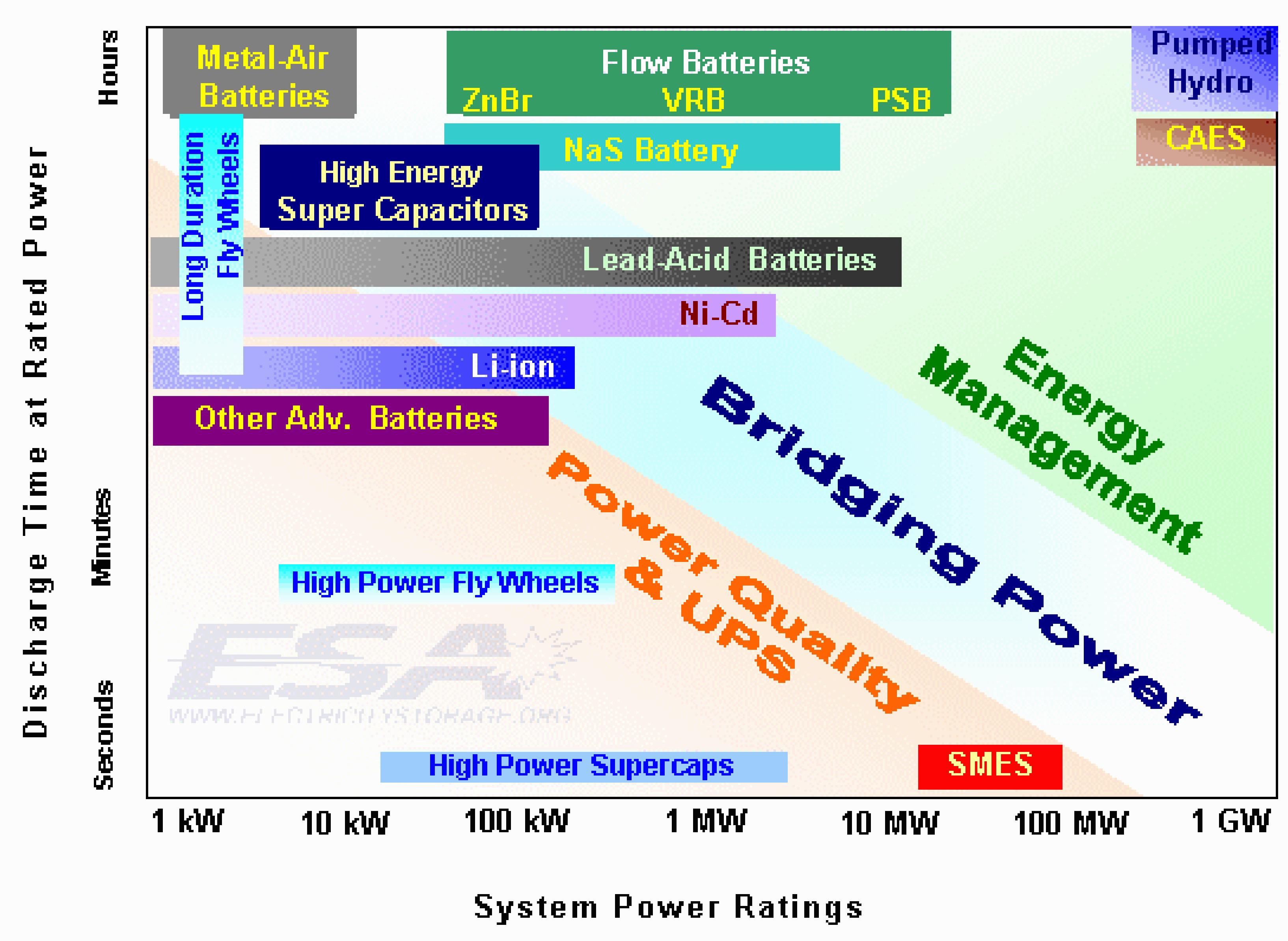
Example 2: Energy storage

Energy storage: several possibilities



CAES = Compressed Air Energy Storage; LAES = Liquid Air Energy Storage; SNG = Synthetic Natural Gas

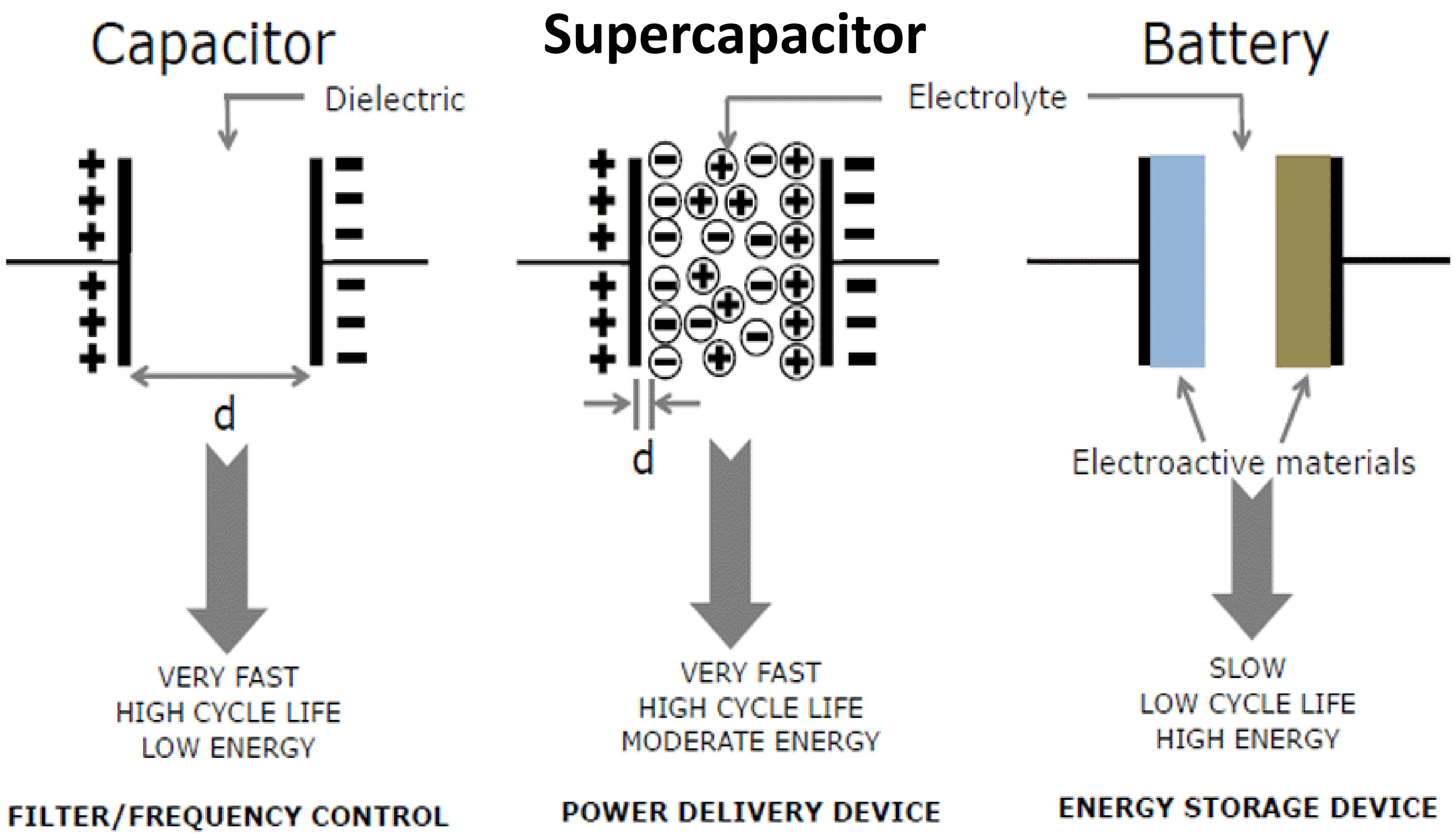
Which type of storage?



Pros and Cons

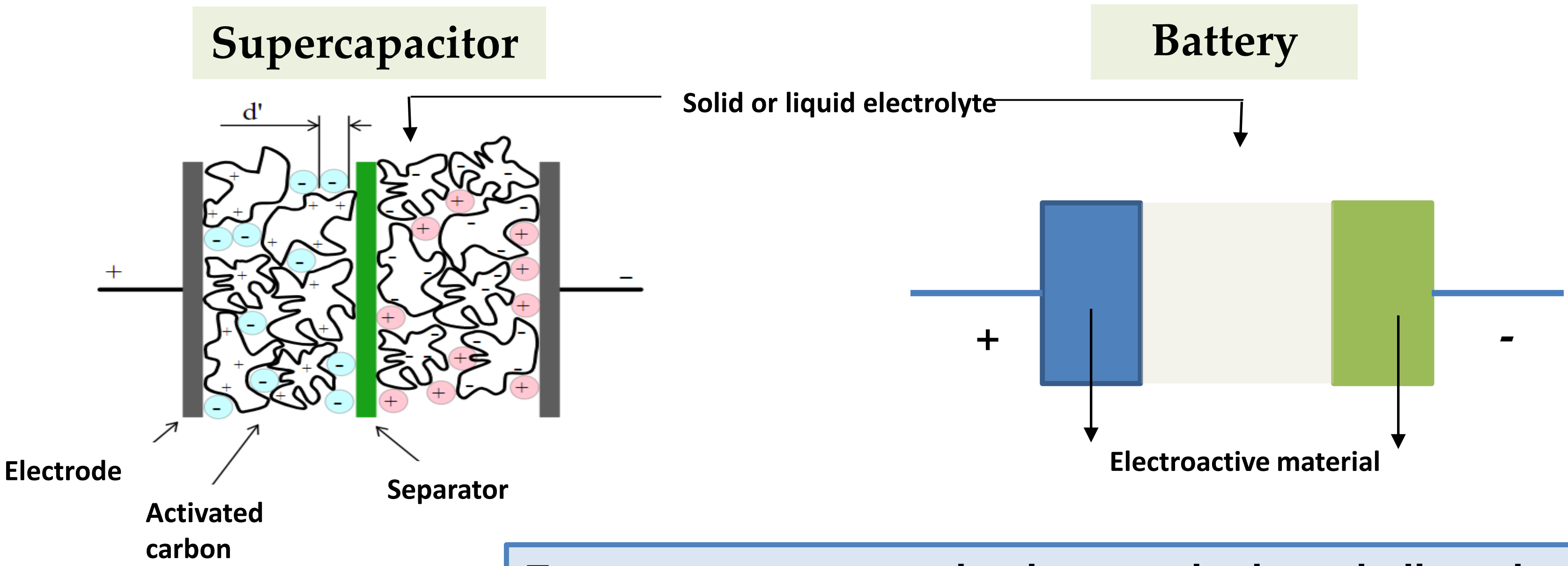
Storage Technologies	Main Advantages (relative)	Disadvantages (Relative)	Power Application	Energy Application
Pumped Storage	High Capacity, Low Cost	Special Site Requirement		●
CAES	High Capacity, Low Cost	Special Site Requirement, Need Gas Fuel		●
Flow Batteries: PSB VRB ZnBr	High Capacity, Independent Power and Energy Ratings	Low Energy Density	◐	●
Metal-Air	Very High Energy Density	Electric Charging is Difficult		●
NaS	High Power & Energy Densities, High Efficiency	Production Cost, Safety Concerns (addressed in design)	●	●
Li-ion	High Power & Energy Densities, High Efficiency	High Production Cost, Requires Special Charging Circuit	●	○
Ni-Cd	High Power & Energy Densities, Efficiency		●	◐
Other Advanced Batteries	High Power & Energy Densities, High Efficiency	High Production Cost	●	○
Lead-Acid	Low Capital Cost	Limited Cycle Life when Deeply Discharged	●	○
Flywheels	High Power	Low Energy density	●	○
SMES, DSMES	High Power	Low Energy Density, High Production Cost	●	
E.C. Capacitors	Long Cycle Life, High Efficiency	Low Energy Density	●	◐

Electrochemical and chemical energy storage devices



J. Xie et al, Journal of Power Sources 401 (2018)

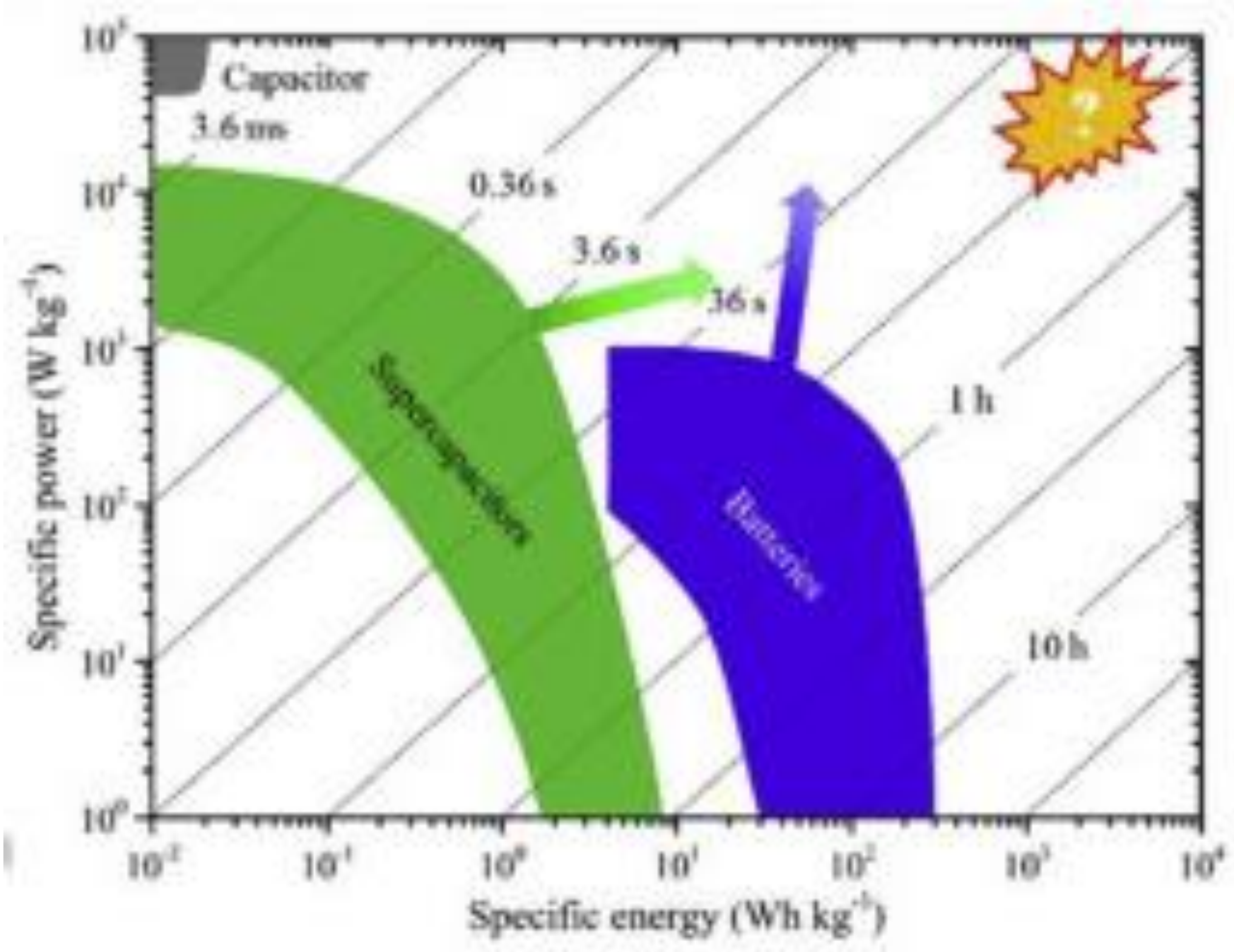
How do they work?



Energy storage mechanism and the similar device configuration/characterization techniques cause confusions.

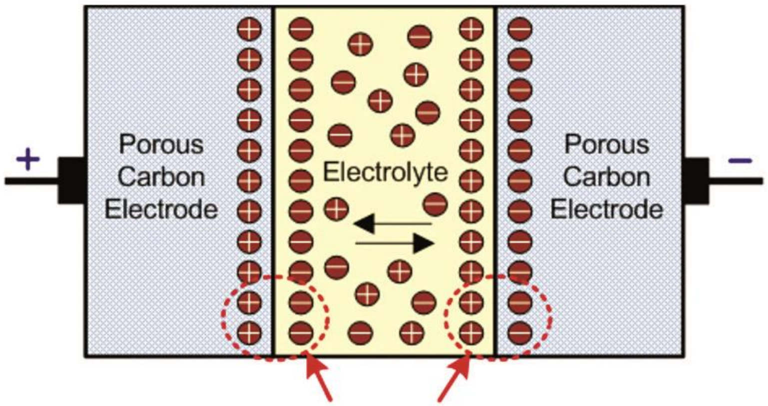
- **Batteries: rapid surface-controlled electrochemical reactions**
- **Supercapacitors: stores energy in the crystal lattices or porous materials through much slower electrochemical reactions with limits from the phase transformation, chemical binding changes or/and reactant diffusions.**

Power vs Energy



J. Xie et al, Journal of Power Sources 401 (2018)

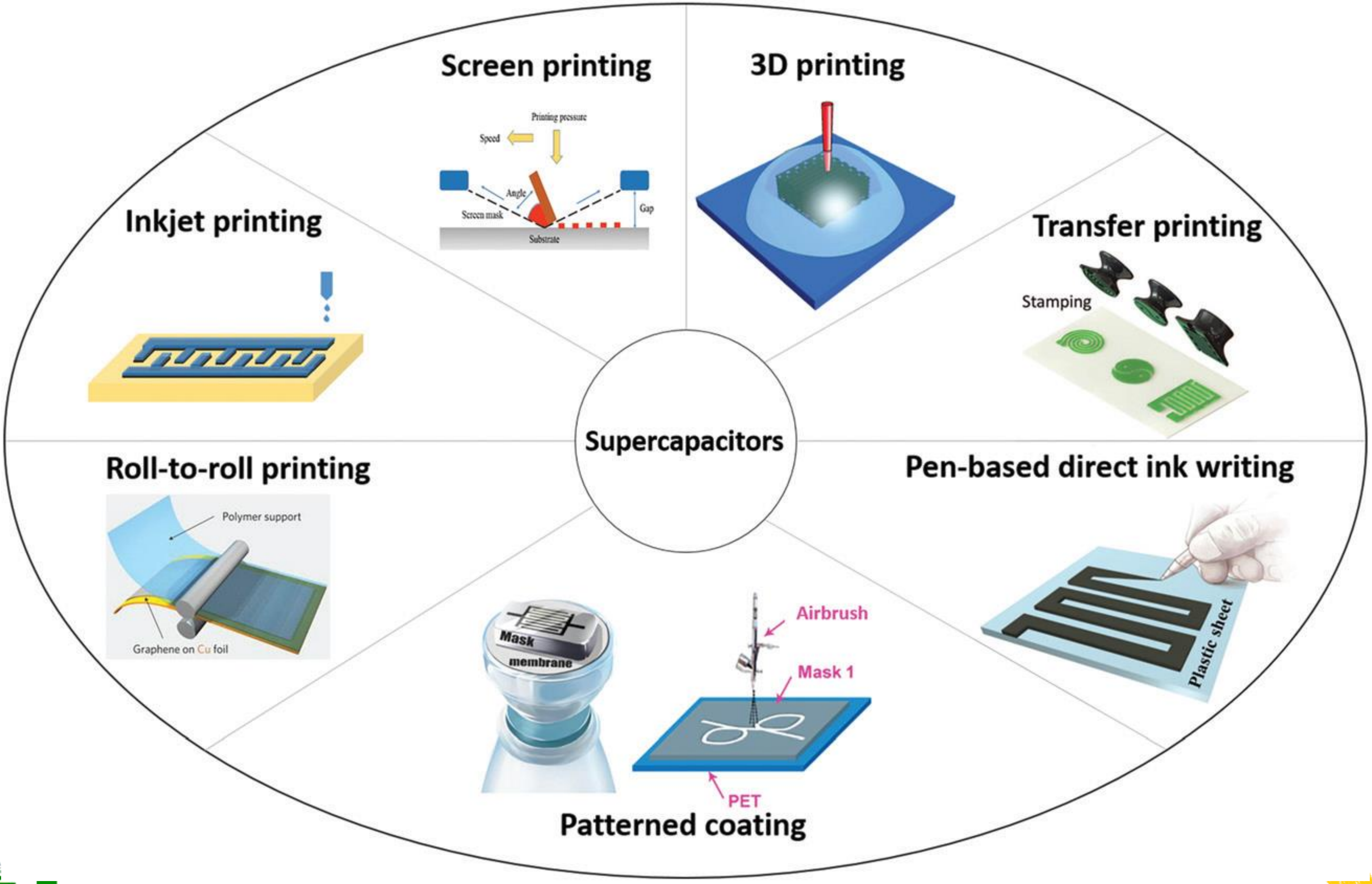
Electric double layer supercapacitors



Electric Double Layer Capacitor (EDLC)

- **EDLCs are supercapacitors that employ electrostatic charge separation only.**
- **The energy storage process of EDLCs takes place at the interface between the electrode surface and the electrolyte**
- **The electrostatic charge transfer is fully reversible, which results in efficient devices with a long life-time**
- **The separator is ion permeable and also prevents short circuits between the electrodes.**
- **The space between the electrodes is filled with electrolyte.**
- **By charging the device, two layers of opposite charge are formed at the interface between the electrode and the electrolyte,**

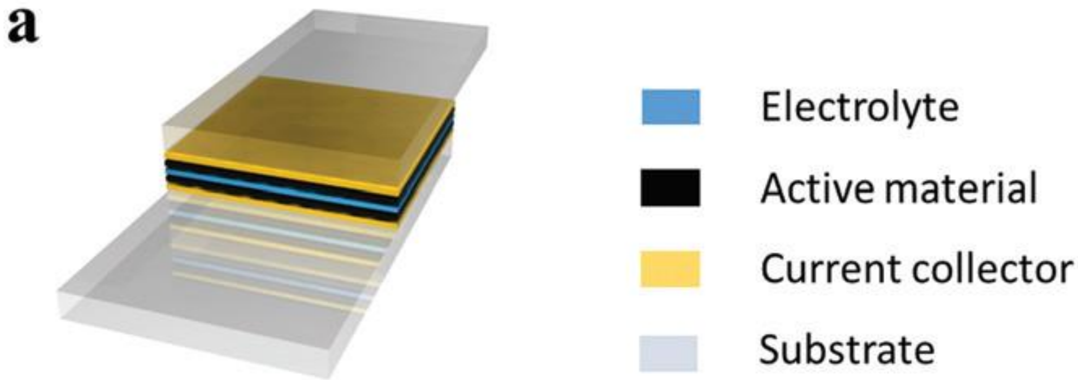
Which printing techniques for Supercaps?

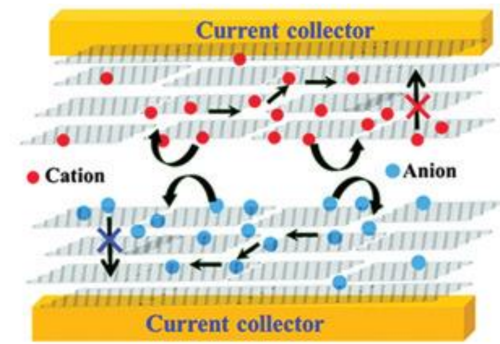


Zang et al. Chem. Soc. Rev., 2019, 48, 3229--3264

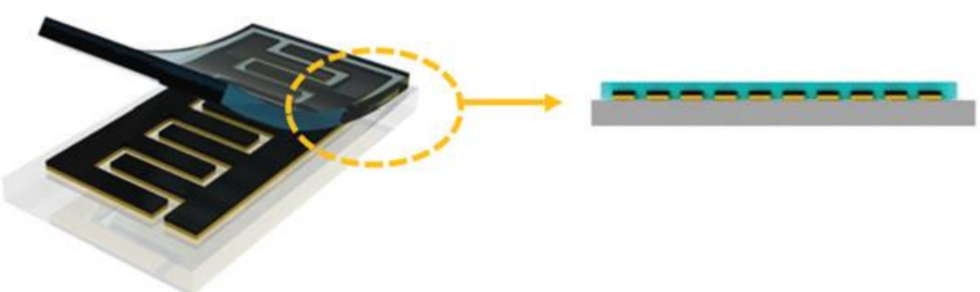
Possible supercap architectures

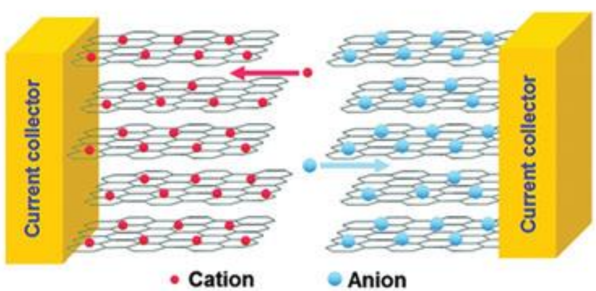
Vertical /sandwich





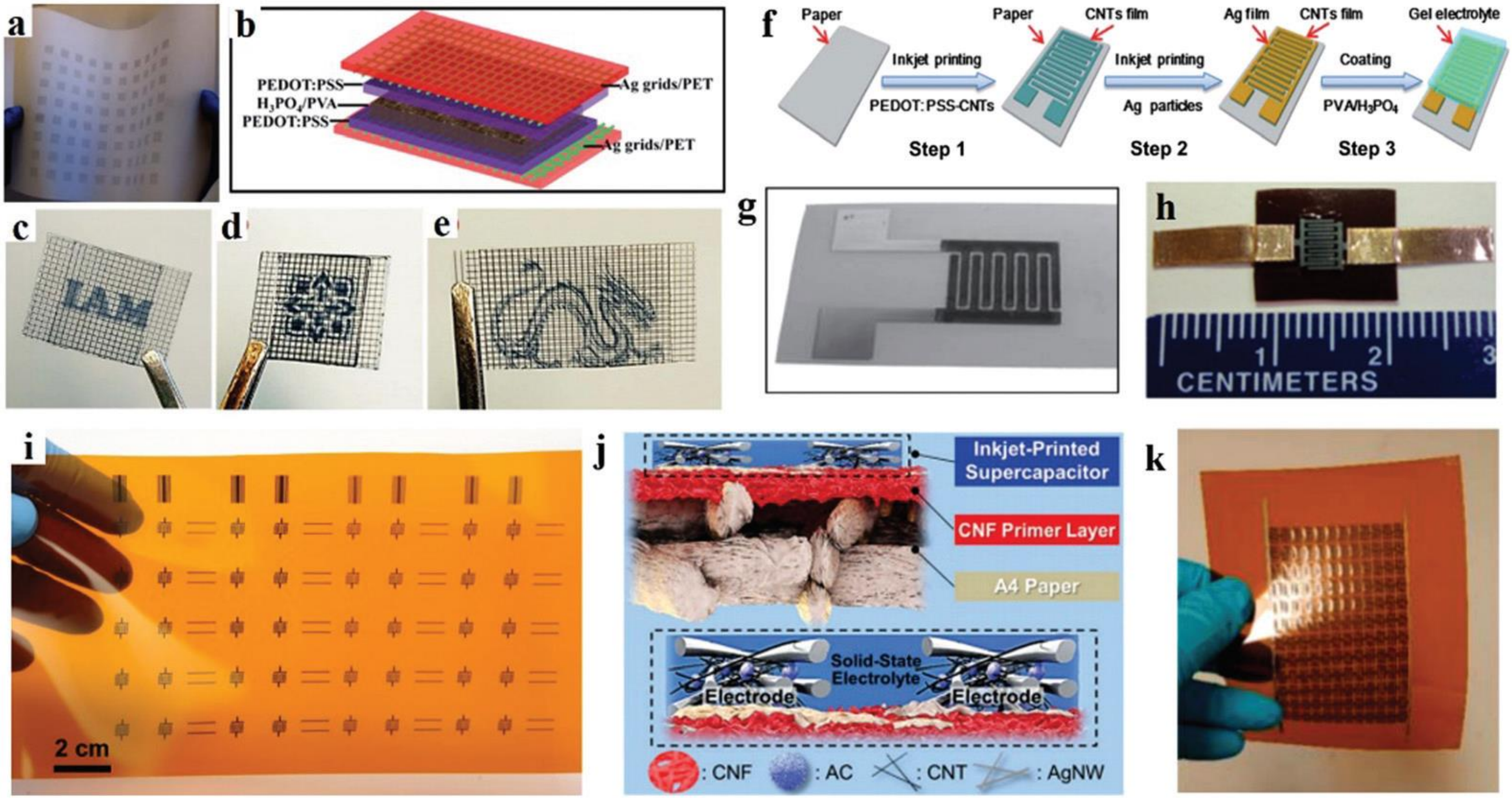
Planar





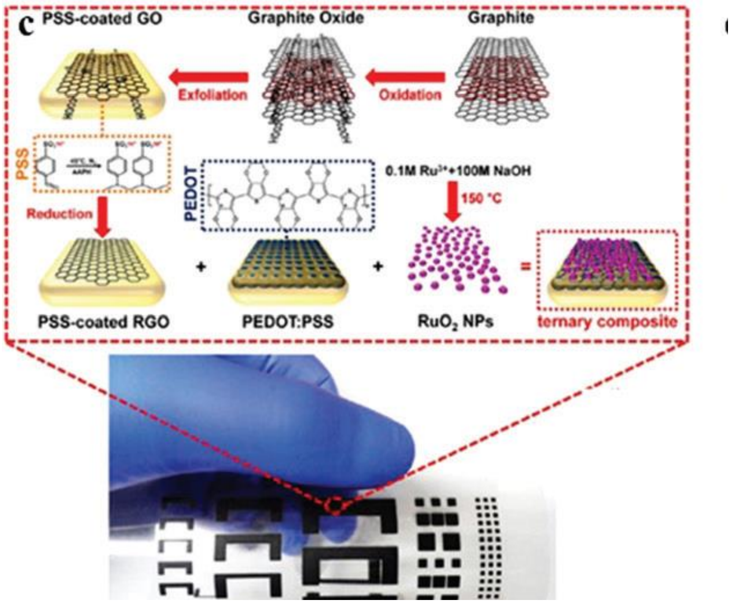
Zang et al. Chem. Soc. Rev., 2019, 48, 3229--3264

Which substrate?

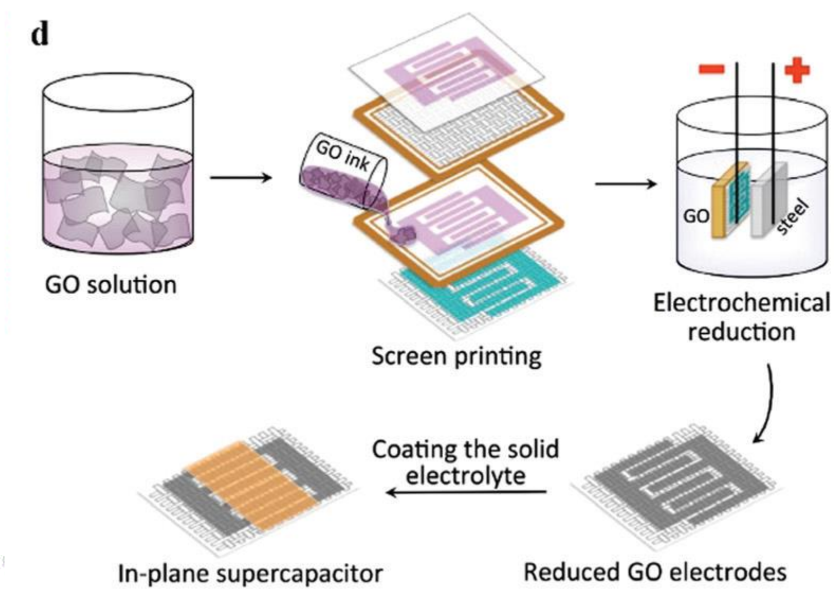


Zang et al. Chem. Soc. Rev., 2019, 48, 3229--3264

Example of screen printed supercap



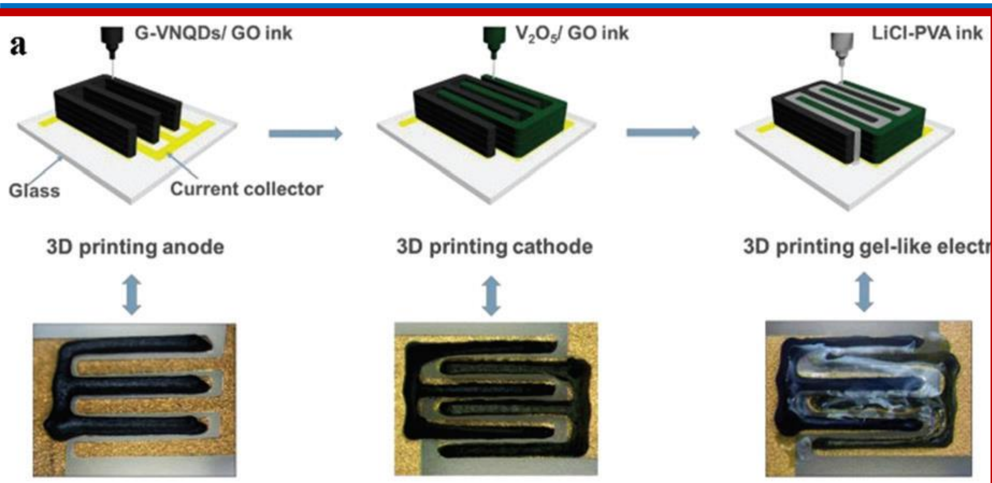
- Simmetric planar supercap
- Electrodes: RuO2/PEDOT:PSS/ graphene
- Electrolyte: 1 M H_2SO_4
- A specific capacitance of 820 F g^{-1}



- Asimmetric planar supercap
- Electrodes: reduced GO
- Electrolyte: H2SO4 PVA gel electrolyte
- Aereal capacitance of 2.5 mF cm^{-2}

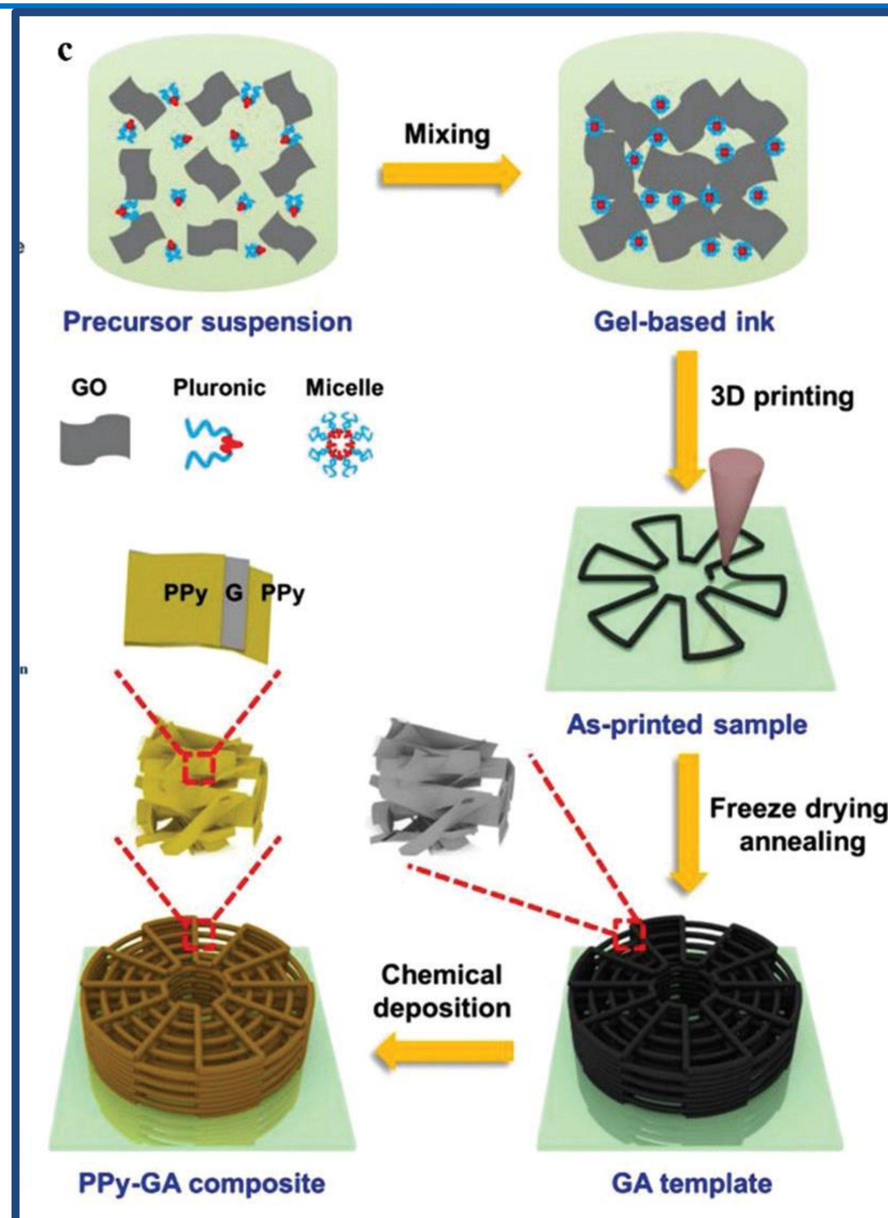
S. Cho, M. Kim and J. Jang, ACS Appl. Mater. Interfaces, 2015, 7, 10213–10227, A. M. Abdelkader, N. Karim, C. Valles, S. Afroj, K. S. Novoselov and S. G. Yeates, 2D Mater., 2017, 4, 035016

3D printed supercap

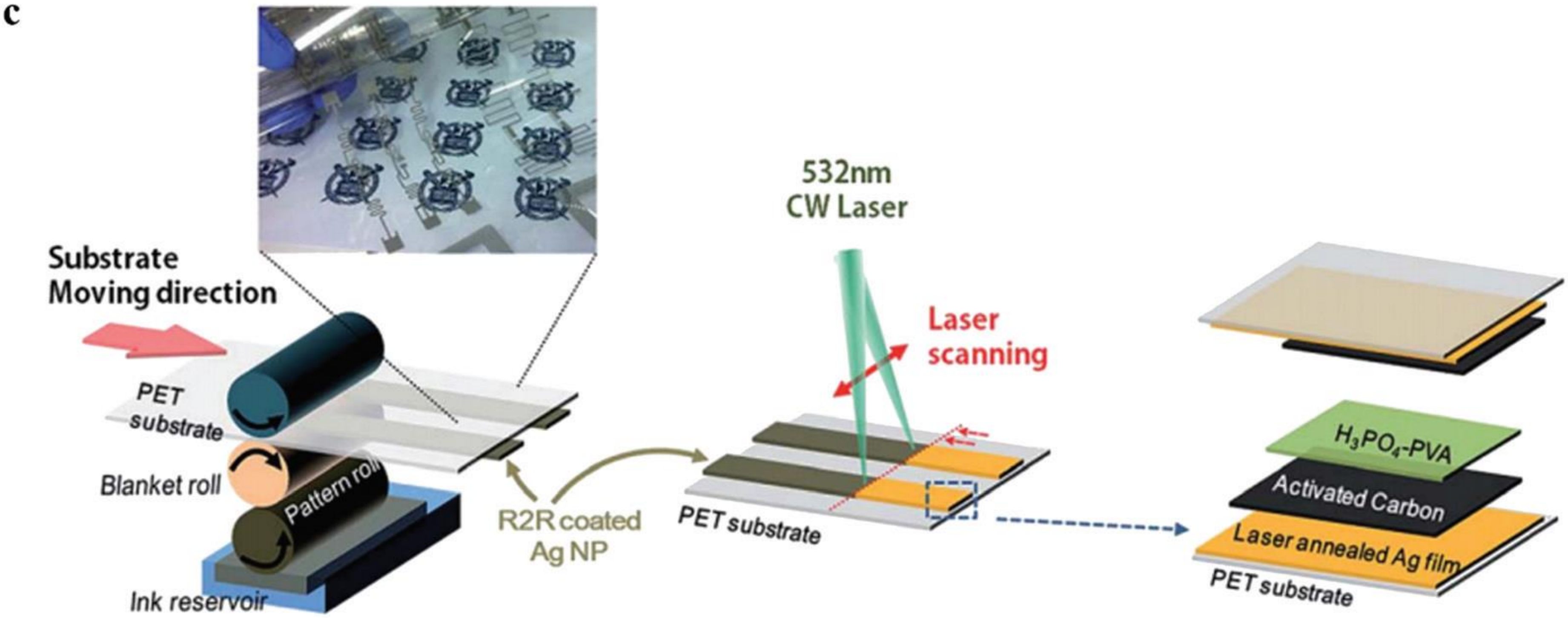


- Asimmetric planar supercap
- Electrodes: V2O5/GO//G-VNQDs/GO
- Electrolyte: PVA/LiCl
- A potential window of 1.6 V, an areal capacitance, of 207.9 mF cm^{-2}, an areal energy density of 73.9 mW h cm^{-2}

- Asimmetric planar supercap
- Electrodes: V2O5/GO//G-VNQDs/GO
- Electrolyte: PVA/LiCl
- A potential window of 1.6 V, an areal capacitance, of 207.9 mF cm^{-2}, an areal energy density of 73.9 mW h cm^{-2}



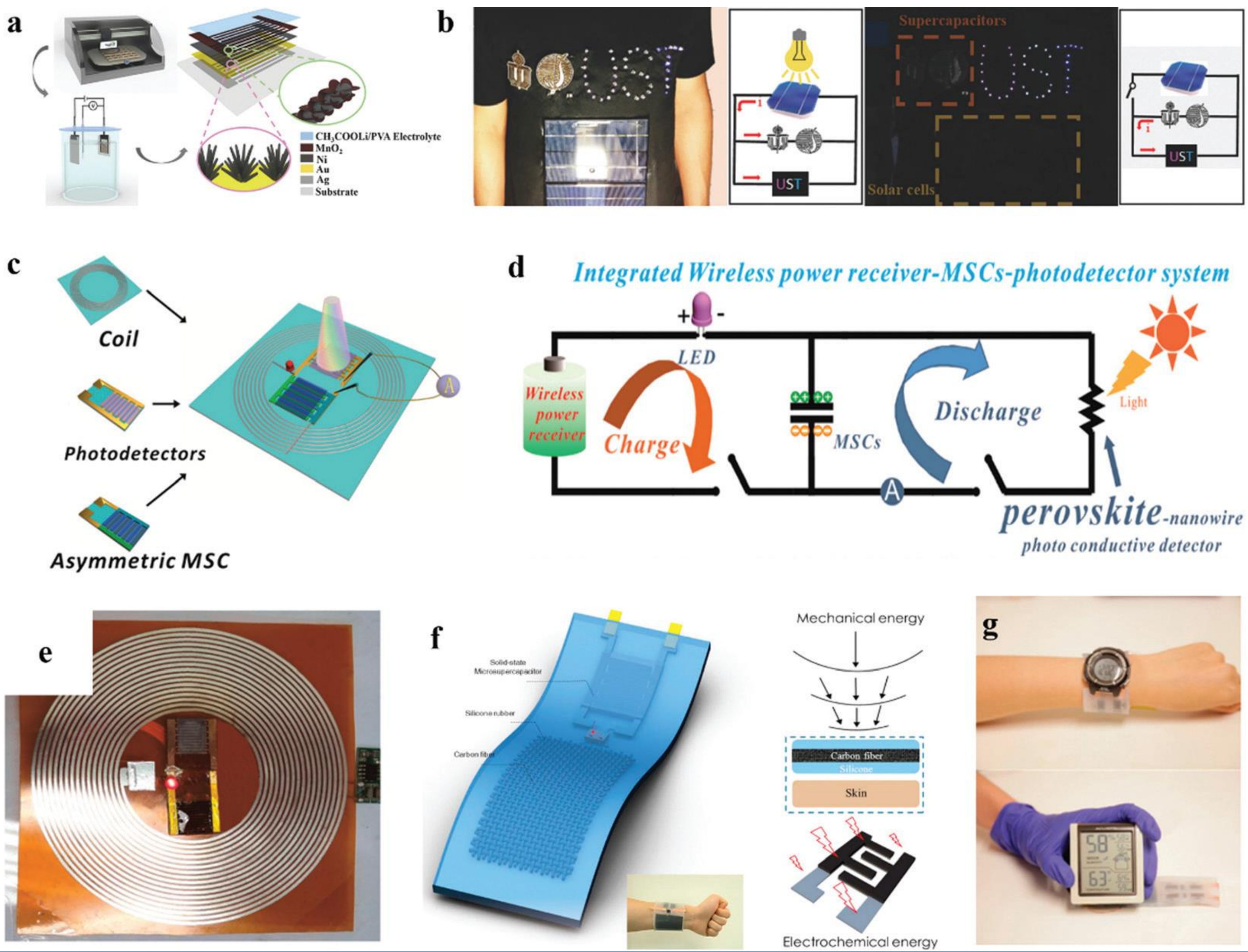
Gravure printing SuperCap



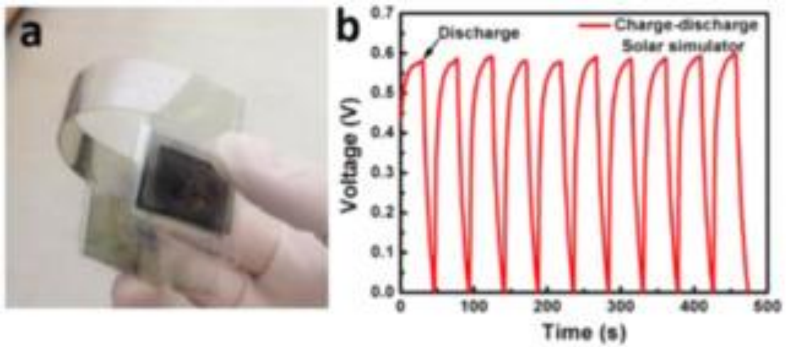
- Symmetric vertical supercap
- Electrodes: Activated carbon
- Electrolyte: PVA/H_3PO_4
- An areal capacitance of 45 mF cm^{-2} at 0.3 mA cm^{-2}

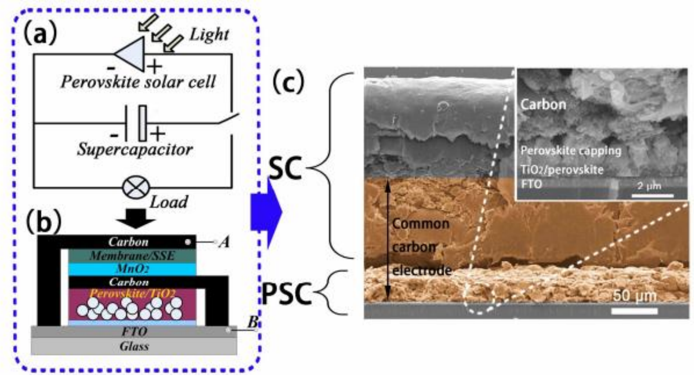
H. Lee, S. Hong, J. Kwon, Y. D. Suh, J. Lee, H. Moon, J. Yeo, and S. H. Ko, J. Mater. Chem. A, 2015, 3, 8339–8345

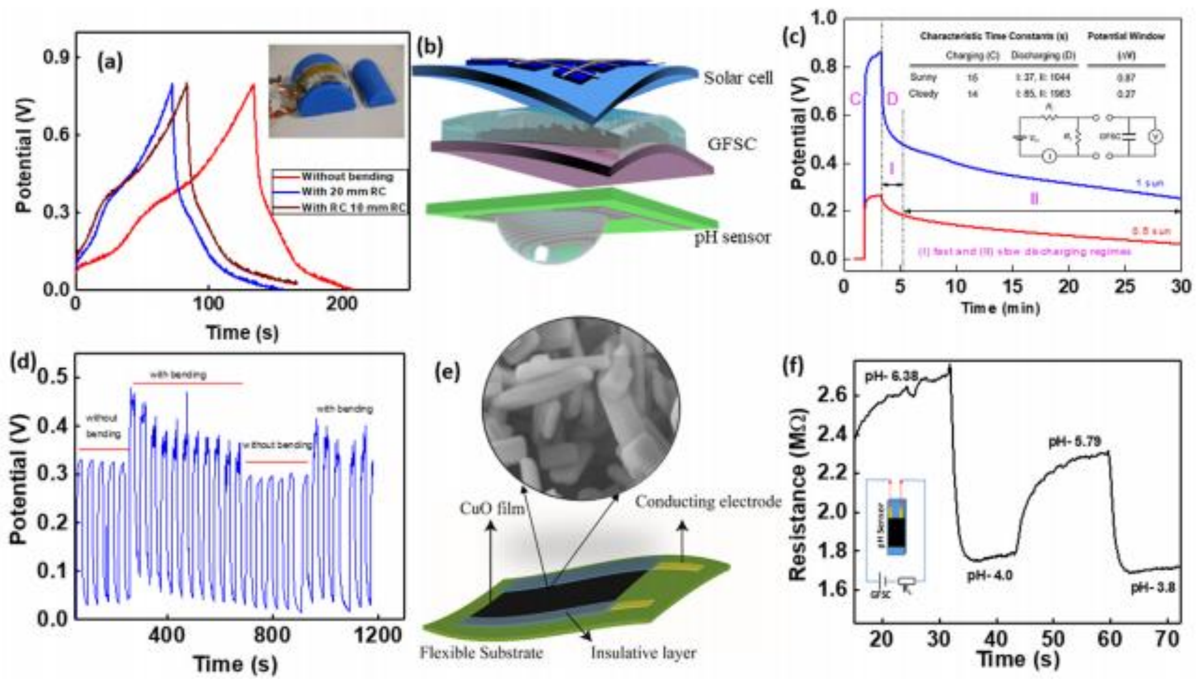
Supercap applications

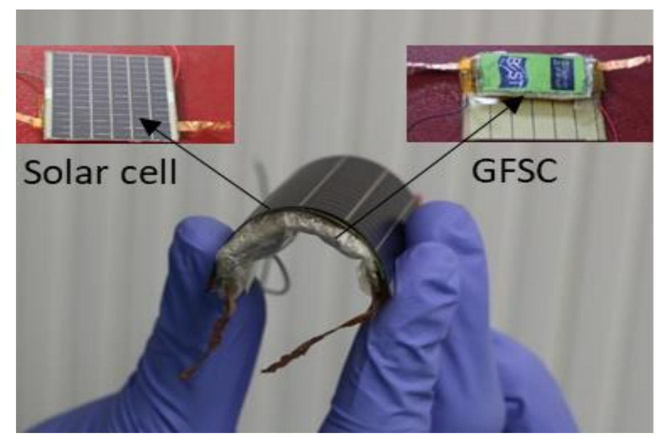


Integration PV and SC









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B.Taheri
L.Cinà

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Thank for your attention

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francesca.brunetti@uniroma2.it