

Introduction to New Generation Solution Processable Solar Cells: Perspectives and Challenges

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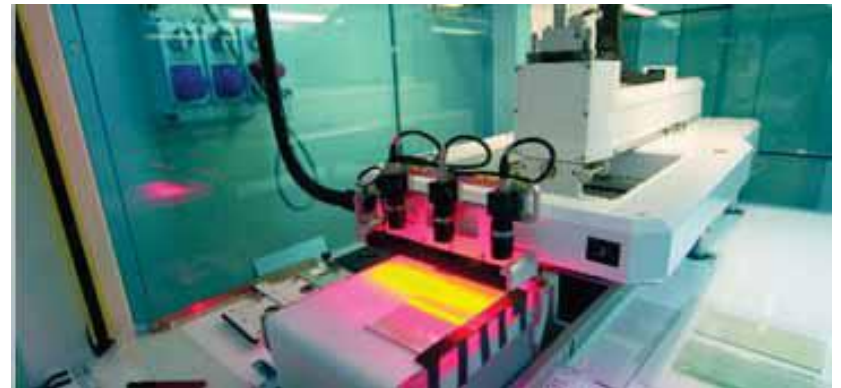


CHOSE- Center for hybrid and organic solar energy

CHOSE is research center with a lab of about 1000 m² located in Rome devoted to the research on DSC and BHJ-SC



www.chose.it



CHOSE- Center for hybrid and organic solar energy

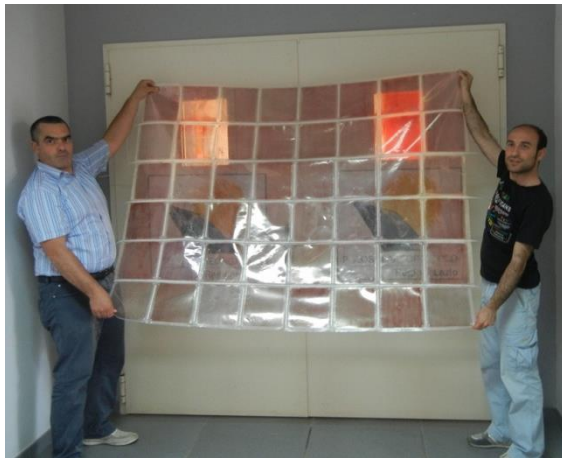
Glass based technology



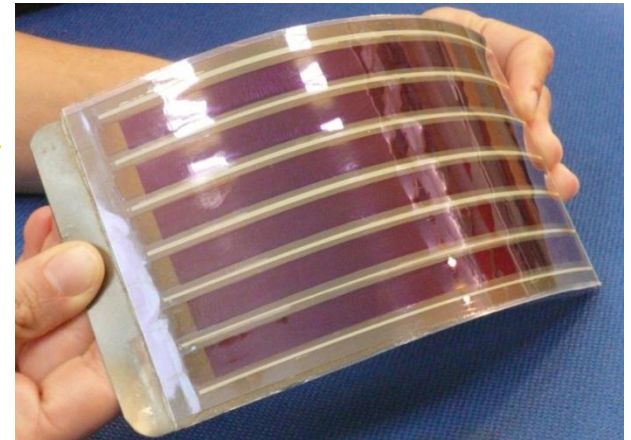
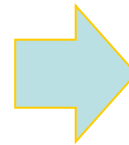
**Dye
Sensitized
Cells**



Flexible solar cells



**Dye
Sensitized
Cells**

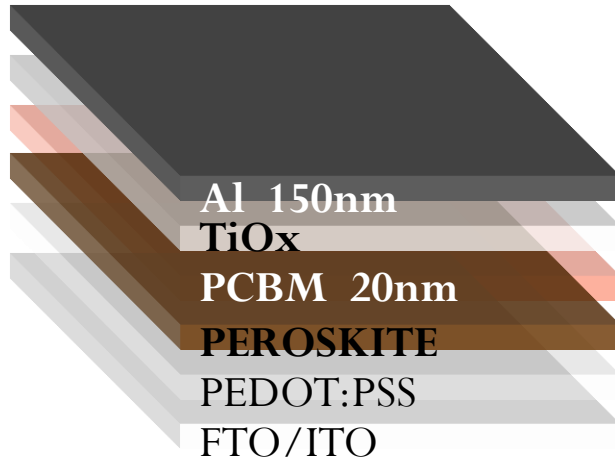


**Polymer
solar cells**

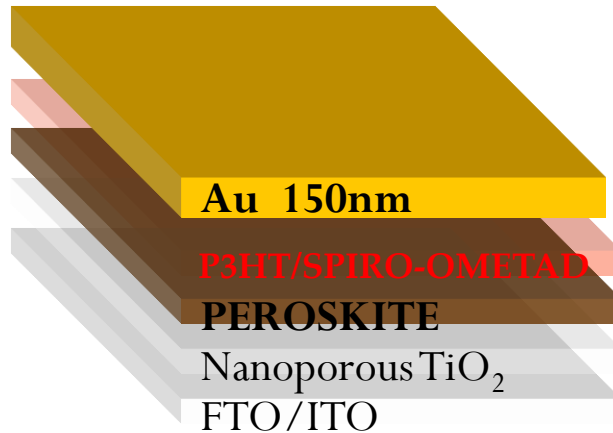
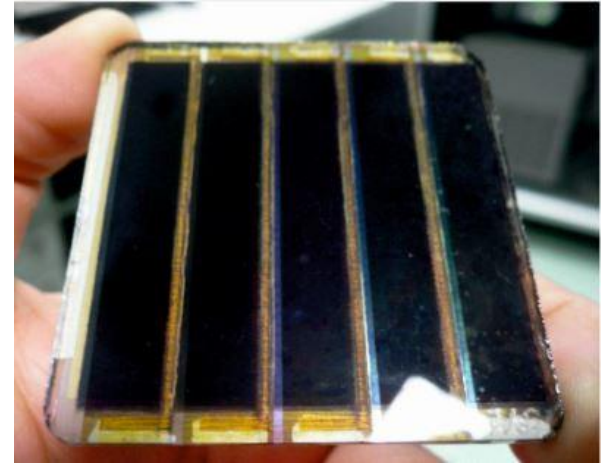


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Perovskites based technology



9% eff.



13% eff.

Perovskite module formed by 5 series connected cells (monolithic architecture). Aperture area = 25 cm², Active area = 16.8 cm², Efficiency on active area = 5.1% (Matteocci et al. PCCP 2014)

SPIN-OFF & START-UP

- Technological transfer with Spin-off and Start-up



8 Engineers and PhD

8 Engineer and PhD



10 Engineer and PhD

5 Engineer
and PhD

INGEM S.R.L.



POLO PER IL
FOTOVOLTAICO A CELLE
ORGANICHE DEL L'INGEGNERIA

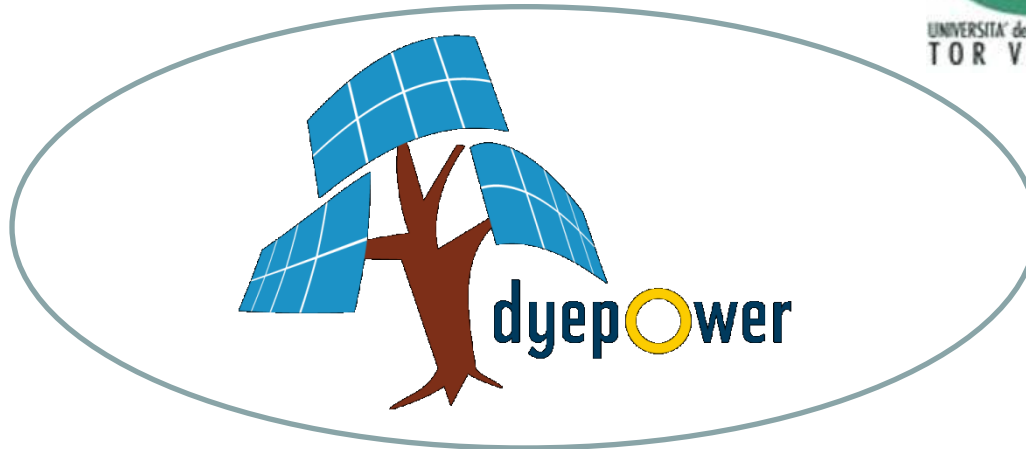


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SOLAR ENERGY

Nanoforum, Roma 14-15 Settembre 2011



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ORGANICHE DEL LAZIO
Nanoforum, Roma 14-15 Settembre 2011



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CELLS ENERGY
SOCIETY



DYEPOWER: Objectives

L'obiettivo del consorzio è lo sviluppo di un processo di produzione industriale per la fabbricazione di pannelli DSC per applicazioni in facciate di vetro. Ciò comporta l'individuazione dei materiali, processi e soluzioni tecnologiche che consentano a tali pannelli di raggiungere livelli adeguati di stabilità, di efficienza energetica e di costo.

Main Milestones

- Prototype of Photovoltaic Glass Envelope based on DSC technology
- Pilot Plan for the production of such DSC Photovoltaic Glass Envelope

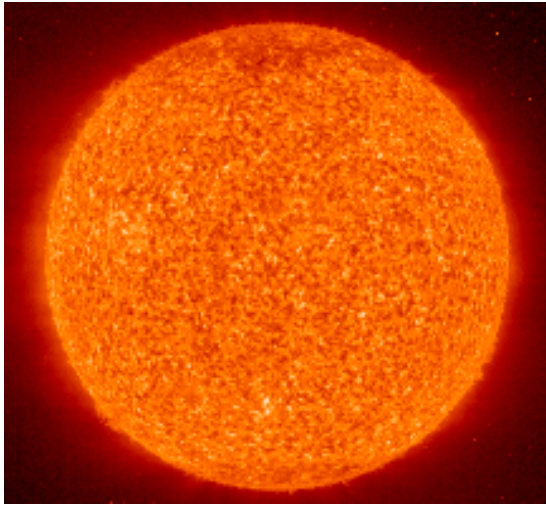


Building Integrated Photovoltaics



Background

Energy from the sun

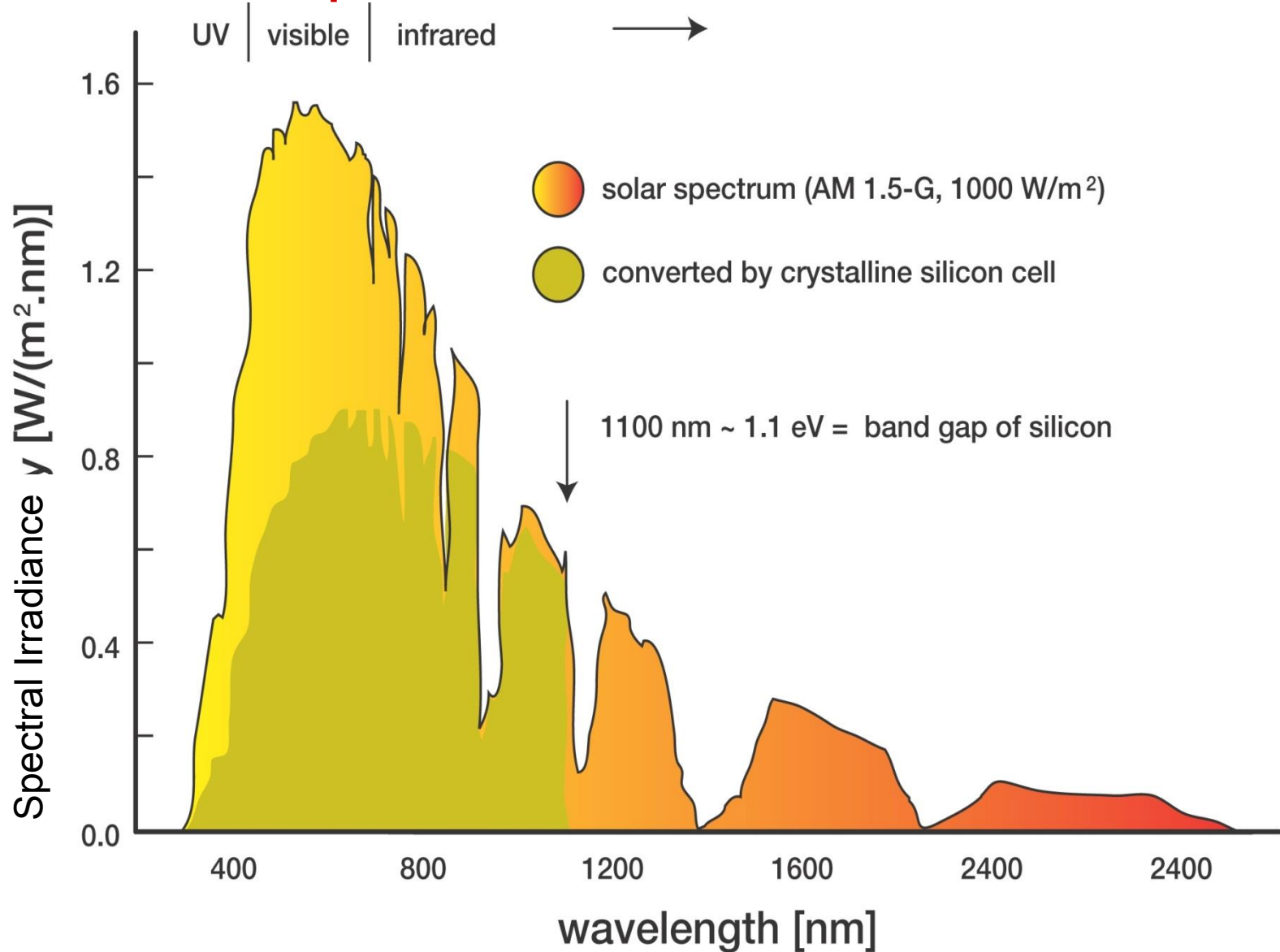


- Averaged over a year humanity consumes over 13 TW of power.
- The sun deposits 120000 TW of power on the earth surface.



- Typical sunlight conditions in central Italy give 1400 kWh/m² per year.
- To satisfy a good fraction of the electricity needs of a typical family one needs at least a 2kWp PV system, i.e. ~20m² of photovoltaic surface (assuming system efficiencies of 10%).

Sun's Spectral Irradiance on earth's Surface



The origins

1941

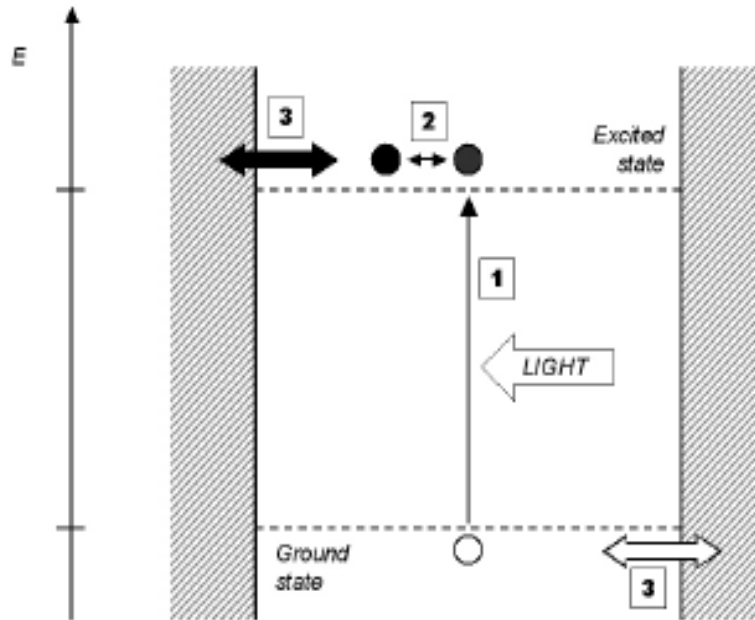
The american Russell Ohl (Bell Labs) discovers accidentally the use of a pn junction as solar cell



1954

The Bell Labs researchers Pearson, Chapin, e Fuller realize a photovoltaic cell with 4.5% power conversion efficiency

Solar Cells (1/2)



- 1- Light harvesting
- 2- Charge separation
- 3- Charge transport

Light harvesting: photons are absorbed and their energy used to excite electrons.

Charge separation: the excited electrons are separated spatially from the ground state to avoid recombination.

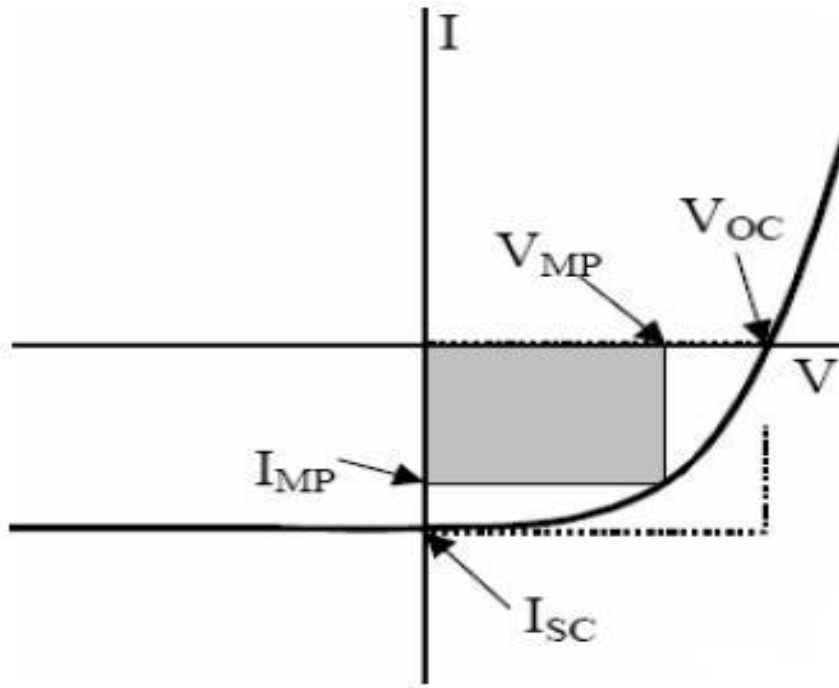
Selective charge transport/extraction: electrons and holes are transported to the terminals of the device, where the high-energy electrons are selectively extracted at one terminal while the holes selectively are replenished from the other terminal.

Ideally, there should be a one-to-one relationship between light and electric current: Each photon that strikes the device deliver its energy to an electron, which in turn transports the energy to an electrical load connected to the terminals of the device. Here the energy can be released in the form of work.

Source: K. West

Solar Cells (2/2)

- The I-V characteristic allows to evaluate the behaviour of the solar cells
- The most important parameters are : the Fill Factor (FF) and the power conversion efficiency (η):



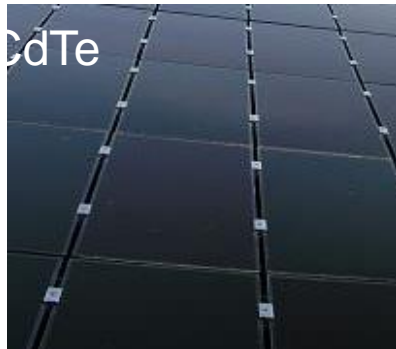
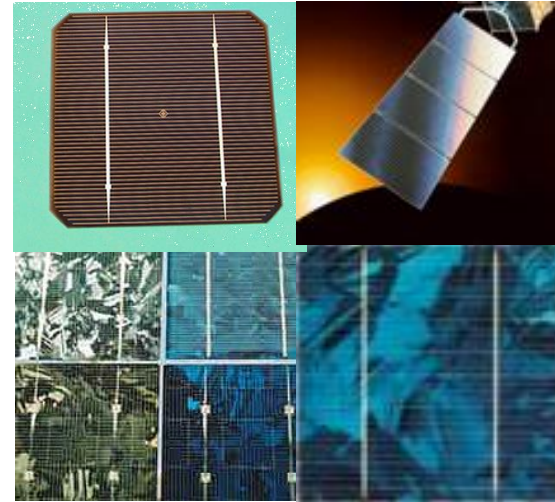
$$FF = \frac{P_{max}}{V_{oc} \cdot I_{sc}}$$

$$\eta = \frac{P_{max}}{P_s}$$

Which materials for the Solar Cells?

Thick crystalline semiconductors

- **Crystalline silicon**
 - Single crystal
 - Polycrystalline
- **Gallium Arsenide (GaAs)**
- **Other materials from the group III-V**



“Thin Films” Materials

- **Amorphous Silicon (a-Si)**
- **Cadmium Telluride (CdTe)**
- **Copper and Indium diselenide (CuInSe₂, o CIS)**
- **Copper Indium gallium diselenide (CIGS)**

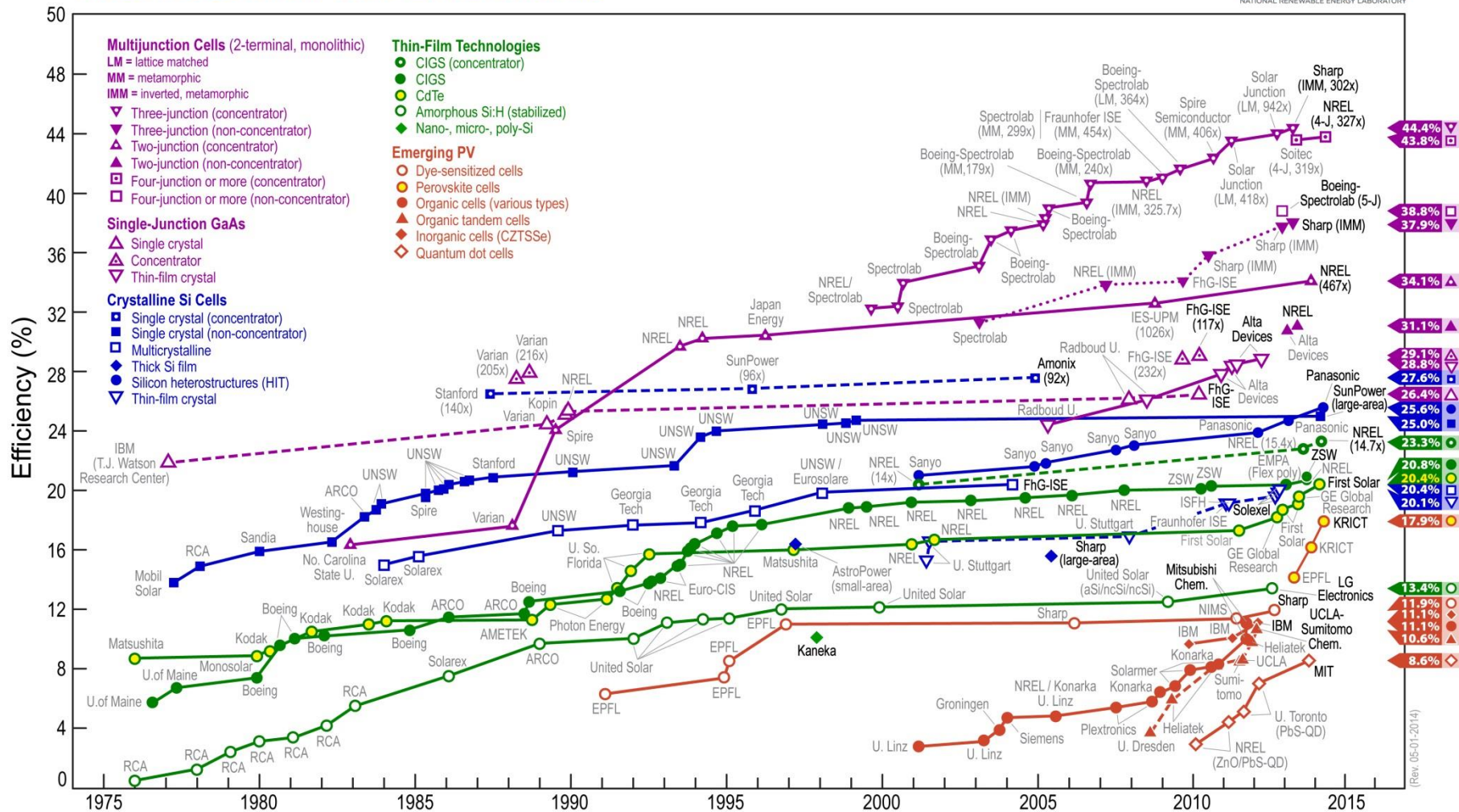
Organic Materials

- **Small molecules (antocyanine etc.)**
- **Polymers**
- **DSC**
- **Perovskites**



Efficiency table

Best Research-Cell Efficiencies



(Rev. 05-01-2014)



POLO PER IL FOTVOLTAICO A CELLE ORGANICHE DEL LAZIO

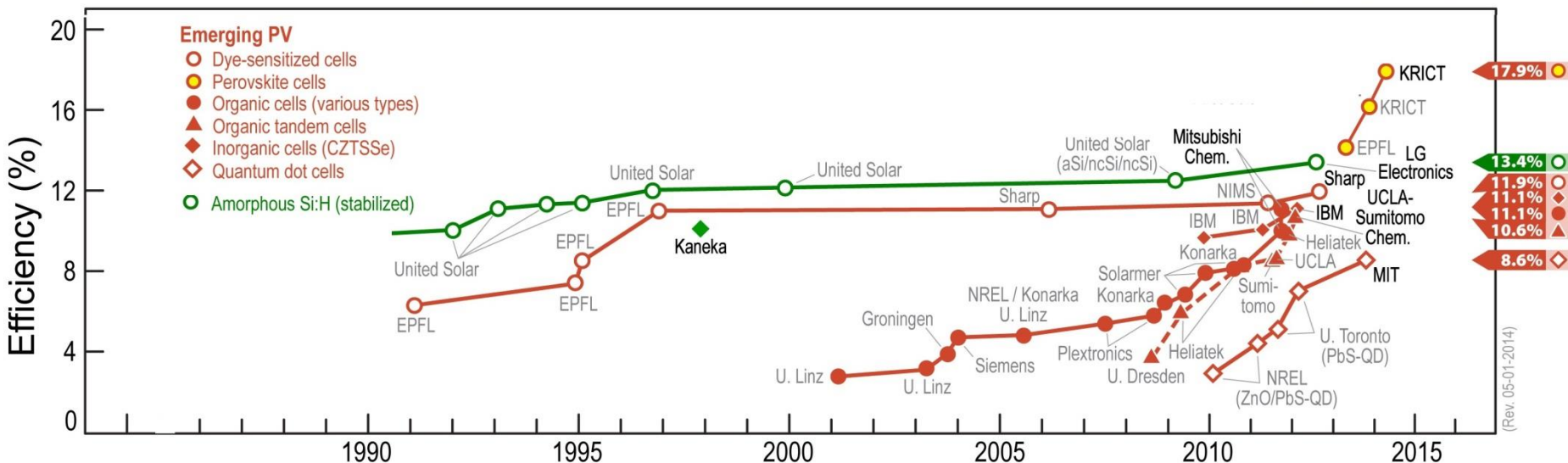


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Efficiency table:detail on organics

Best Research-Cell Efficiencies



Different approaches have been developed to achieve high efficiency devices:

- OPV standard architecture: 9.15%
- OPV tandem architecture: 10.6%
 - Planar perovskites: 12.1%
- Perovskites with scaffold: 17.9%



Outline

- Solution processable OPV devices
 - Working principle
 - Architectures
- Fabrication process
- New carbon based electrodes
- Conclusions



Solution processable OPV devices

Organic Photovoltaics-New Perspectives

The fabrication processes of the “conventional” solar cells are expensive and complex.

The cost for the setting of a production factory is very high

Is it possible to reduce both the material and the production costs for the realization of solar cells?

Yes! With the introduction of new materials and new fabrication techniques

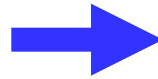


Solution processable solar cells



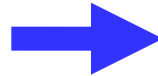
"New" manufacture processes

Conventional Electronics

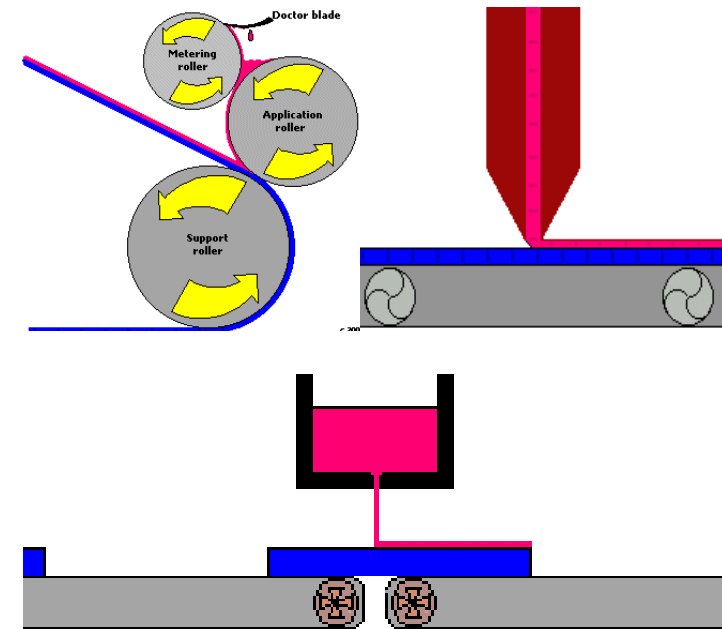
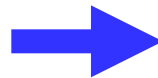


Organic Electronics

Conventional semiconductor industry



Printing methods



High temperature, doping, vacuum

Liquid deposition

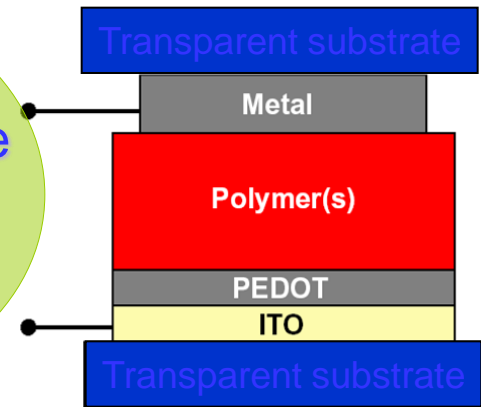
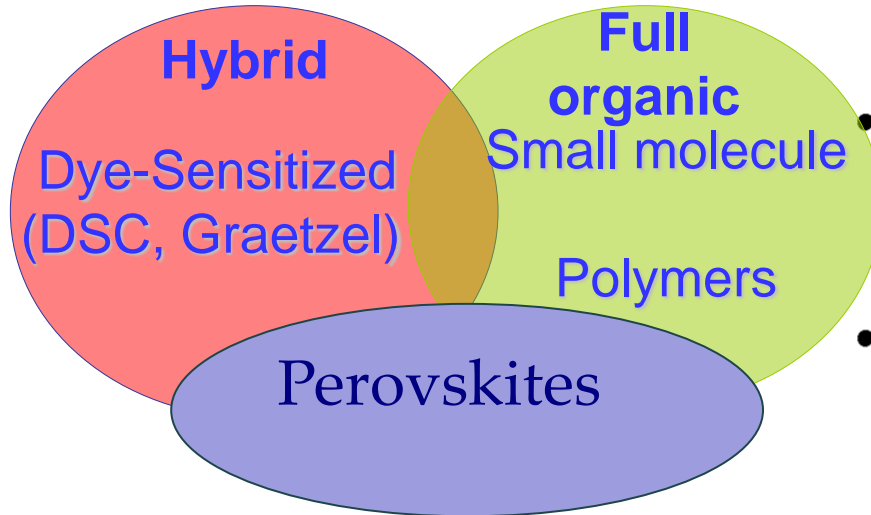
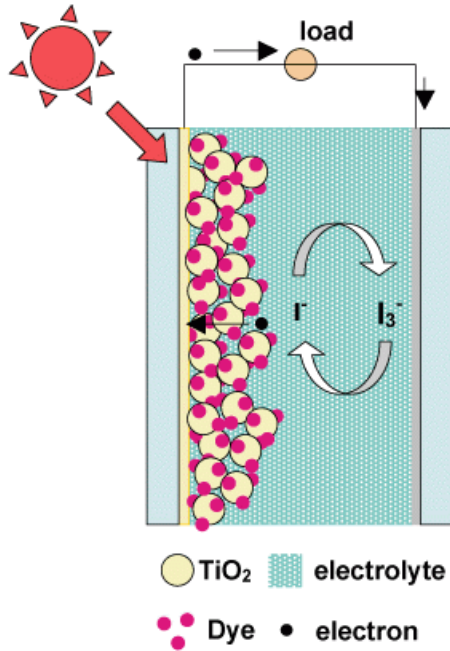
Very Large enterprises



Small Medium enterprises /local productions



Organic photovoltaics



Type	Max lab efficiency	Stability	R&D
Hybrid Dye Sensitized (Graetzel)	~ 11-12%	IEC 61646	University and industry
Full organic solar cells	~ 10%	IEC 61646	University and industry
Perovskites	~ 18%	-	University

Organic Photovoltaic

DSSC Façade System
at the CSIRO Energy Centre
Newcastle, Australia



DYEPOWER



KONARKA

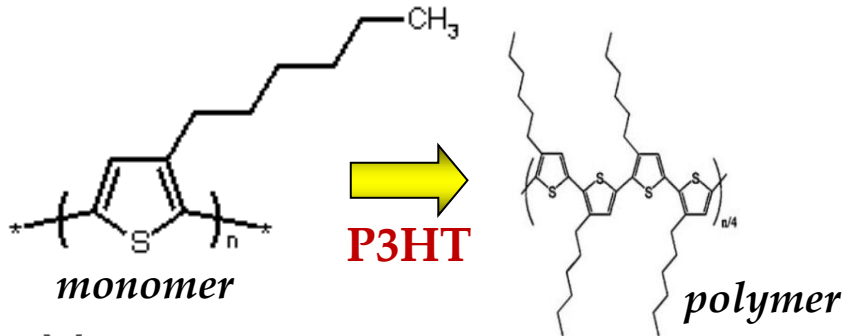


Working principle



Polymers

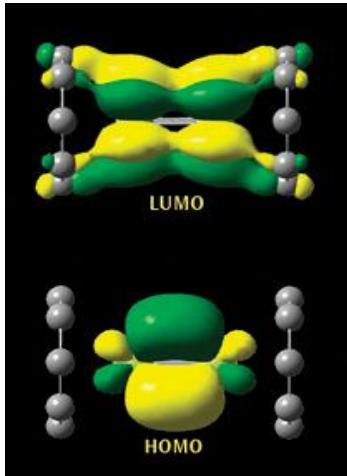
Conjugated polymers: macromolecules based on repetition of monomers (same or different species); principally made of carbon (C), they can have different and distinctive properties (both optical and electrical), and can be tailored “*ad hoc*” for several purposes.



Pro

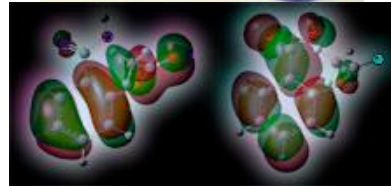
- ✓ low-cost fabrication (solution-processing)
- ✓ large-area and mass production
- ✓ flexible devices
- ✓ customizable

2.7 eV

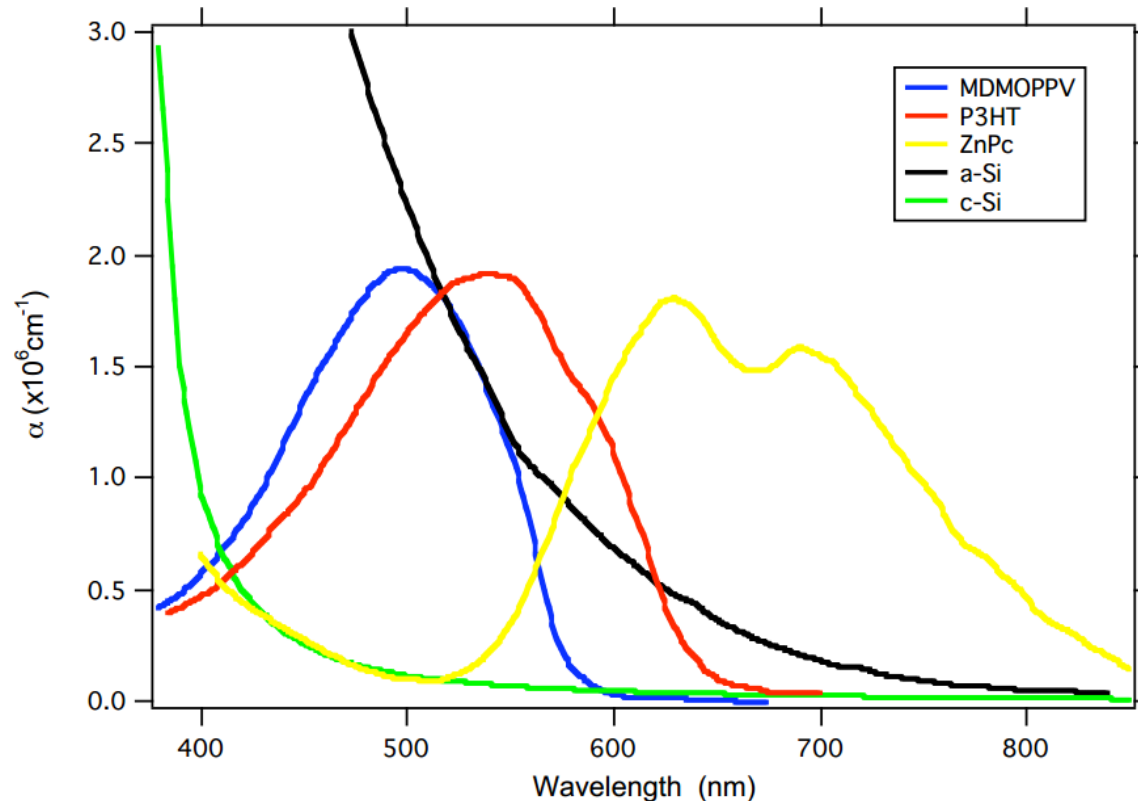


P3HT

4.9 eV



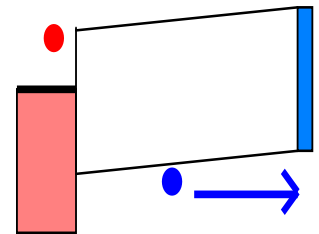
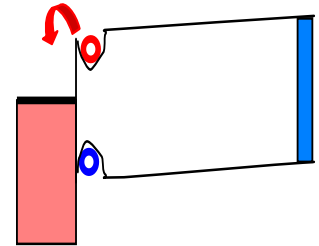
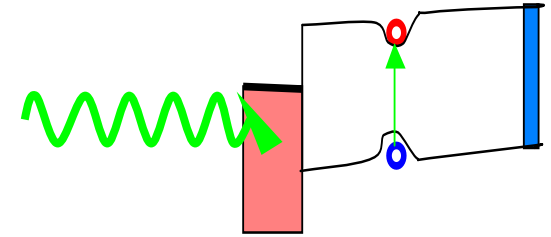
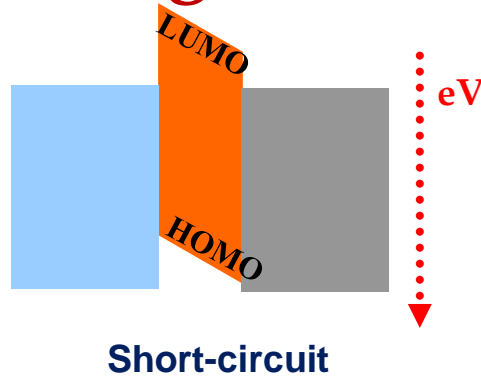
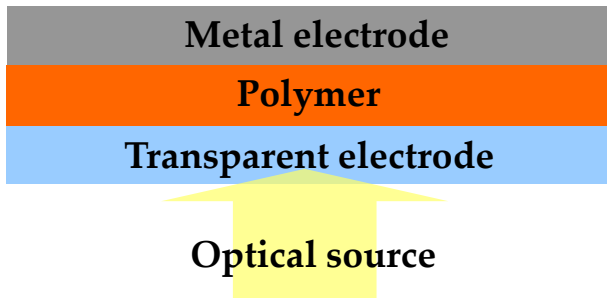
Absorption Coeff. of Organic Semiconductors



Generally the optical absorption coefficient (α) of organic materials is much higher than that of crystalline or multicrystalline silicon as shown in Figure. For the conjugated polymers MDMO-PPV and P3HT and for the molecular dye, zinc phthalocyanine (ZnPc) α exceeds $1 \times 10^5 \text{cm}^{-1}$ in the major part of the visible spectrum. Effective thicknesses of the order of $\sim 100 \text{nm}$ are required.



Single layer Organic Solar Cell



- ❑ Excitons are mobile, electrically neutral, optically excited states, which exist because they do not have enough energy to separate into an electron and a hole.
- ❑ The exciton separates at the interfaces
- ❑ Exciton diffusion length 1-10 nm, absorption depth >100 nm

A Key Cell Parameter
the exciton diffusion length

$$L_n = \sqrt{D\tau}$$

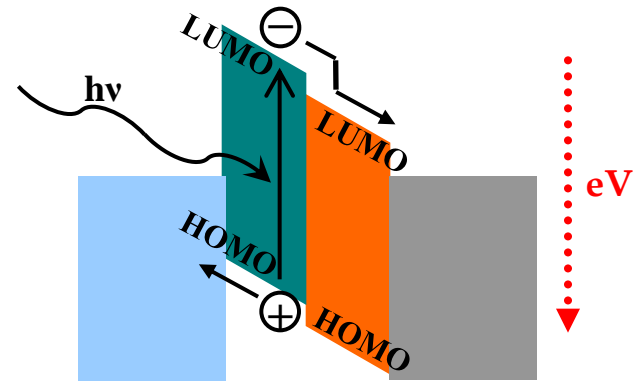
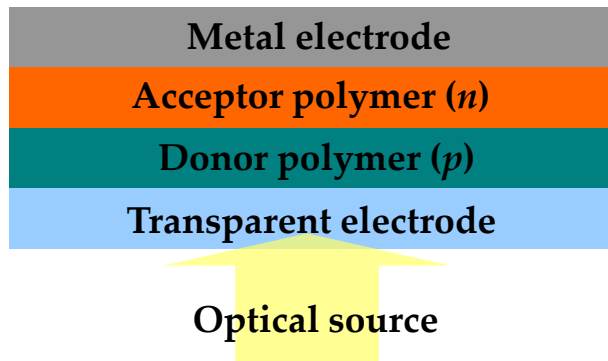
The exciton diffusion length is shorter than the light absorption length

Power efficiency
 $\eta < 0.1\%$

Source: J. Nelson, ICCMP 2004

Double-layer

Bi-layer device (heterojunction)



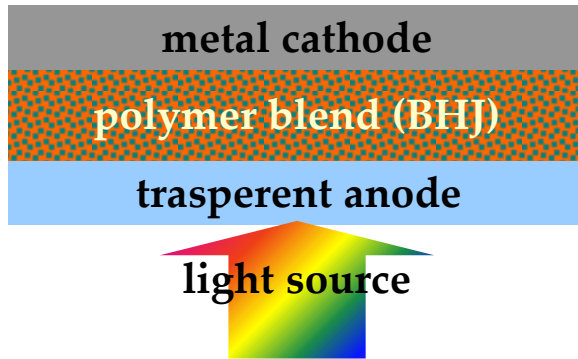
Use of two polymers, **donor** and **acceptor** (*p* and *n* type) → better conversion efficiency (~1%)

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

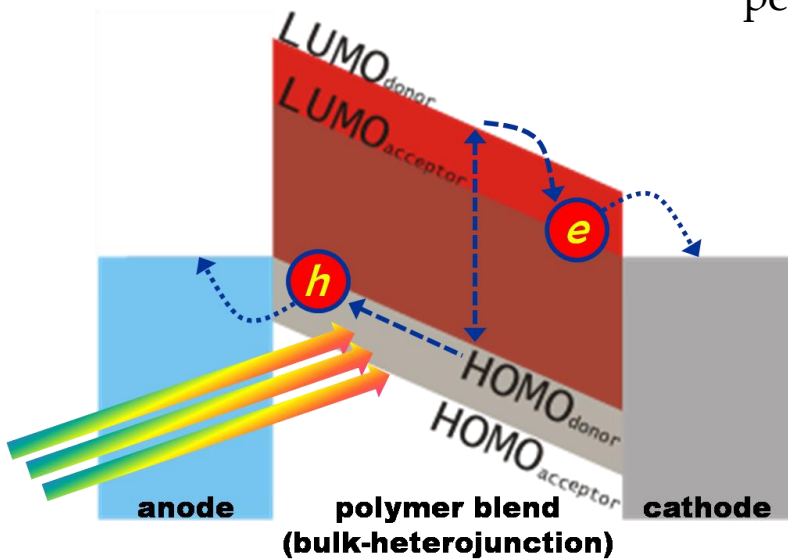
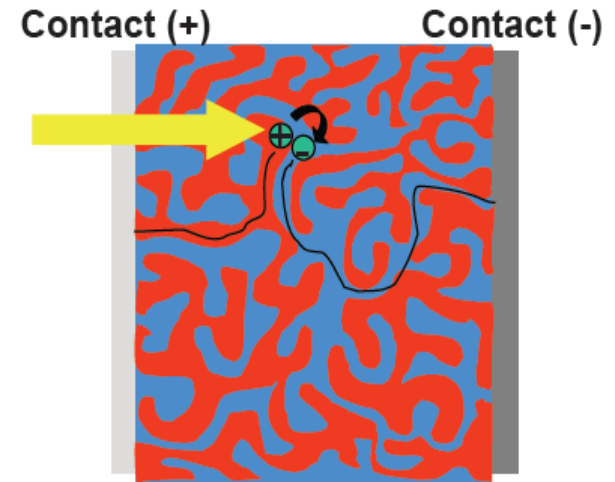
Remaining problems:

- ? higher **series resistance**
- ? **solvent-crossing**

Bulk-Heterojunction (BHJ-layer)

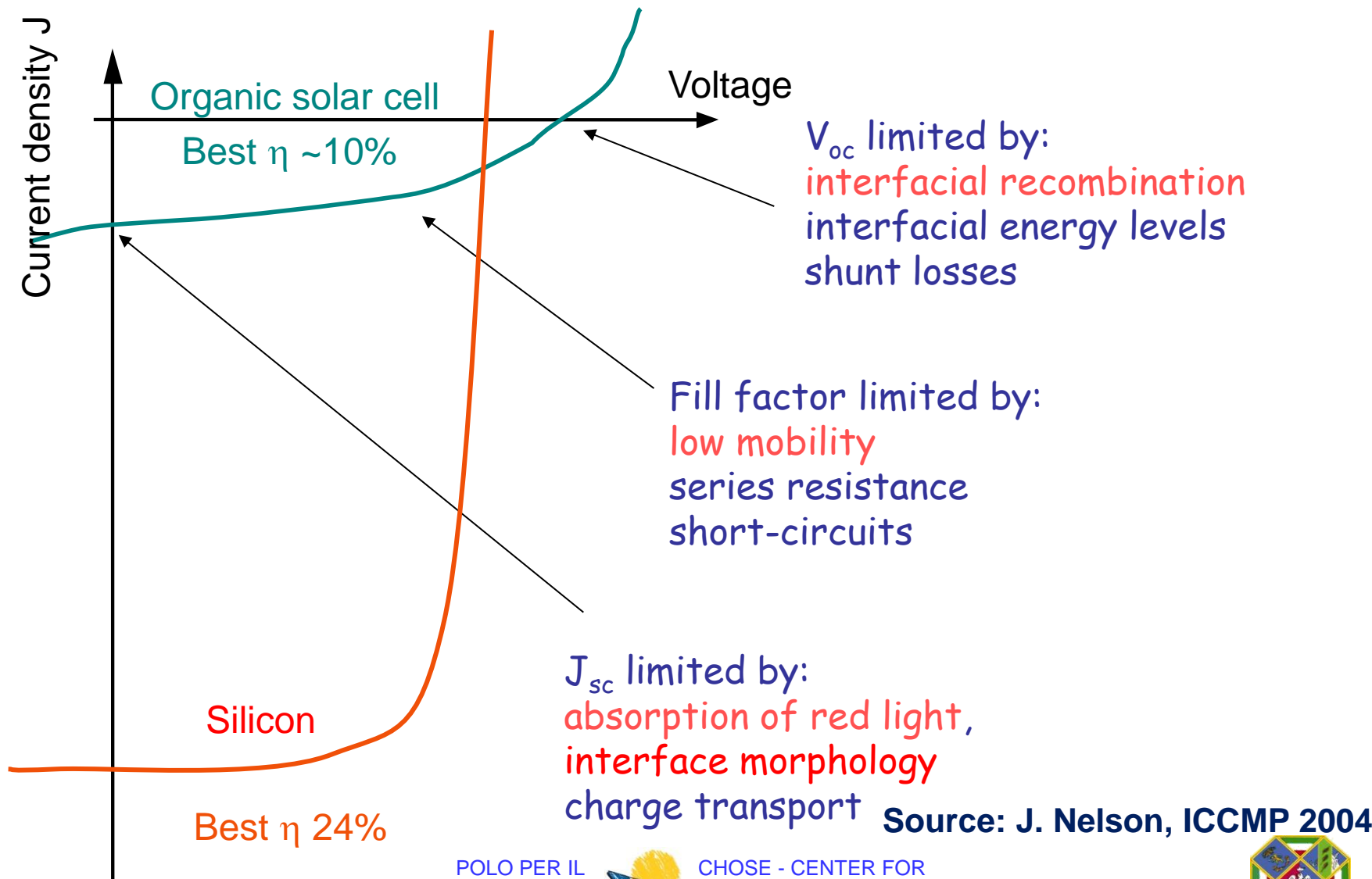


- Blend hole accepting with electron accepting material
- Length scale of blend \sim exciton diffusion length
- Charge separation at D-A interface
- Continuous paths for electron and hole percolation



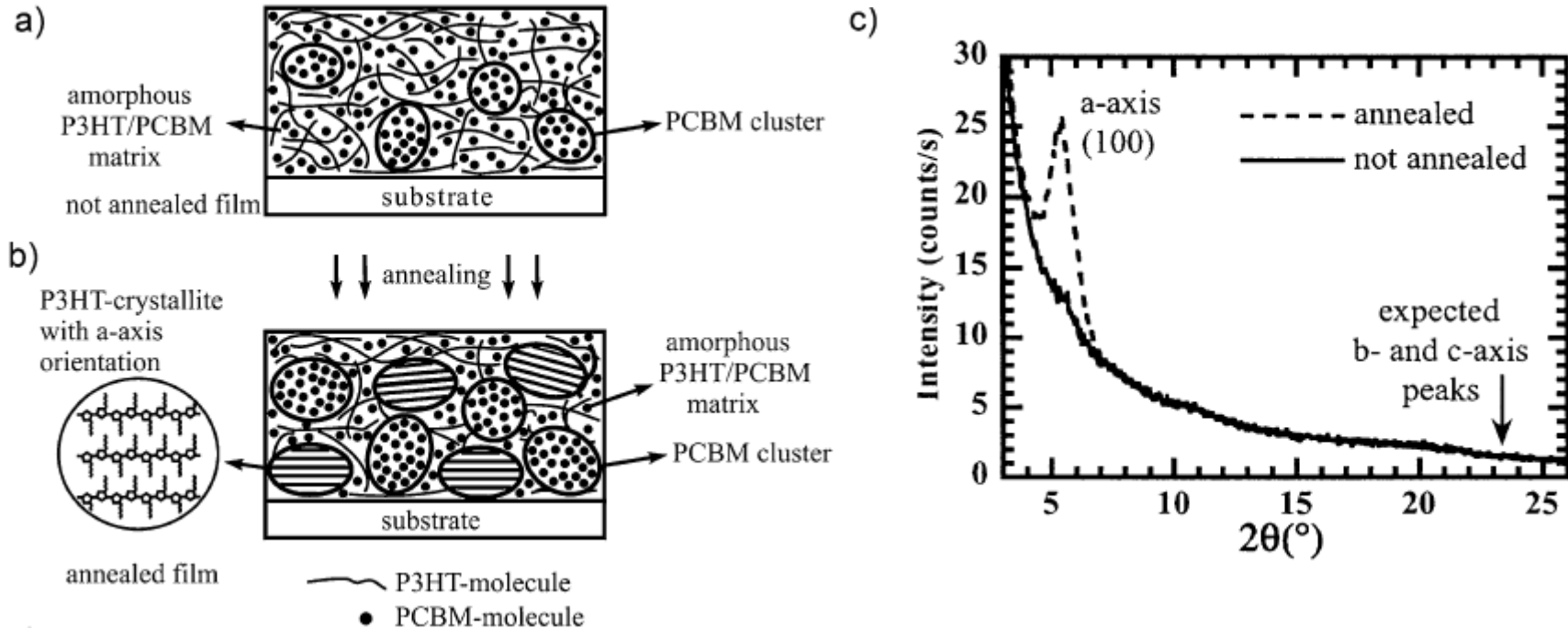
- Photo-Voltaic effect** in organic bulk-heterojunction:
- 1) Photon absorption
 - 2) Exciton formation
 - 3) Exciton diffusion to heterojunction *a-d* (acceptor-donor)
 - 4) Exciton dissociation (electrons "*hop*" from LUMO_{donor} to LUMO_{acceptor})
 - 5) Carriers transport towards electrodes
 - 6)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

Improving organic solar cell efficiency



Morphology

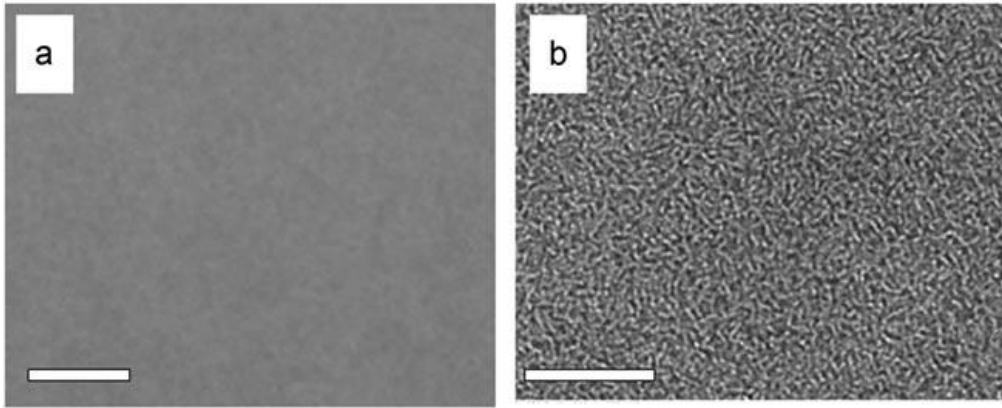
Morphology



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.

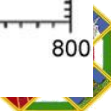
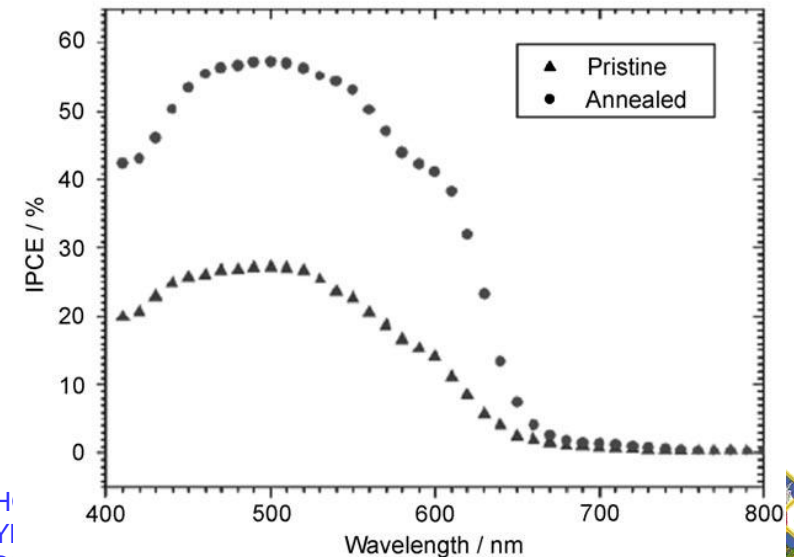
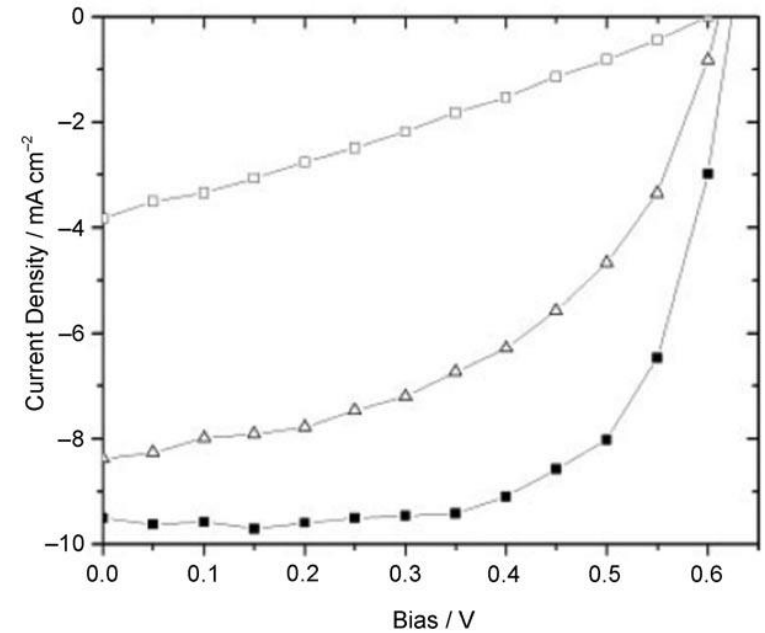
Dennler et al., *Adv. Mater.*, 2009, 21, 1–16

Effect of thermal annealing

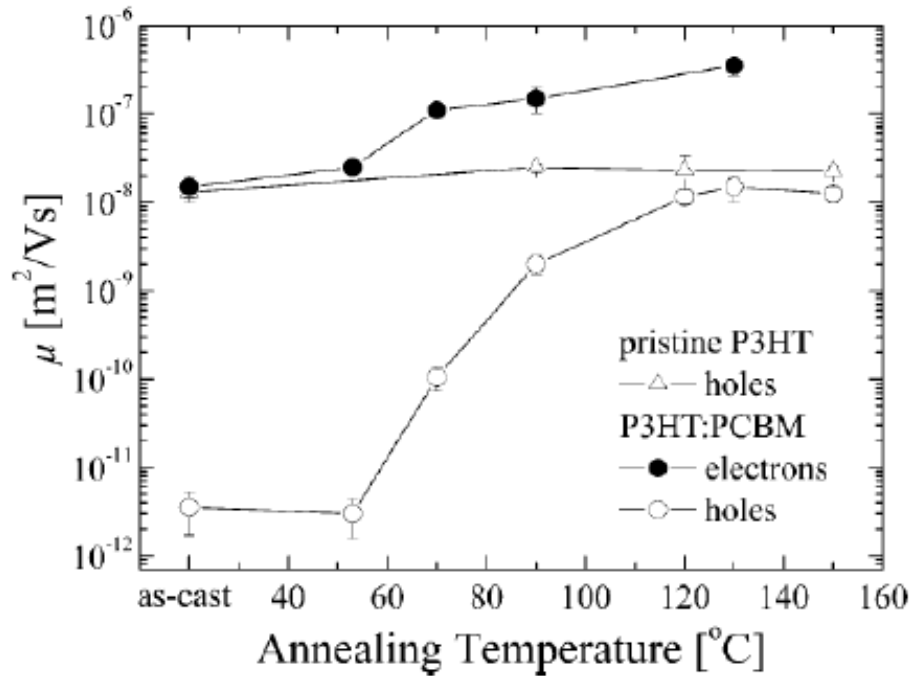


TEM images of 1:1 blend of P3HT and PCBM prior (a) and after (b) thermal annealing at 150°C for 30 minutes (scale bar 0.5 μm).

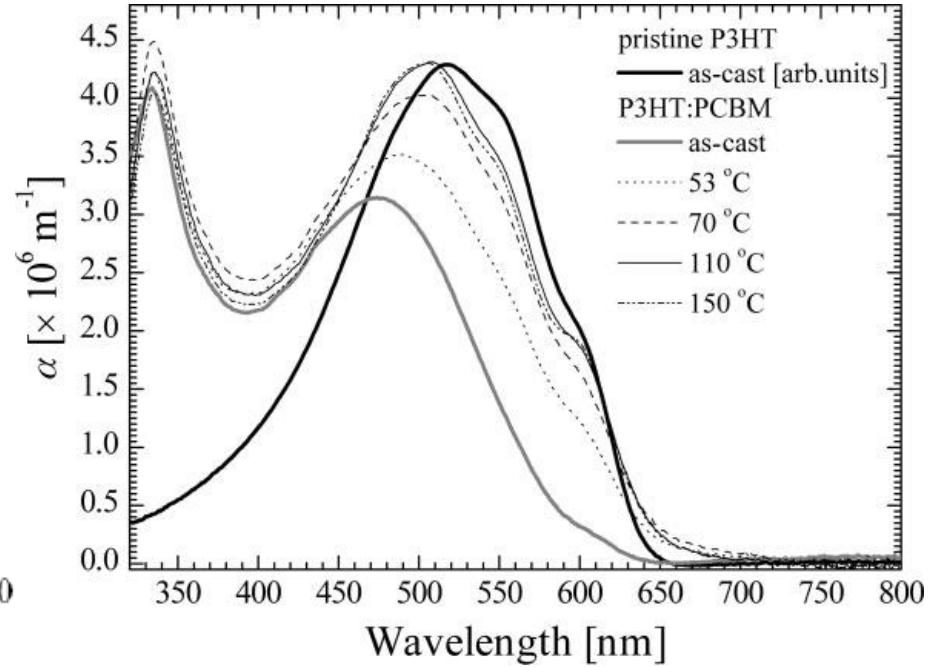
Thomson et al., *Angew. Chem. Int. Ed.*, 2008, 47, 58–77



Effects of morphology



Room-temperature electron (●) and hole (○) 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.

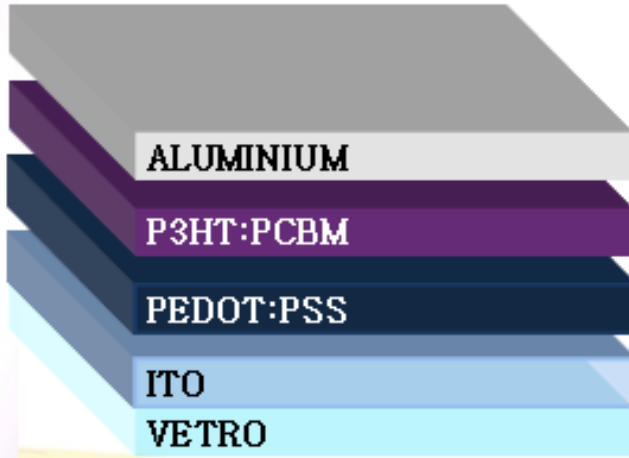


Absorption spectra of P3HT:PCBM blend films for different annealing temperatures.

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

Architectures

Standard architecture

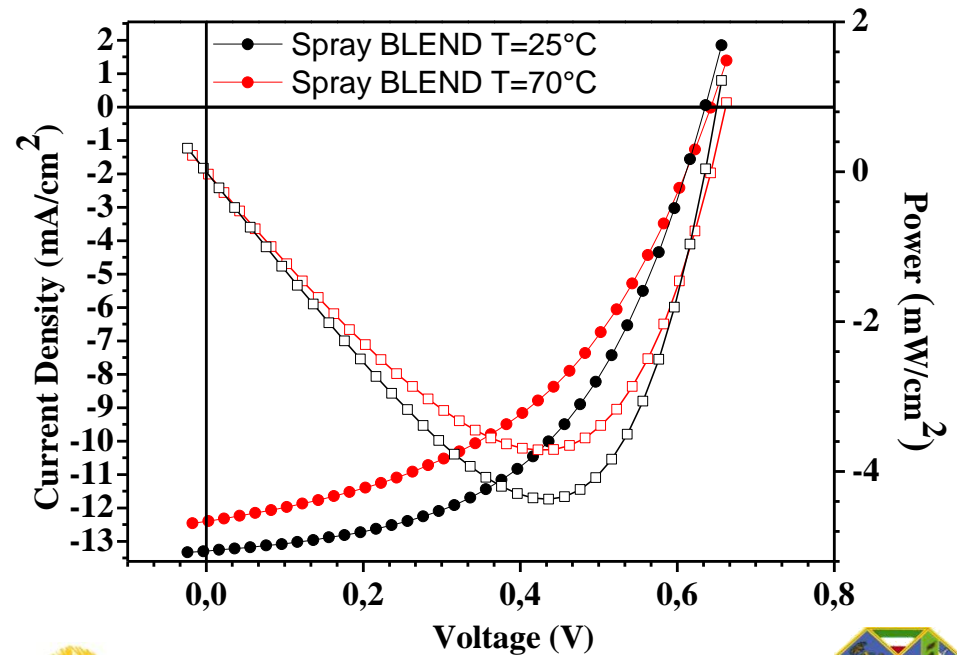
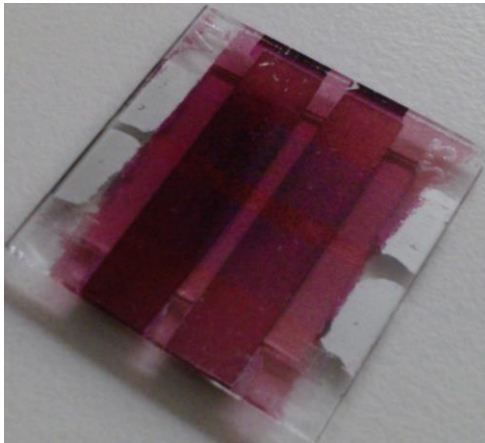


← Cathode: Al, Ca/Al

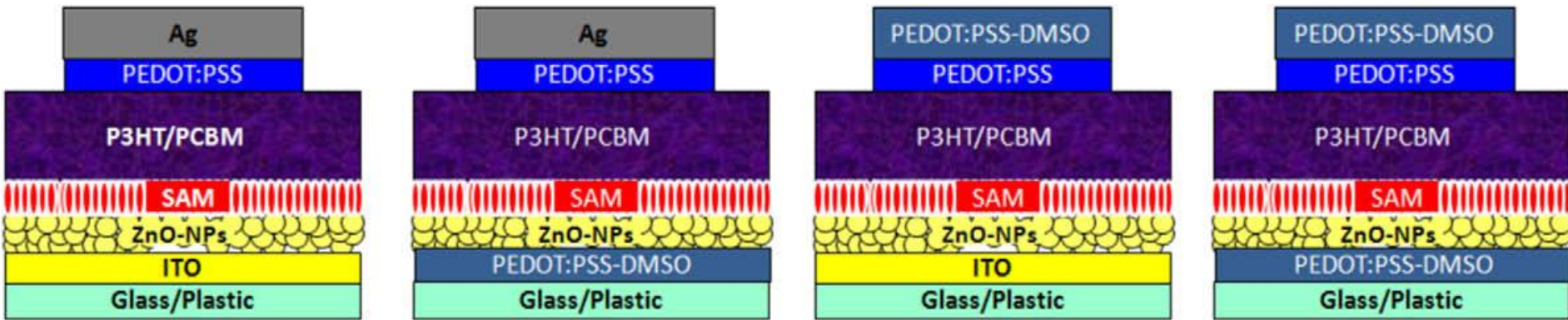
← Active layer

← HTL: PEDOT:PSS, MoO₃, Cs₂Co₃,
V₂O₅, TiO₂, ZnO, NiO

← Anode: ITO/FTO



Inverted Solar Cells

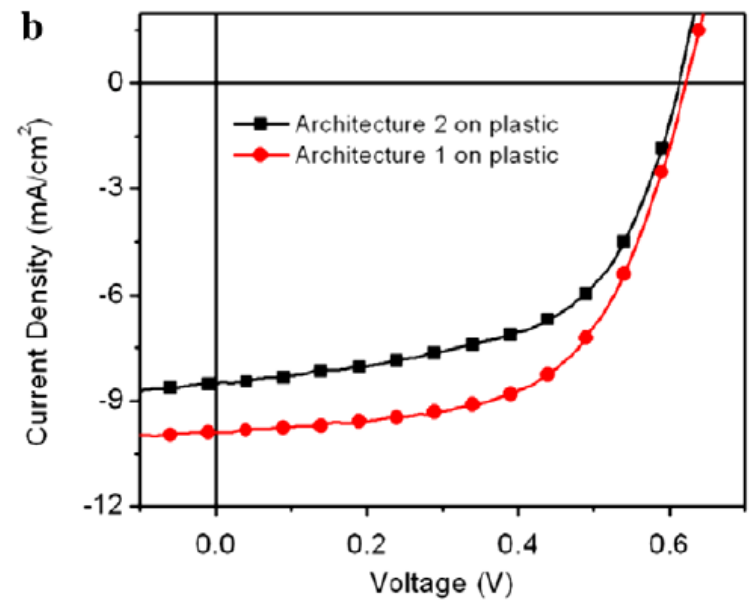
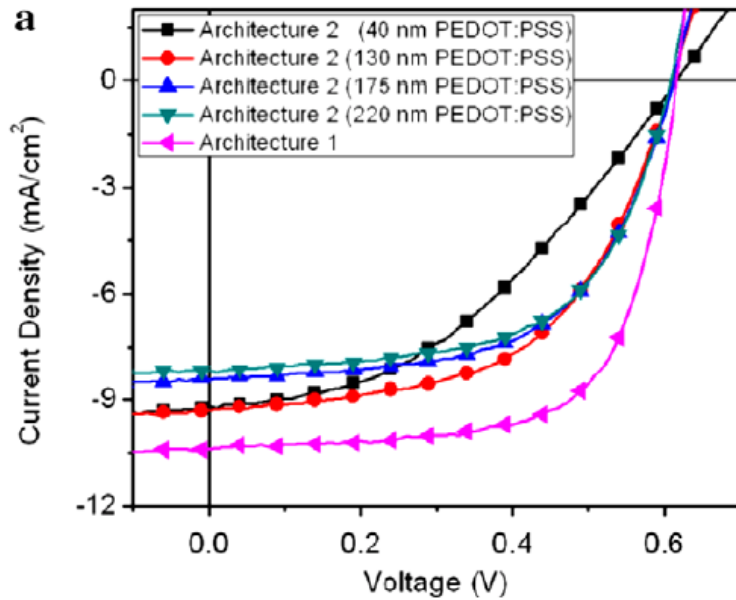


Architecture 1

Architecture 2

Architecture 3

Architecture 4



Hau et al., *Org. Electr.*, 2009, 10, 1401–1407

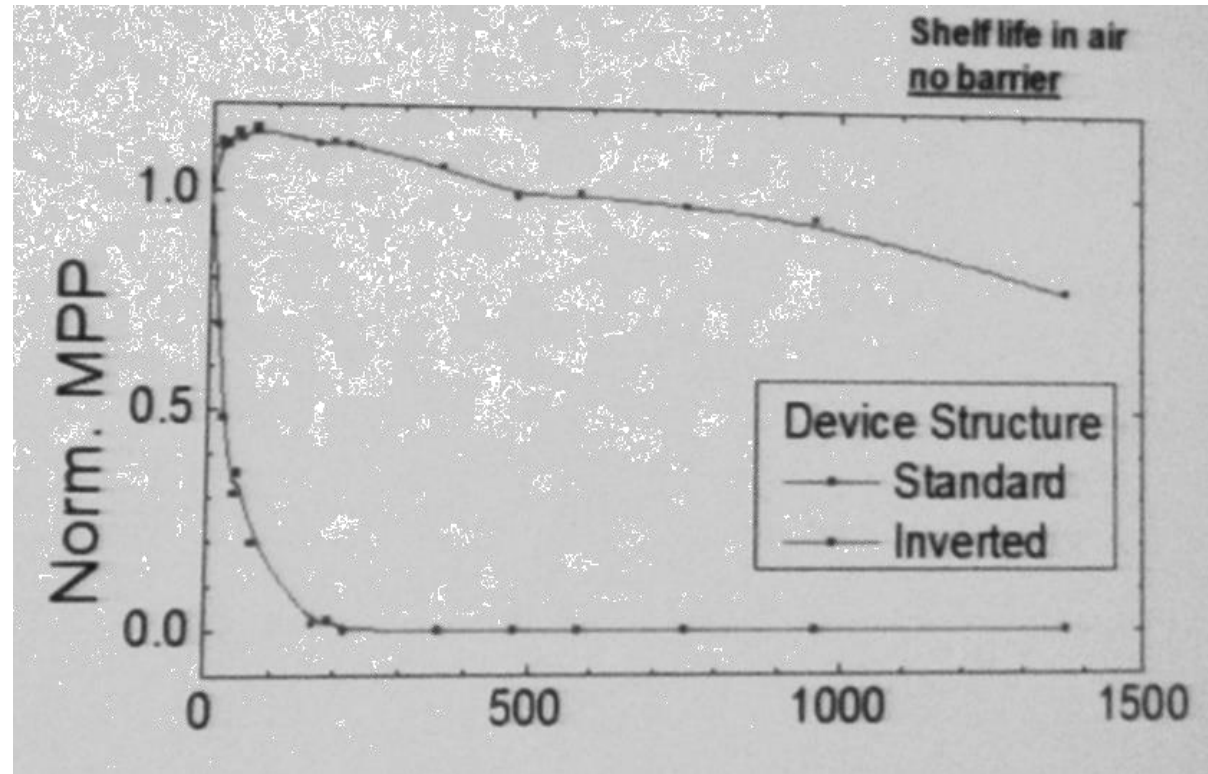
Inverted solar cells: higher stability

LiF/Al
Blend
PEDOT
ITO
Glass

Standard

Ag
PEDOT
Blend
ZnO
ITO
Glass

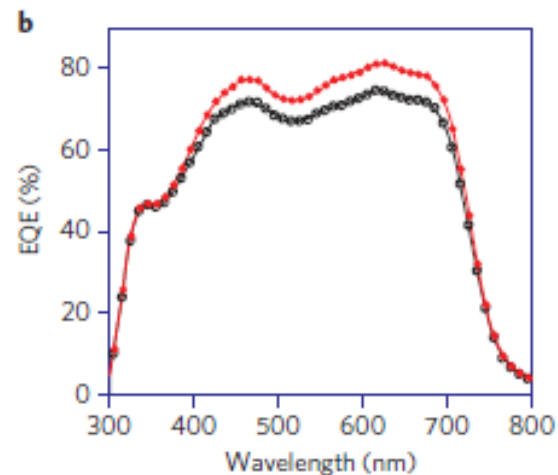
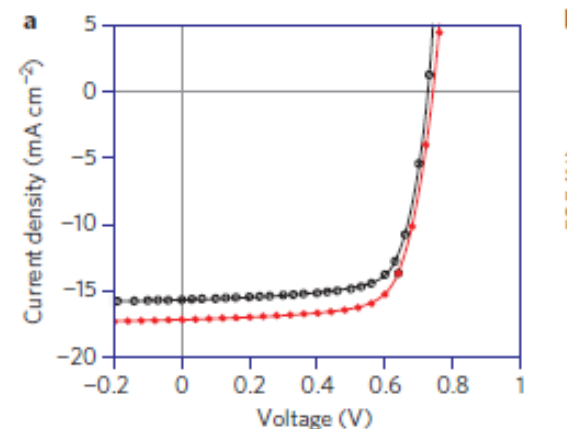
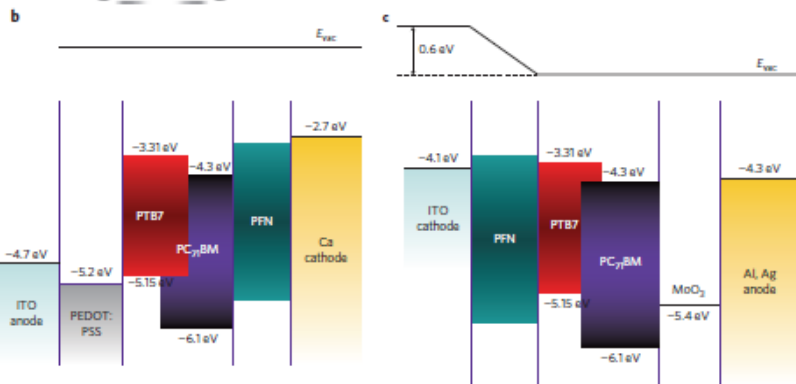
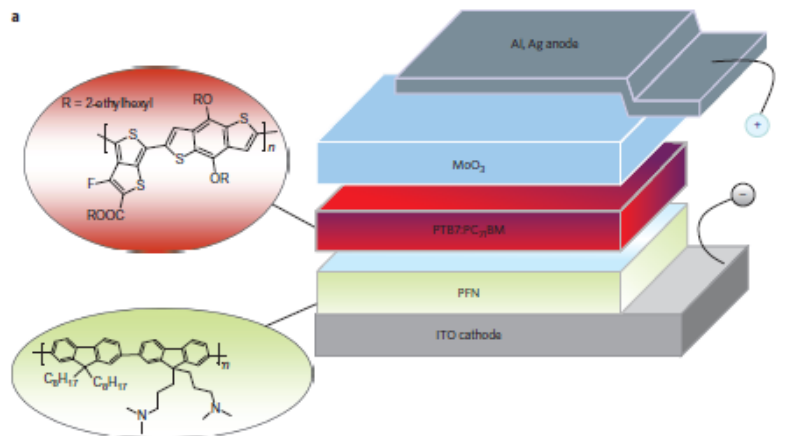
Inverted



The use of an inverted architecture leads to a substantial increase of the device lifetime

Holdst center PVSEC 2011

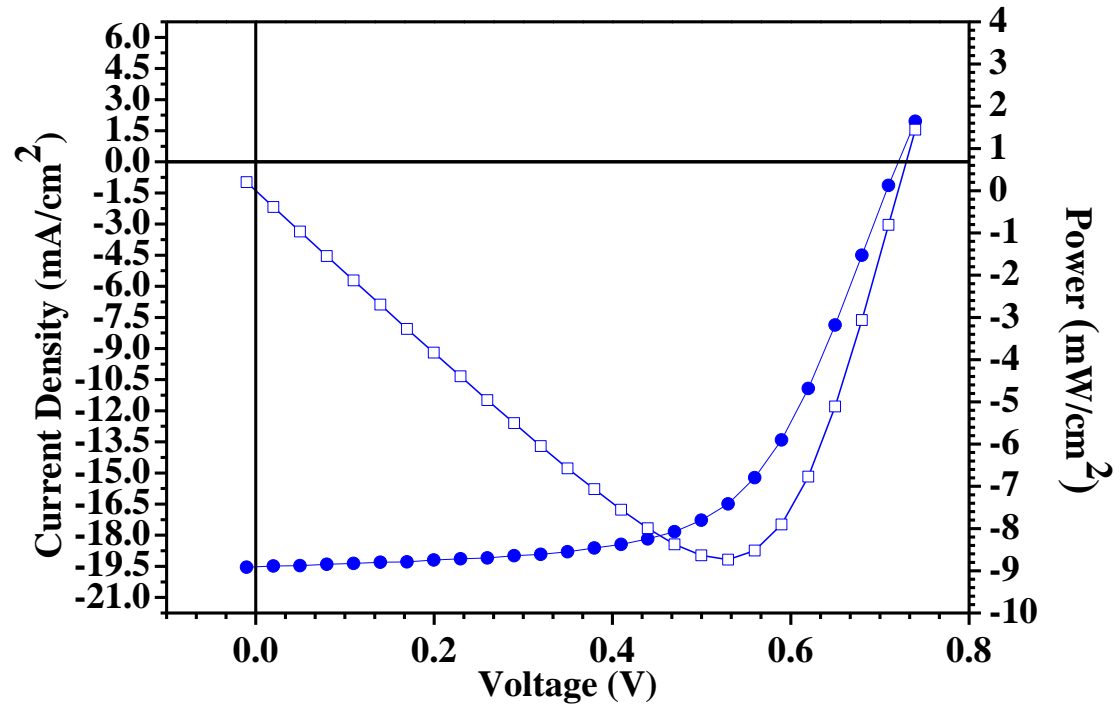
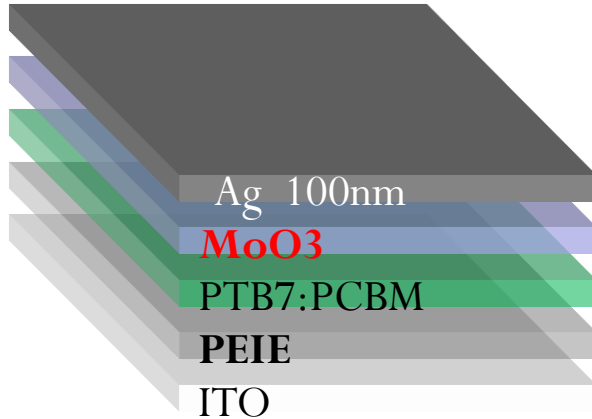
Inverted architecture: the record for a single junction BHJ



Device type	PCE (%)	J_{SC} (mA cm^{-2})	FF (%)	V_{OC} (V)
Conventional	8.24	15.4	70.6	0.759
Inverted	9.15	17.2	72.0	0.740
Inverted, tested by CPVT	9.214	17.46	69.99	0.754

Z. He et al. NATURE PHOTONICS, VOL 6, pp591-595 SEPTEMBER 2012

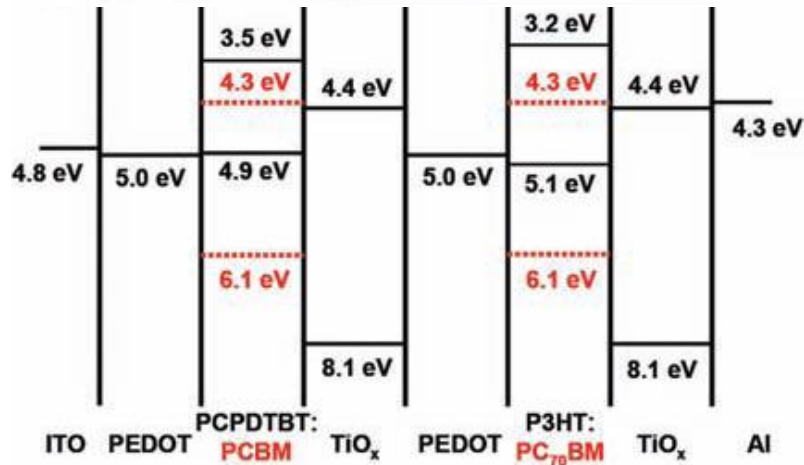
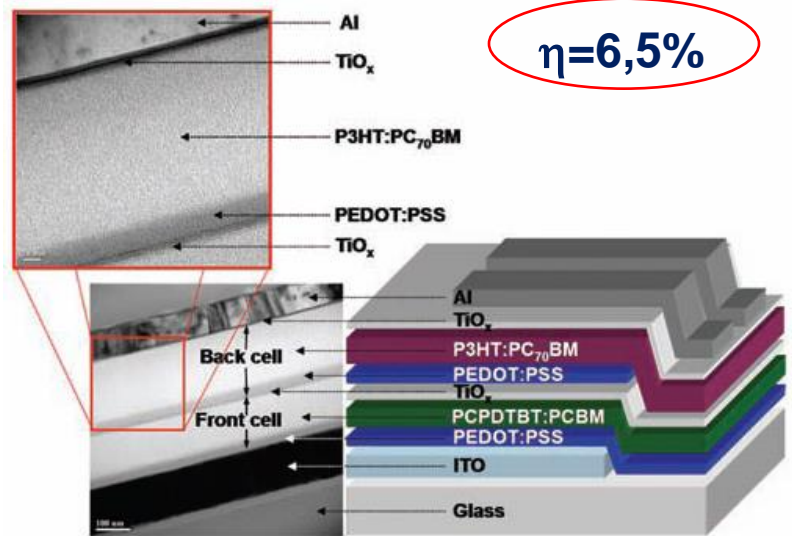
PTB7:PCBM active layer/inverted architecture



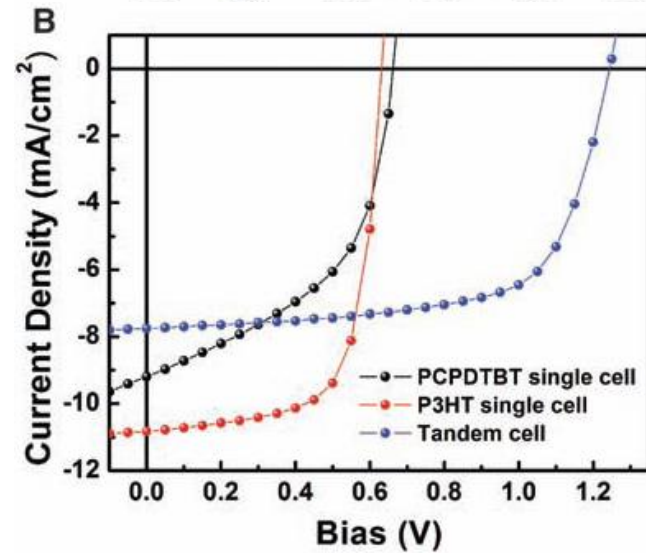
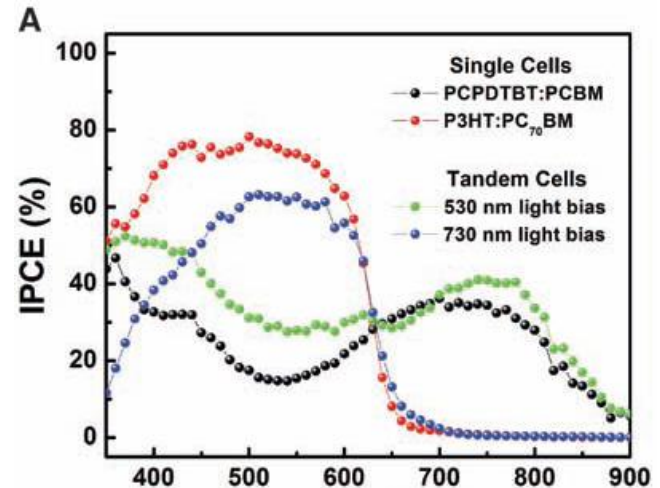
		Voc(V)	Jsc(mA/cm ²)	FF(%)	PCE(%)
PEIE	CHOSE	0.72	19.52	63.55	8.73
	Reference	0.74	17.2	72	9.15
Z.He et al., Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure, NATURE PHOTONICS DOI:10.1038/nphoton.2012.190					

Susanna et al. Submitted

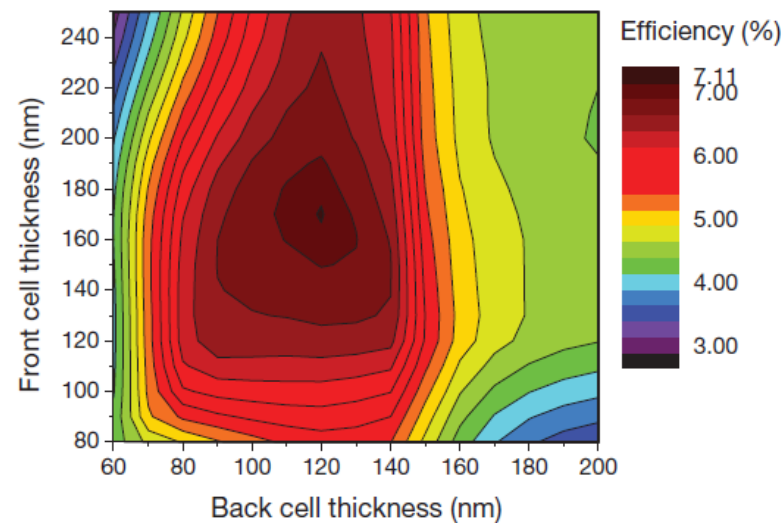
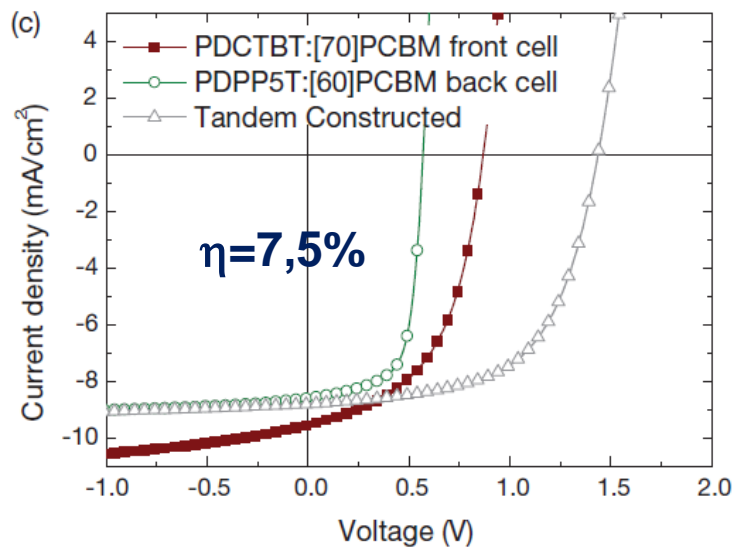
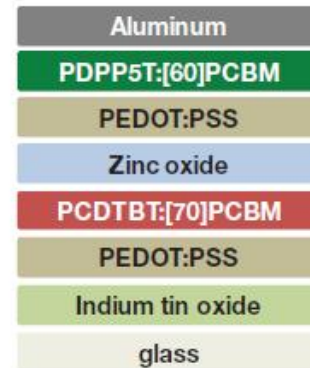
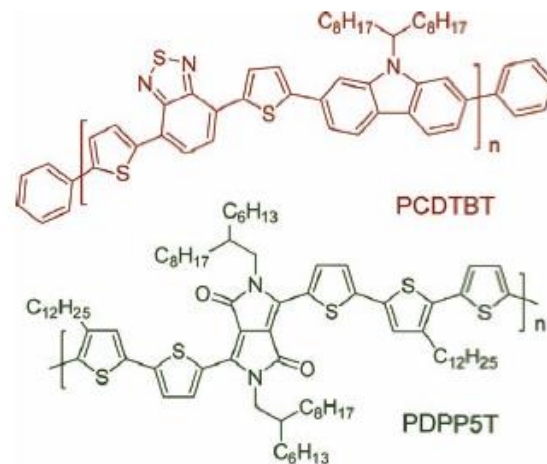
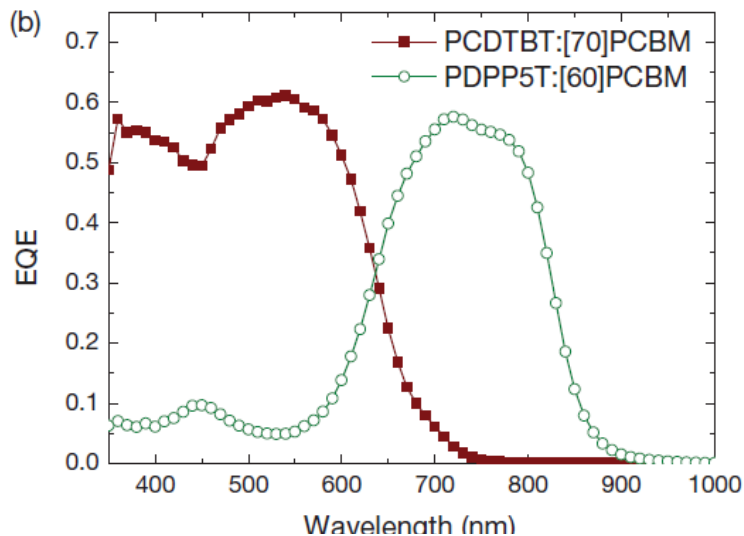
Tandem Solar Cells



Kim et al., *Science*, 2007, 317, 222



Optimization of tandem solar cells



Veronique S. Gevaerts et al *Adv. Mater.* 2012, 24, 2130–2134

Large area realization techniques

Large area BHJ processing

The requirements for an ideal process on large area are:

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

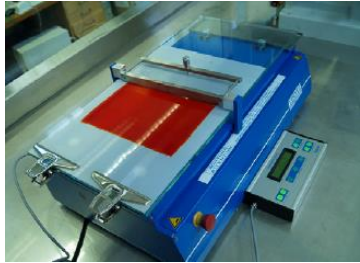
Roll to roll approach represent the preferred solution



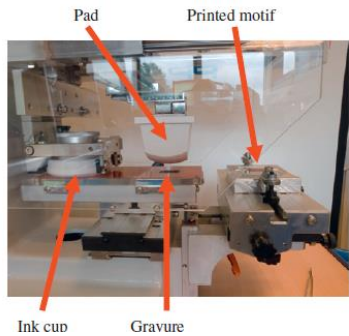
Konarka Technologies, Inc.

Large area coating techniques

There is a huge amount of film-forming techniques, but still no established approach for the realization of polymer solar cells.

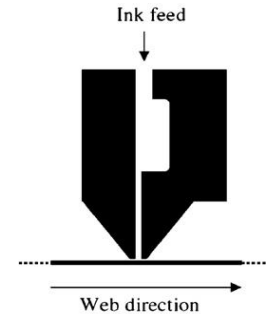
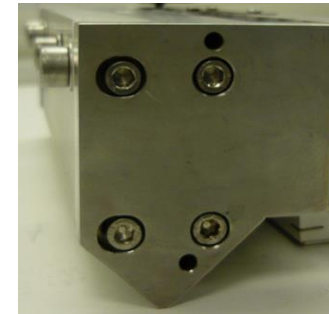


← **SCREEN-PRINTING**
DOCTOR BLADING →



← **PAD-PRINTING**

SLOT-DIE →



← **SPRAY-COATING**

INK-JET PRINTING →



Comparison of the deposition techniques

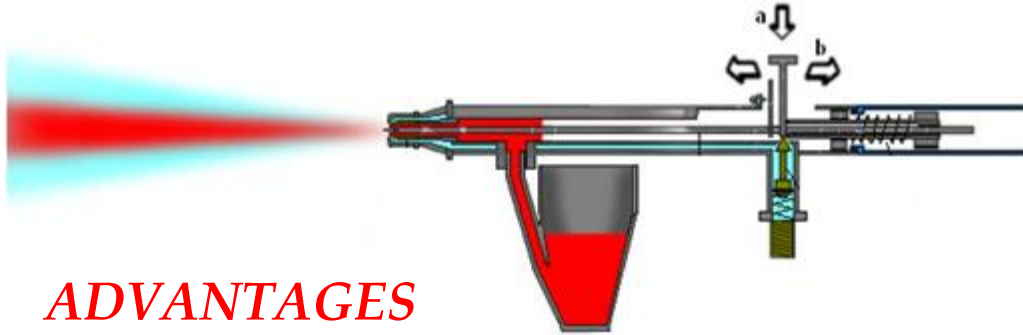
Technique	Ink waste	Pattern	Speed	Ink preparation	Ink viscosity (cP)	Wet thickness (μm)	R2R compatible
Spincoating	5	0	-	1	1	0-100	No
Doctor blade	2	0	-	1	1	0-100	Yes
Casting	1	0	-	2	1	5-500	No
Spraying	3	0	1-4	2	2-3	1-500	Yes
Knife-over-edge	1	0	2-4	2	3-5	20-700	Yes
Meniscus	1	0	3-4	1	1-3	5-500	Yes
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 $< 1 \text{ m min}^{-1}$), 3 (medium $1-10 \text{ m min}^{-1}$), 4 (fast $10-100 \text{ m min}^{-1}$), 5 (very fast $100-1000 \text{ m min}^{-1}$). Ink preparation: 1 (simple), 2 (moderate), 3 (demanding), 4 (difficult), 5 (critical). Ink viscosity: 1 (very low $< 10 \text{ cP}$), 2 (low $10-100 \text{ cP}$), 3 (medium $100-1000 \text{ cP}$), 4 (high $1000-10,000 \text{ cP}$), 5 (very high $10,000-100,000 \text{ cP}$).

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

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 set-up

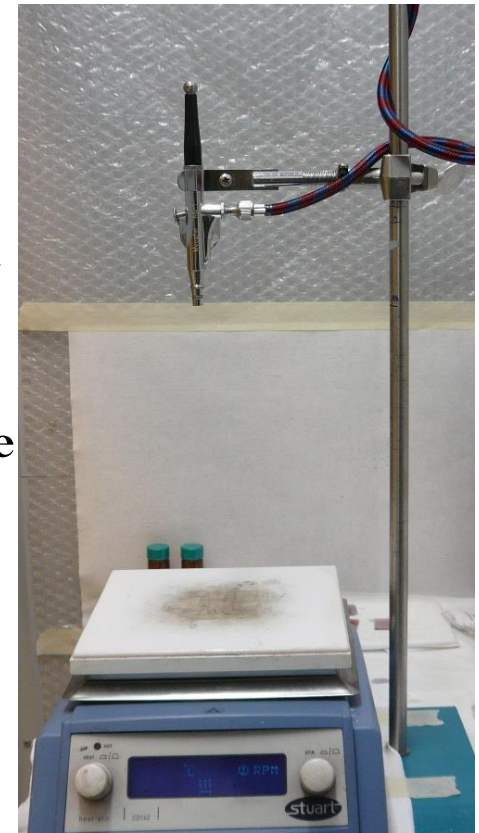
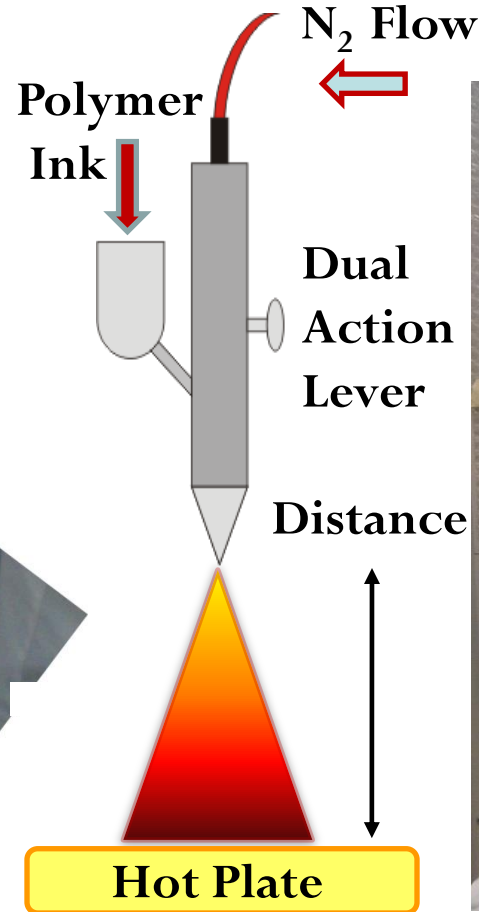
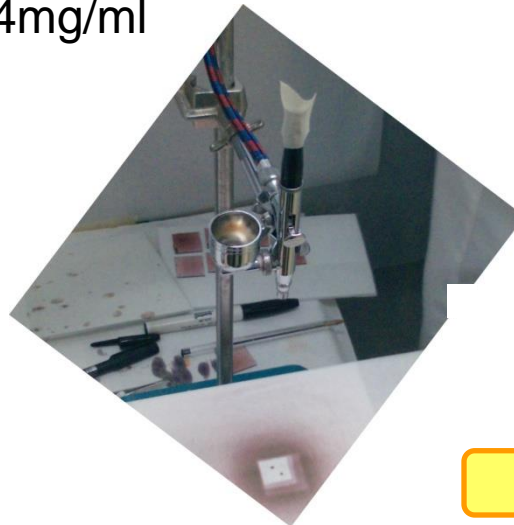
Instrument variables

1. **Distance** sample / airbrush: 10-18cm
2. **Flow Rate:** $\sim 17\text{-}25\mu\text{l/s}$ ($\sim 1\text{-}1,5\text{ml/min}$)
3. **Pressure** N_2 flow : 10-15 Psi
4. **Substrate Temperature** : $25^\circ\text{-}70^\circ\text{C}$

Conventional environment
(under chemical hood)

Film Parameters

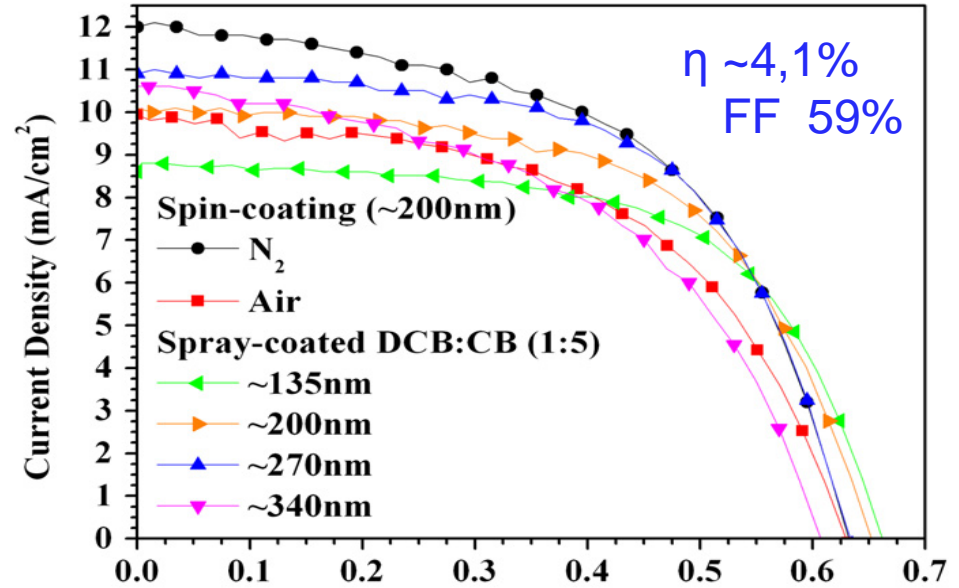
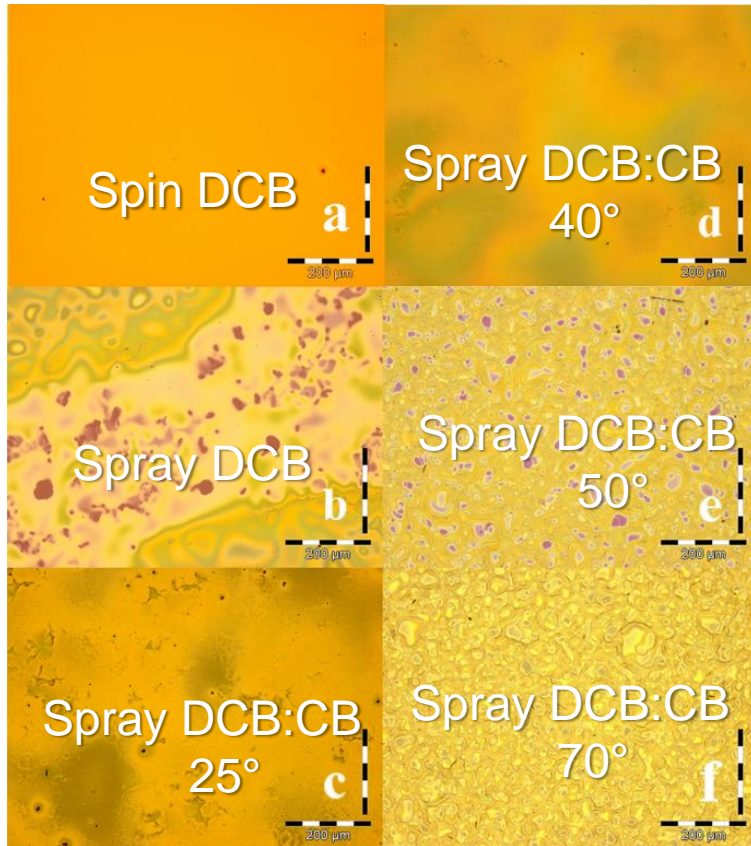
5. **Time of spray:** 10-60s
 6. **Number of passes:** 1- }
 7. **Concentration:** 1-4mg/ml
 8. **Solvents**
- Thickness



Co-Solvent optimization: temperature effect

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

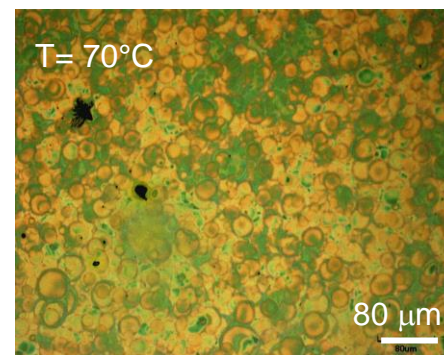
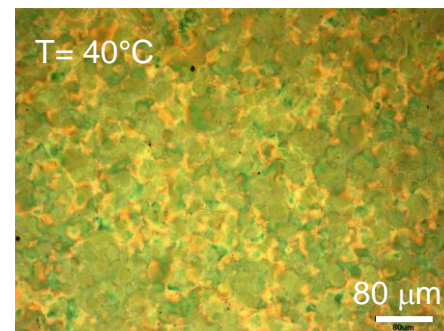
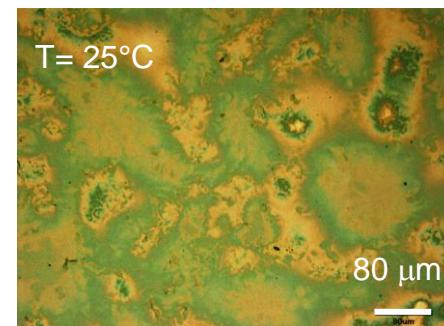
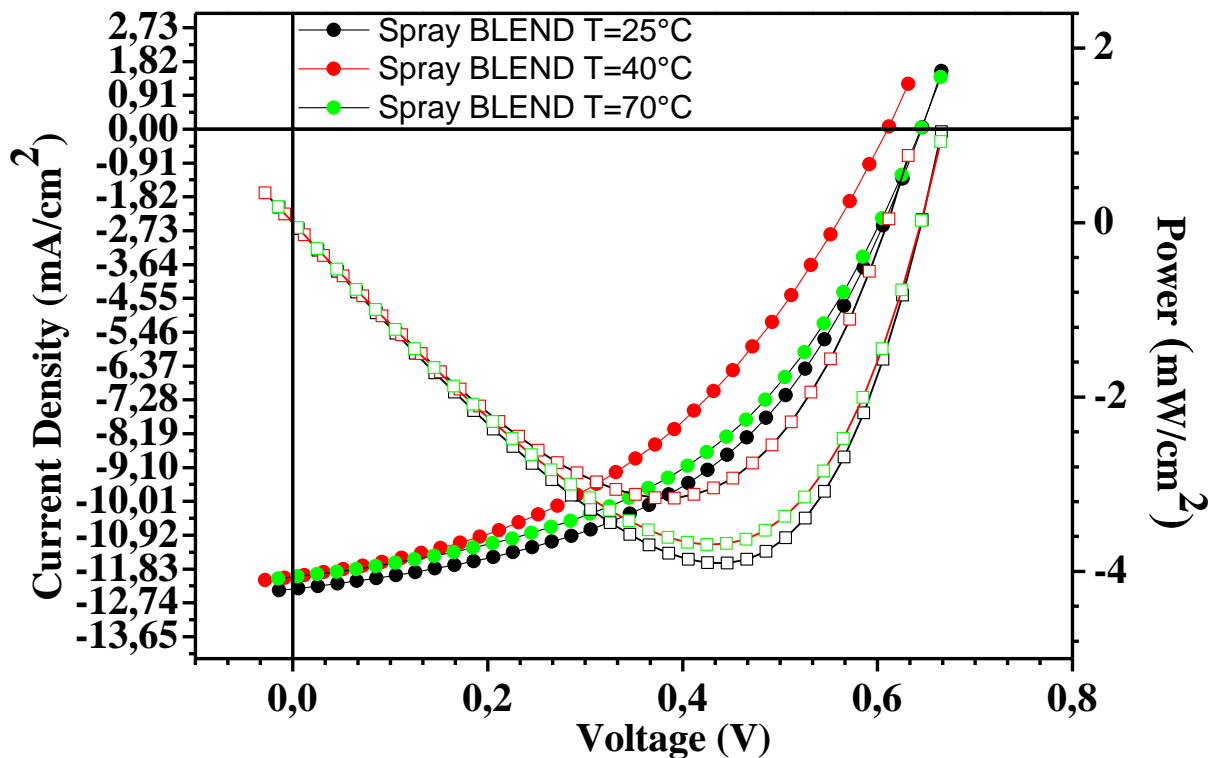
DCB: improves the phase separation
CB: allows better spray deposition



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
				9.97	53	3.3
Spray	Air	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

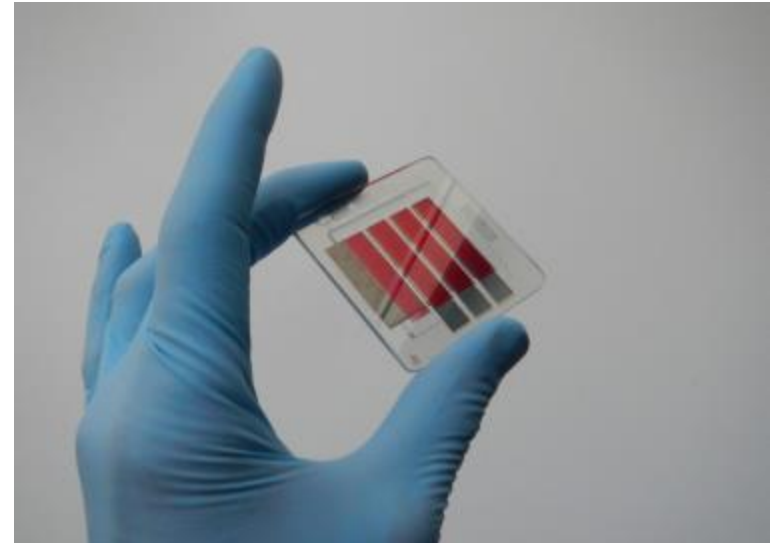
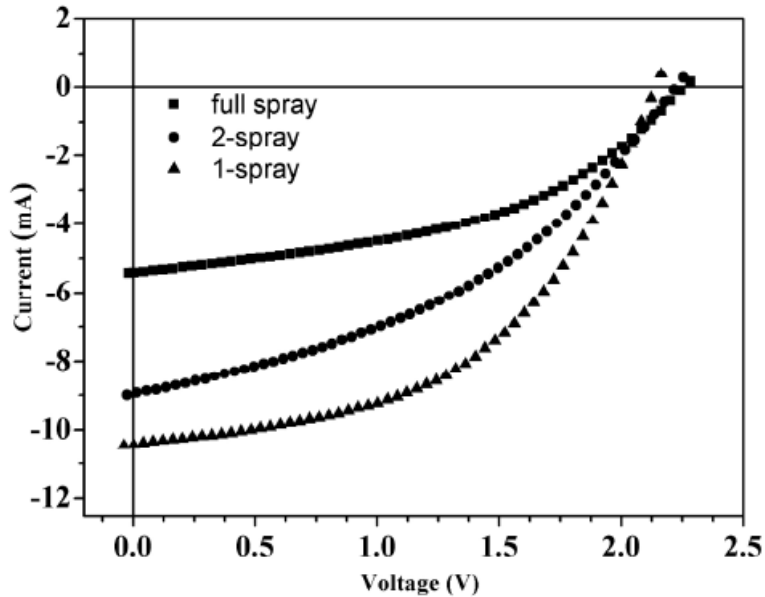
G. Susanna et al., Solar Energy Materials & Solar Cells 95 (2011) 1775–1778

Spray coating HTL + Active layer



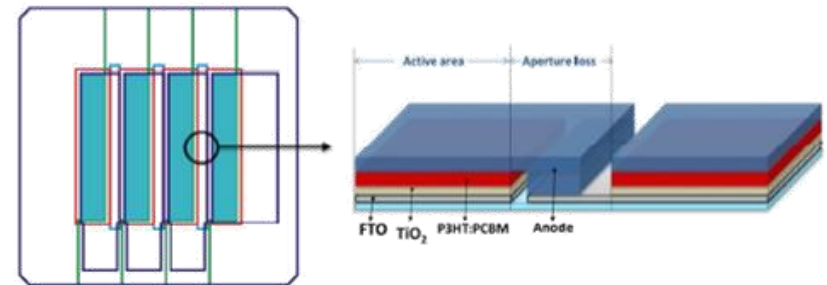
T _{substrate}	PCE %	FF %	Voc (V)	Jsc (mA/cm ²)
25 °C	3.9	49	0.64	12.4
40 °C	3.5	48	0.62	11.62
70 °C	3.7	46	0.64	12.04

Fully spray coated solar cell



Active Area: 6 cm²

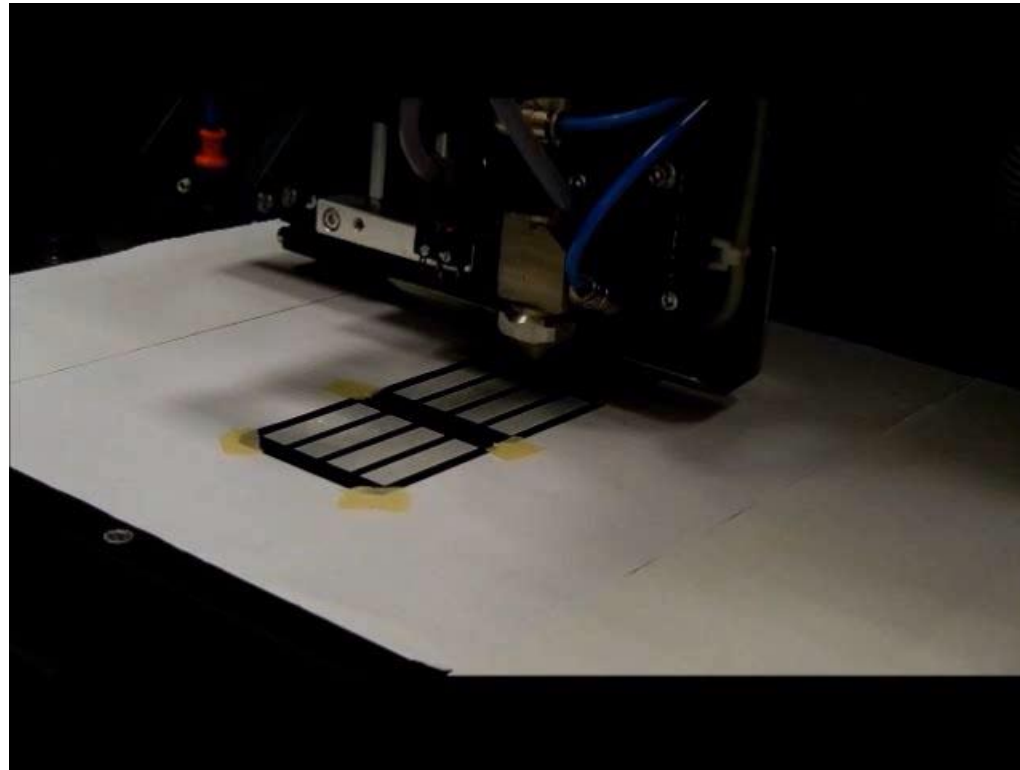
Efficiency: 1,8%



246x92mm (96 x 96 DPI)

L. La Notte, et al., Energy Technology, 1, 12 (2013) 709.

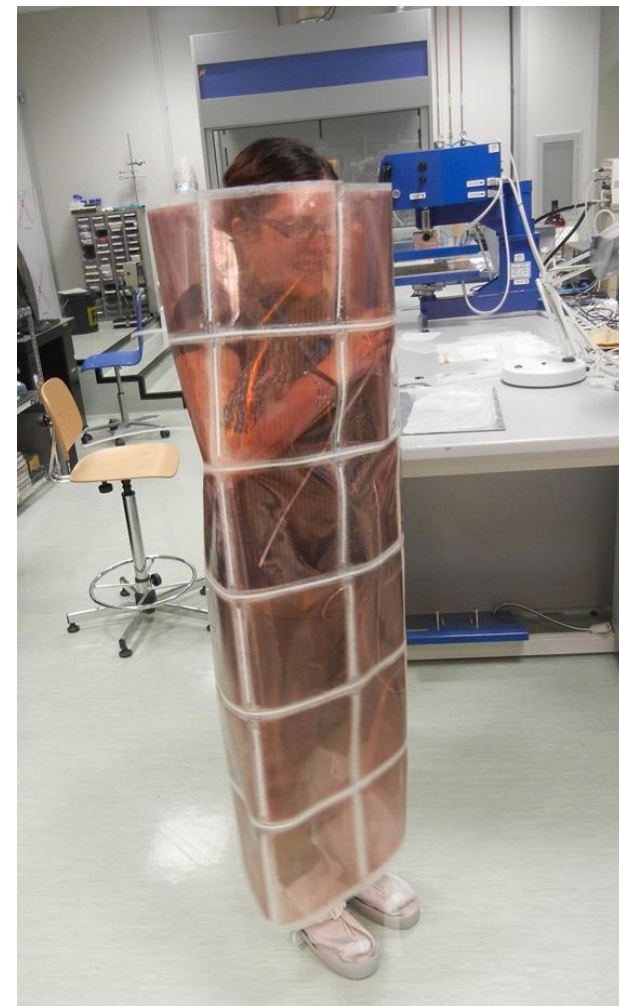
Perspectives: large area OPV using spray coating techniques



Devices on flexible substrates



Semi-trasparent

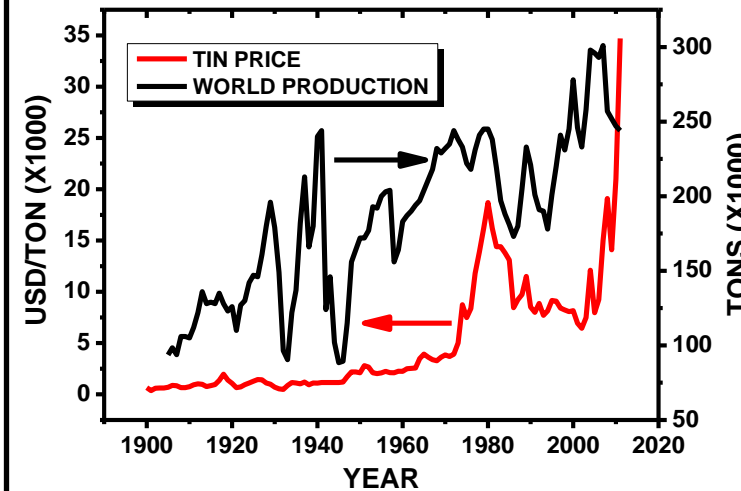
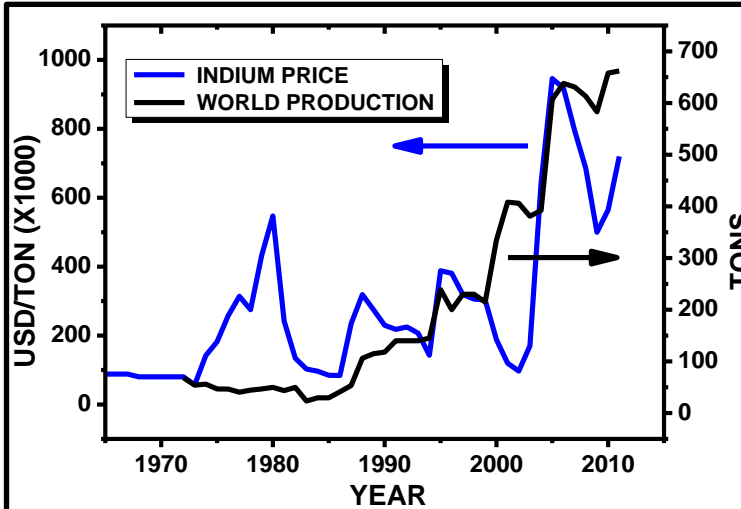


Flexible

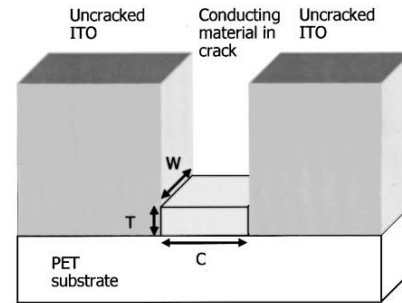
Carbon based semitransparent electrodes in new generation solar cells

The Indium Tin Oxide issue

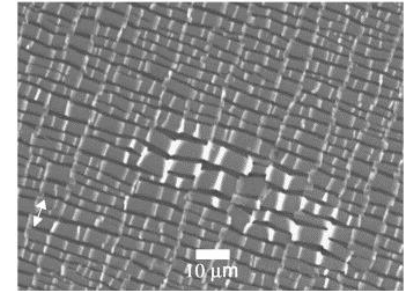
INDIUM AND TIN PRICE



CRACK AND FRACTURE AT STRAIN OF 2÷6%

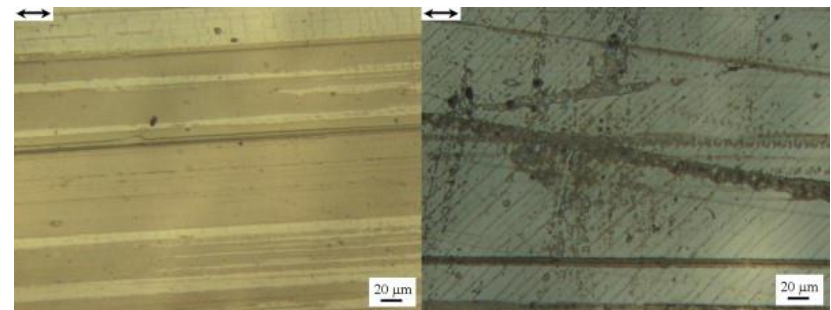


Cairns *et al.* 2000



Sierros *et al.* 2009

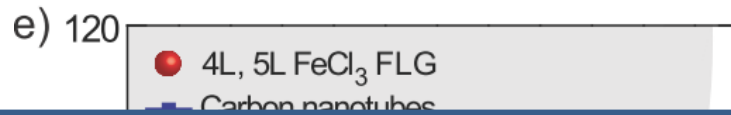
SALTS AND ACIDS CAN REDUCE LIFETIME



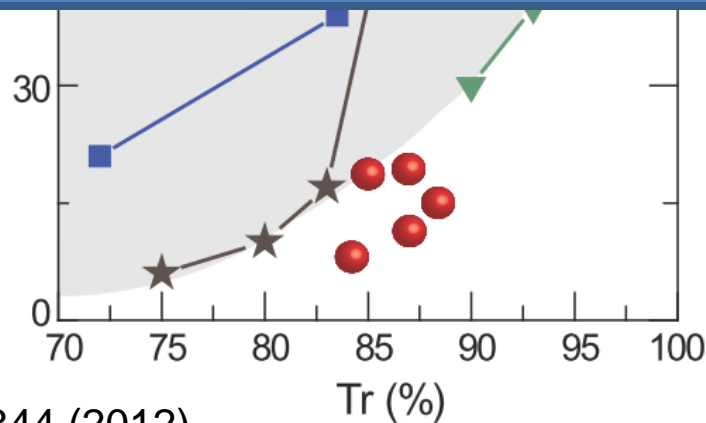
Sierros *et al.* 2009

U.S. Geological Survey 2012

Carbon based alternatives to TCO



Not only conductivity and transparency, but new functionalities can be achieved



I. Khrapach et al., Adv. Mat. 24,2844 (2012).

CNTs as TCO in new generation solar cells

CNTs Transparent Electrodes

CNTs TRANSPARENT CONDUCTIVE LAYERS

- HIGH TRANSPARENCY
- FLEXIBLE
- EXCELLENT ELECTRICAL CONDUCTIVITY
- COMPATIBLE WITH INDUSTRIAL PROCESS



Kim *et al.* 2010



Tenent *et al.* 2009



Hu *et al.* 2007

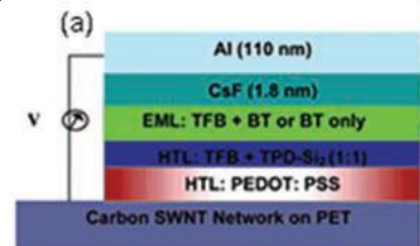
APPLICATIONS

DISPLAY



Unidym/Samsung

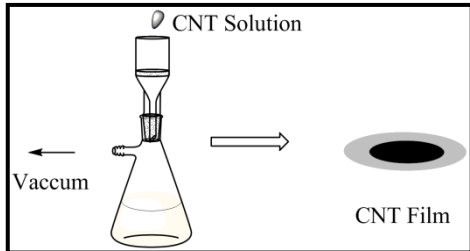
SOLAR CELL



Yu *et al.* 2009



CNTs Deposition Techniques



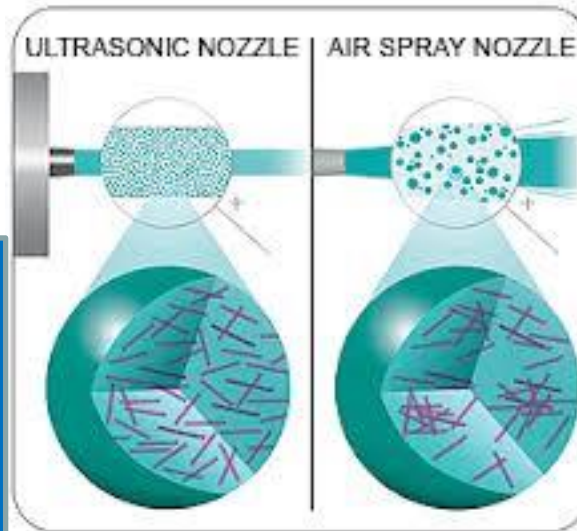
VACUUM ASSISTED FILTRATION

PRO:

- INEXPENSIVE
- CONTROL OVER FILM THICKNESS
- NO SURFACTANTS

CONS:

- VERY LIMITED FILM SIZE
- SLOW PROCESS



Sono-Tek Corp.

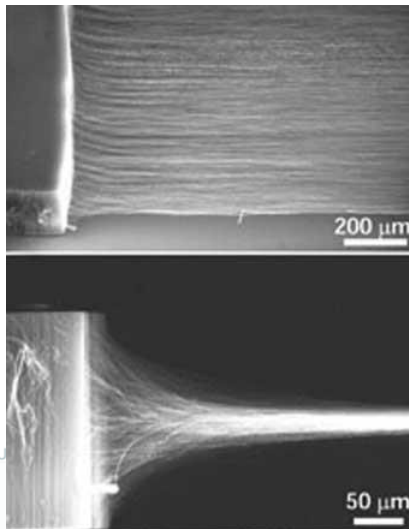
SPRAY COATING

PRO:

- SCALABLE
- EFFECTIVE FOR CONTOURED SURFACES

CONS:

- INHOMOGENEOUS IF NOT AUTOMATIC
- AVERAGE ADHESION



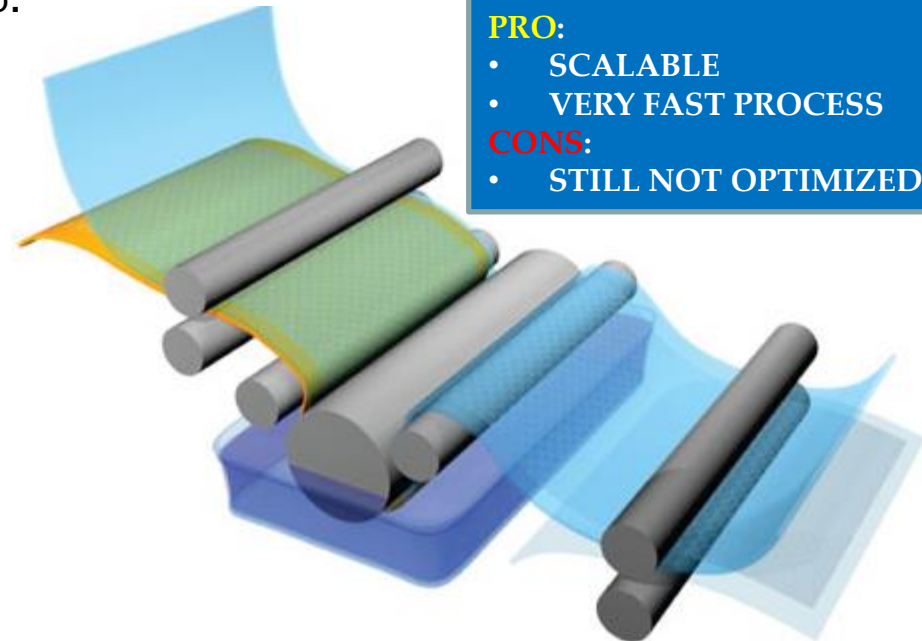
EXTRUSION OF THREADS FROM CNTs FORESTS

PRO:

- SCALABLE
- VERY STRONG THREAD

CONS:

- RELATIVELY COMPLEX PROCESS



ROLL-TO-ROLL

PRO:

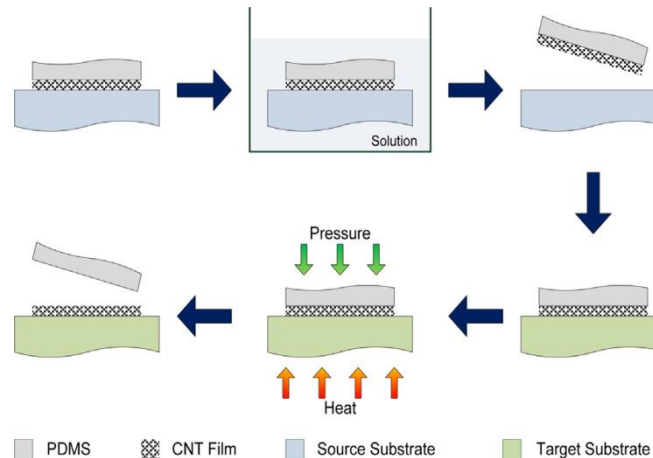
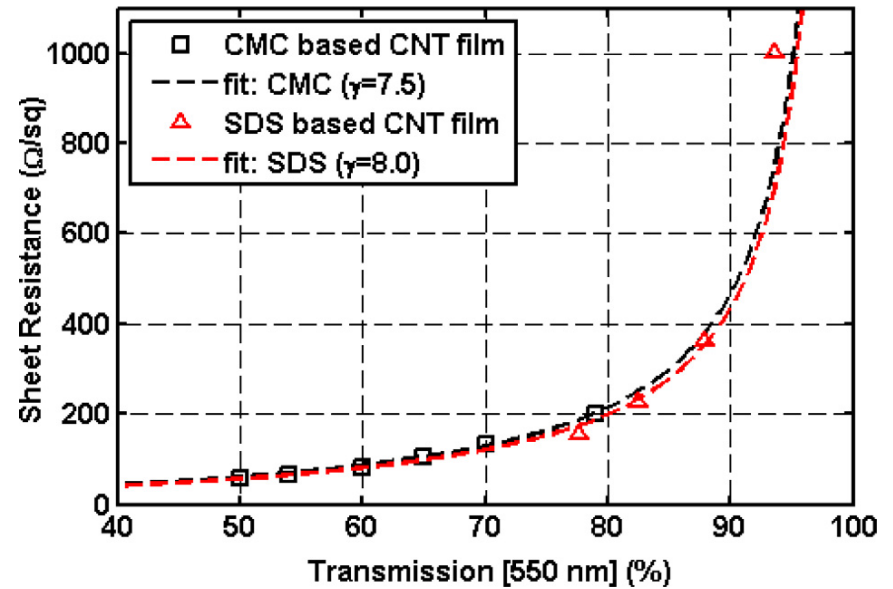
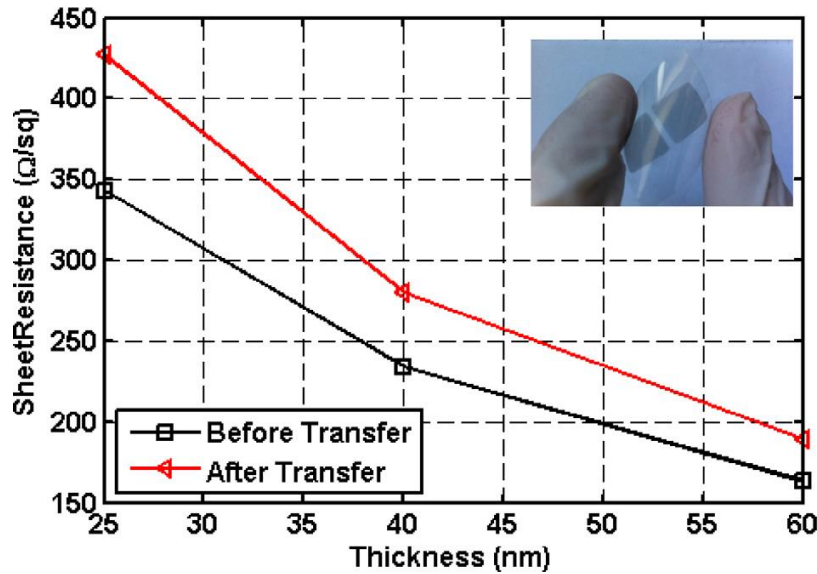
- SCALABLE
- VERY FAST PROCESS

CONS:

- STILL NOT OPTIMIZED

POLO PER IL
FOTOVOLTAICO A CELLE
ORGANICHE DEL LAZIO

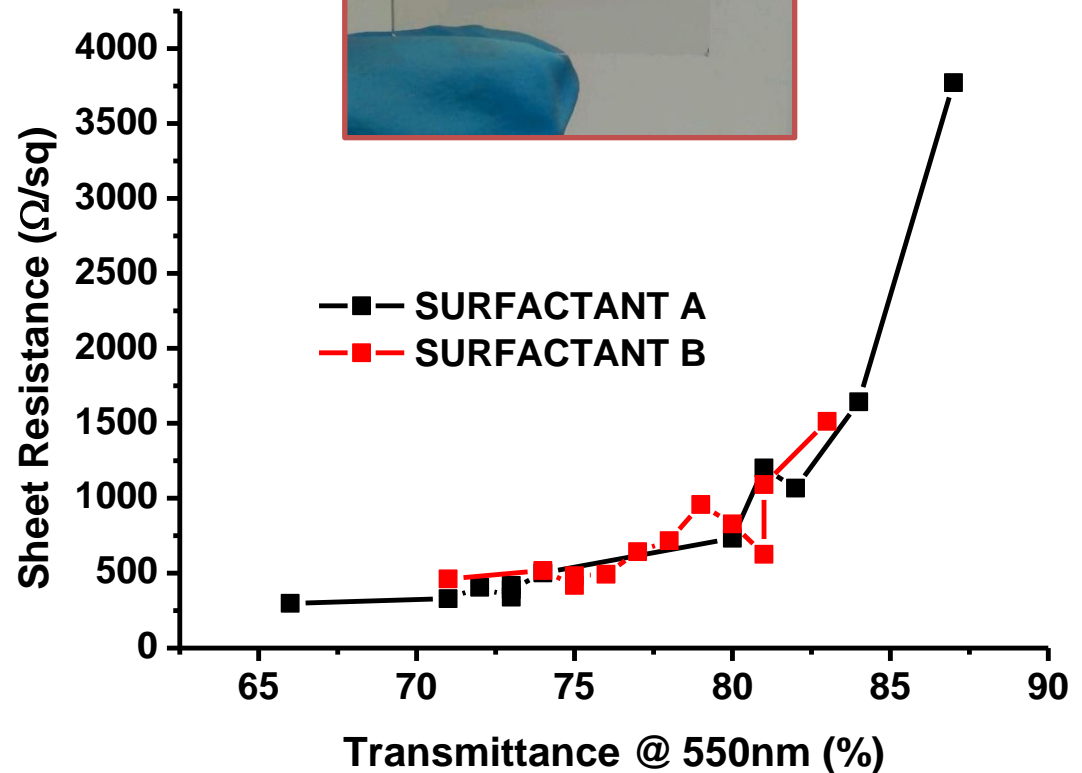
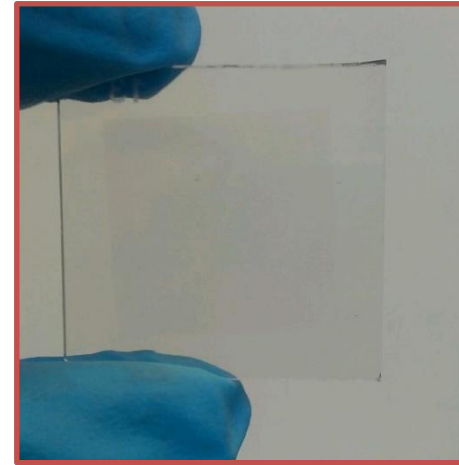
Spray coating CNTs on flexible substrates



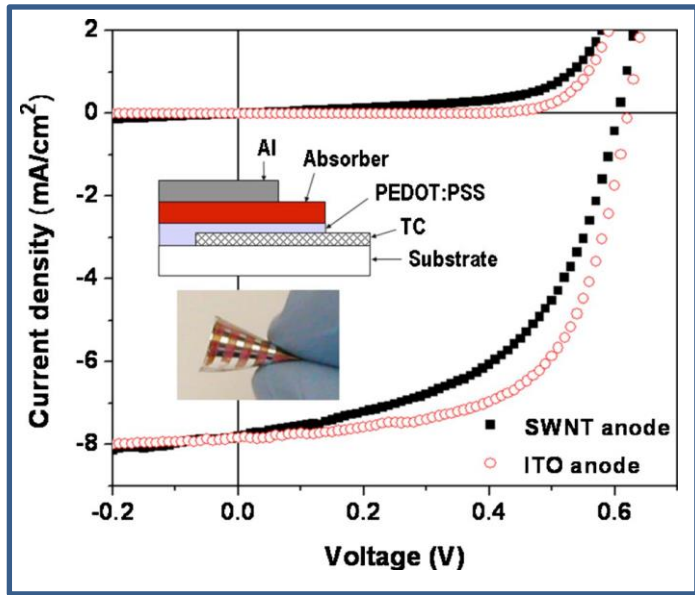
Transmittance 86% at a sheet resistance of 250 Ω/sq have been fabricated on flexible substrates

Spray Deposited CNTs @CHOSE

Sample	Transmittance (%)	Sheet-Resist. (Ω/\square)	Transmittance (%)	Sheet-Resist. (Ω/\square)
	SURFACTANT A		SURFACTANT B	
1	66	298	71	461
2	71	329	74	518
3	72	406	75	417
4	73	339	75	482
5	73	391	76	492
6	73	418	77	643
7	74	501	78	716
8	80	733	79	958
10	81	1202	80	828
11	82	1067	81	626
12	84	1643	81	1091
13	87	3773	83	1512

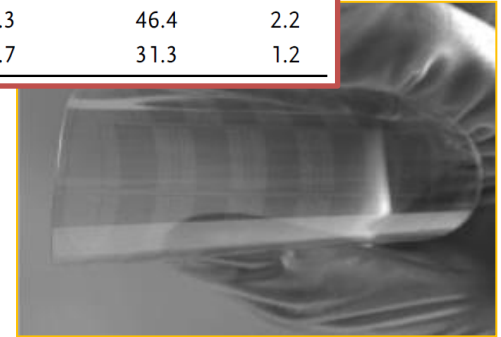
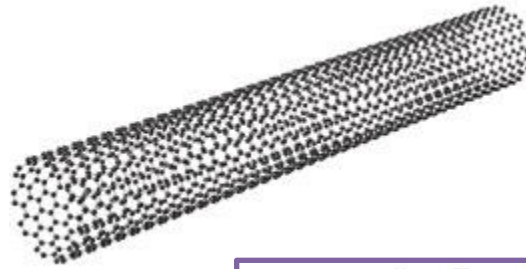


CNTs Electrodes in OPV

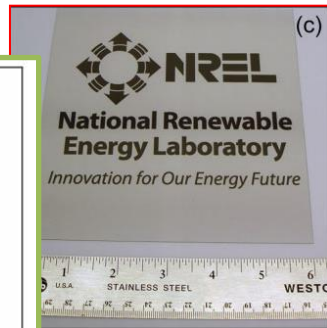
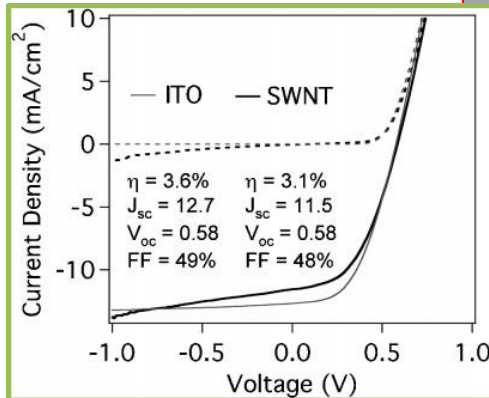


Anode	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
ITO/glass	0.55	8.4	50.0	2.3
SWCNT/glass (DCE)	0.55	9.9	43.1	2.3
SWCNT/glass (H ₂ O:SDS)	0.59	7.3	46.4	2.2
SWCNT/glass (H ₂ O:SDBS)	0.55	6.7	31.3	1.2

Kim *et al.* 2010



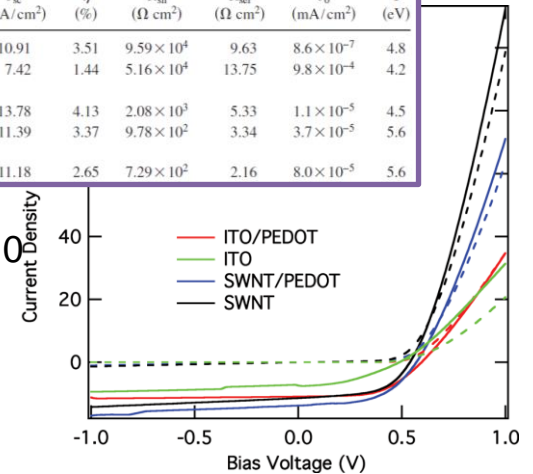
Rowell *et al.* 2006



Tenent *et al.* 2009

Electrode	V_{oc} (V)	FF (%)	J_{sc} (mA/cm ²)	η (%)	R_{sh} (Ω cm ²)	R_{ser} (Ω cm ²)	J_0 (mA/cm ²)	Φ (eV)
ITO/PEDOT	594.9	55.3	10.91	3.51	9.59×10^4	9.63	8.6×10^{-7}	4.8
ITO 56 Ω /sq	487.3	40.6	7.42	1.44	5.16×10^4	13.75	9.8×10^{-4}	4.2
SWNT/PEDOT	570.2	52.9	13.78	4.13	2.08×10^3	5.33	1.1×10^{-5}	4.5
24 Ω /sq SWNT	539.8	55.4	11.39	3.37	9.78×10^2	3.34	3.7×10^{-5}	5.6
Certified Device— 60 Ω /sq SWNT	517	45.9	11.18	2.65	7.29×10^2	2.16	8.0×10^{-5}	5.6

Barnes *et al.* 2010

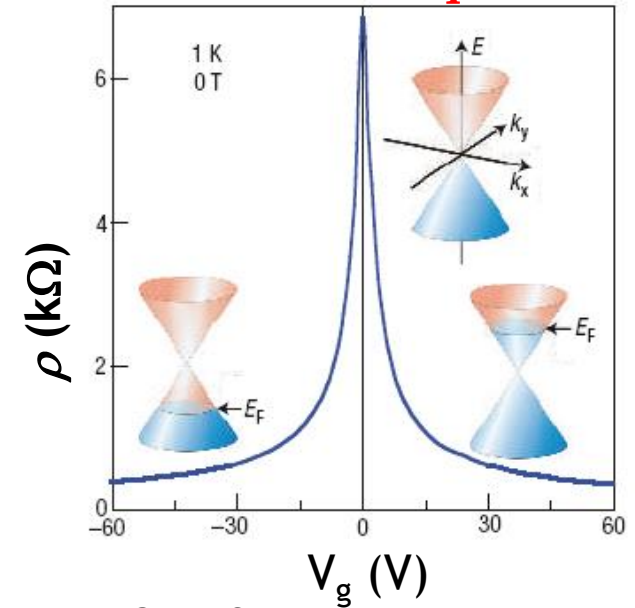
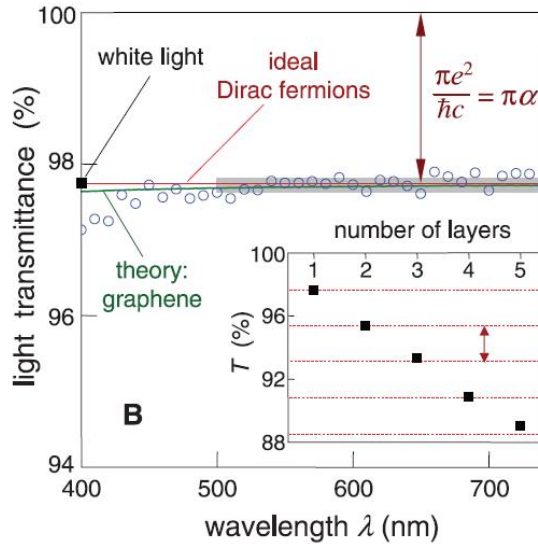
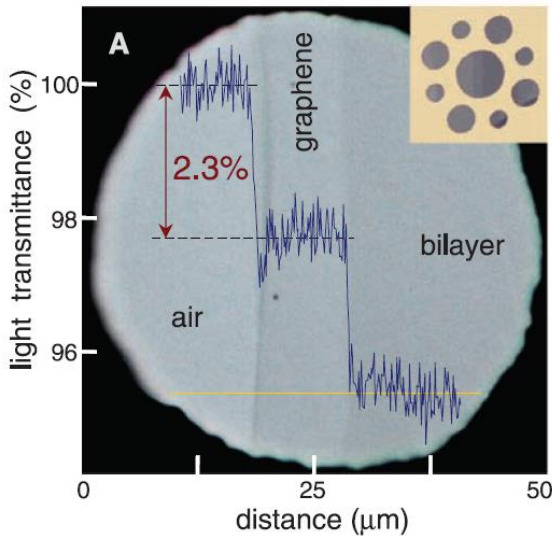


Graphene based BHJ solar cells

Graphene for Transparent Electrodes

Transparency of graphene monolayer: ~97.7 %

Intrinsic sheet resistance ($h/4e^2$): ~ 6 k Ω /square

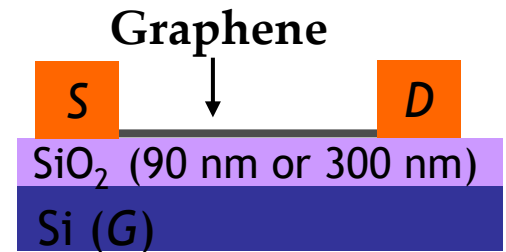
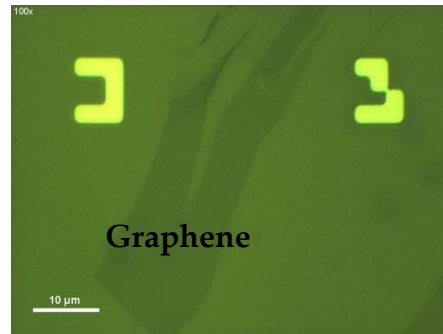
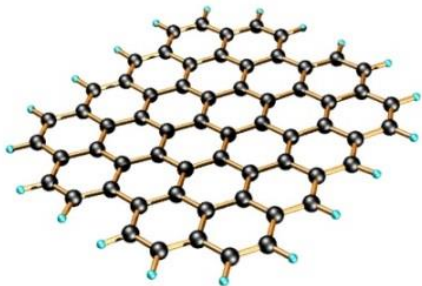


Geim & Novoselov
Nature Materials 6, 184, (2007)

Mechanically exfoliated graphene

Nair et al. *Science* 320, 1308, (2008)

Graphene is very susceptible to ambient adsorbates.



CVD of graphene

CVD Method (on Cu, Ni or Pt catalyst layer), e.g.,

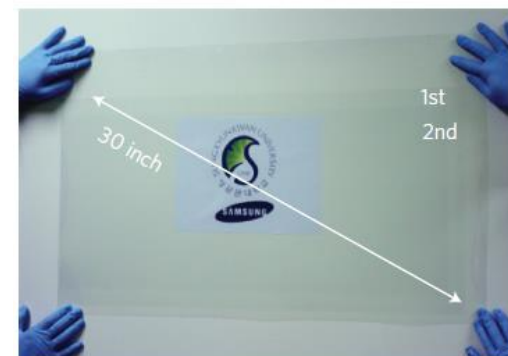
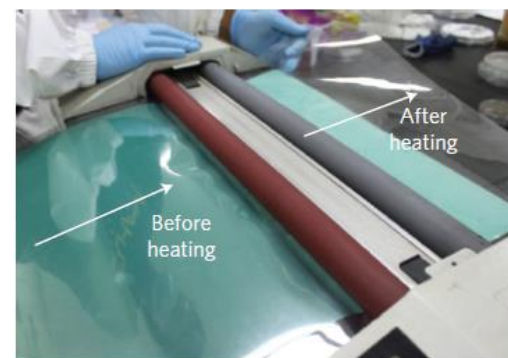
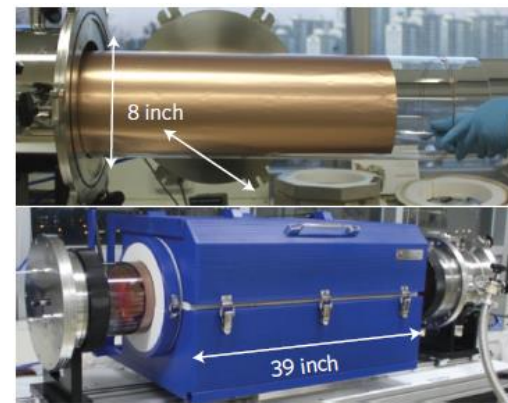
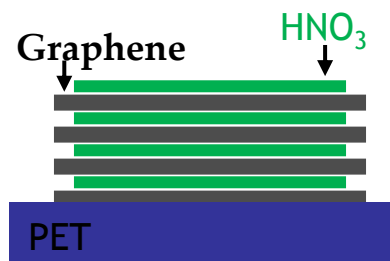
- Cu foil (catalyst, 25 μm thick), heated in H_2 at 1000°C to increase grain size
- CVD of CH_4 & H_2 at 1000°C
- Cool down, spin-on protective polymer layer (100 nm), etch away Cu foil (.....residue)
- Transfer graphene to substrate, dissolve polymer (...residue)

Properties

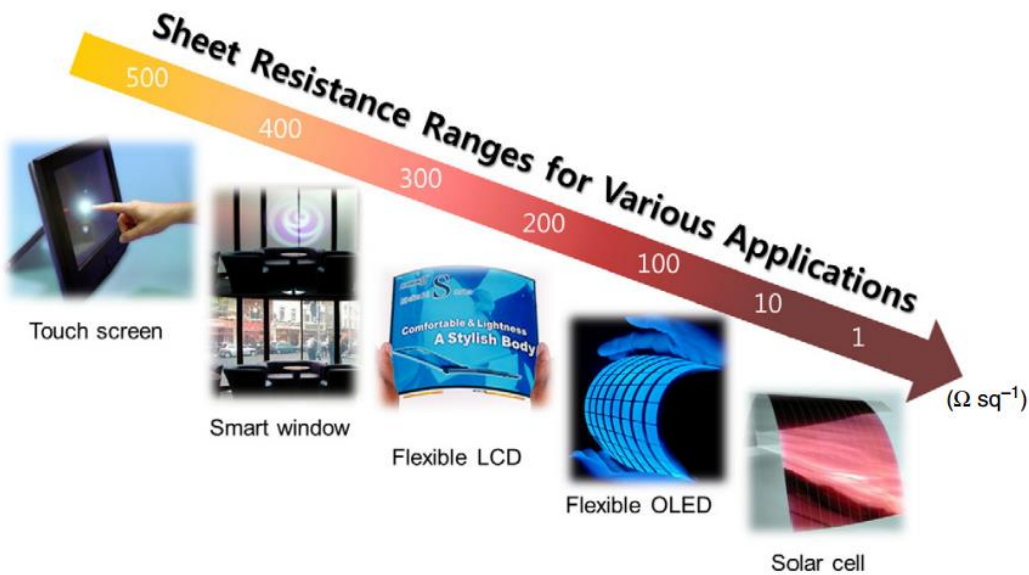
- Monolayer graphene transmission: ~97.7%
- Intrinsic graphene: $R \sim 6 \text{ k}\Omega/\text{sq.}$ (1 - 5 $\text{k}\Omega/\text{sq.}$ for best CVD)
- Adsorbate-doped graphene:
 $R \sim 100 \Omega/\text{sq.}$ using HNO_3 (record! Stability concerns)
- Stack of 4 monolayers (resistors in parallel):
 - $R \sim 25 \Omega/\text{sq.}$
 - (400 - 800 $\Omega/\text{sq.}$ at AMO: cm-scale)
 - ~90% transmission

Ruoff Group, X. S. Li *et al.*, *Science* 324, 1312 (2009)

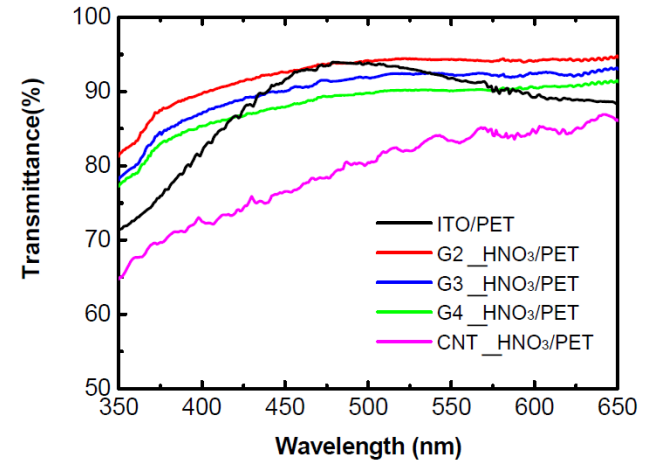
Bae *et al.*, SKKU, Samsung *Nat. Nano* 5 574 (2010)



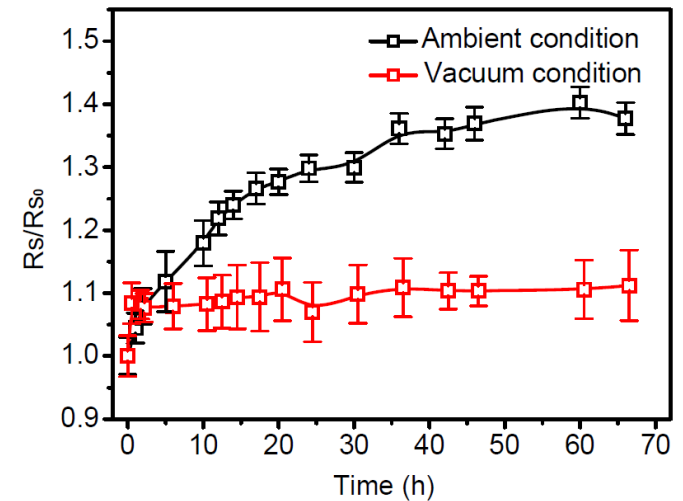
State of the art



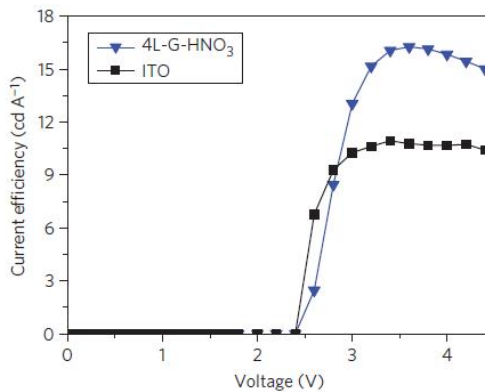
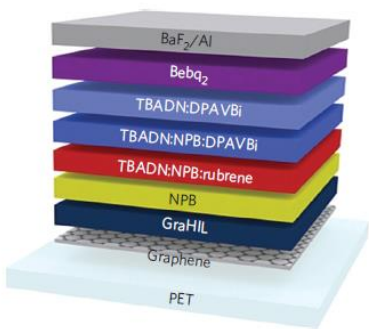
Transmission for 2, 3 & 4 layer graphene sheets doped with HNO_3



Stability of sheet resistance after doping with HNO_3

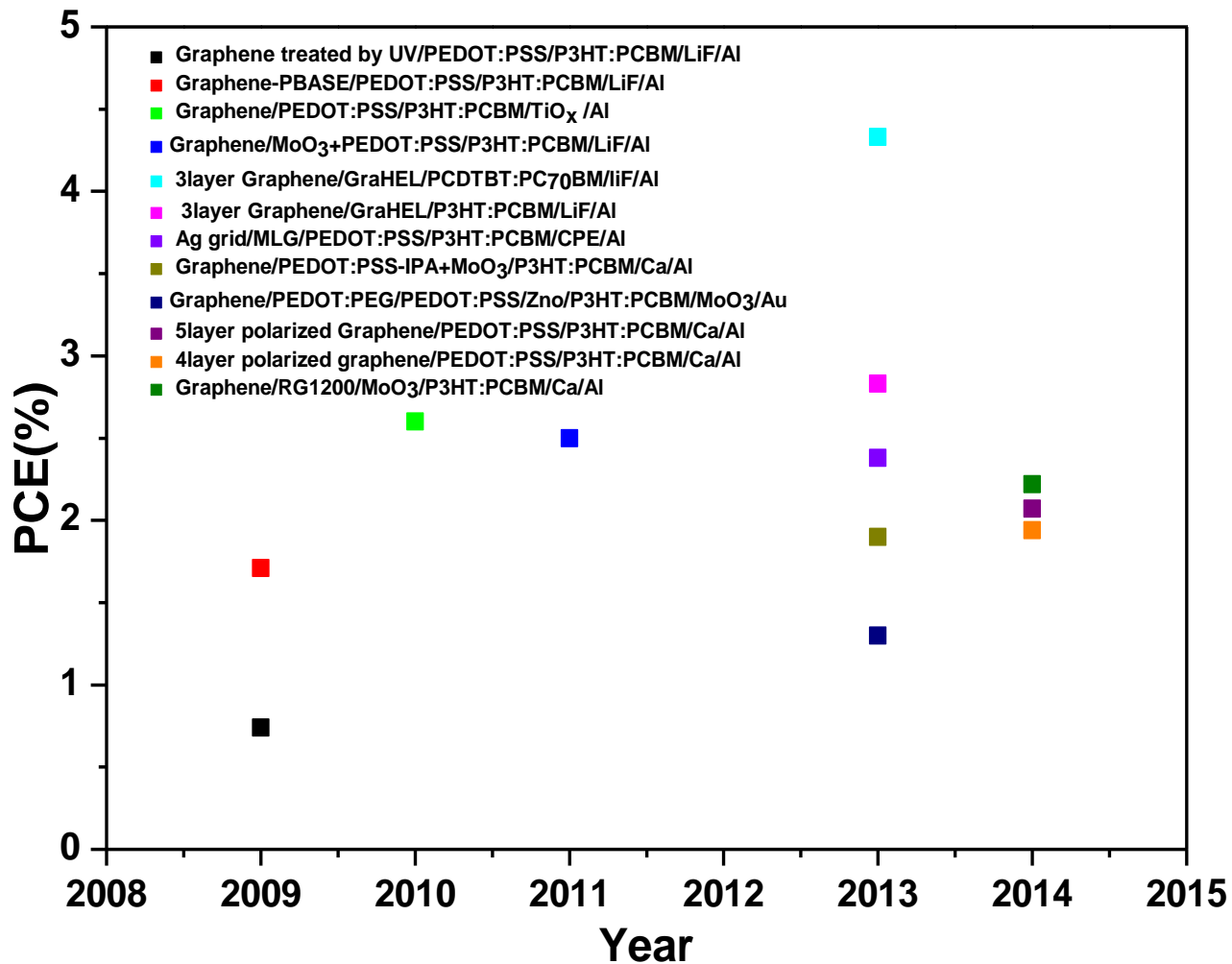


Graphene OLED

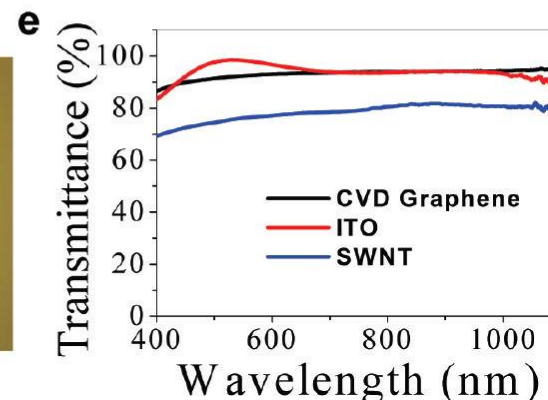
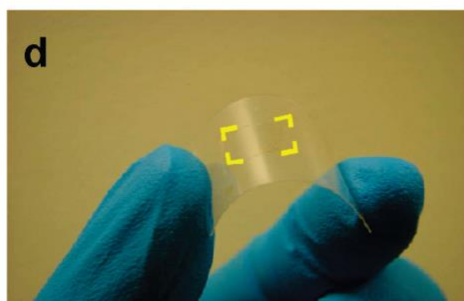
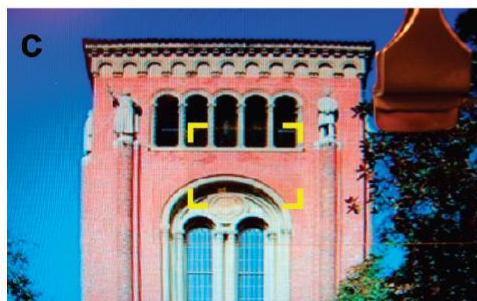
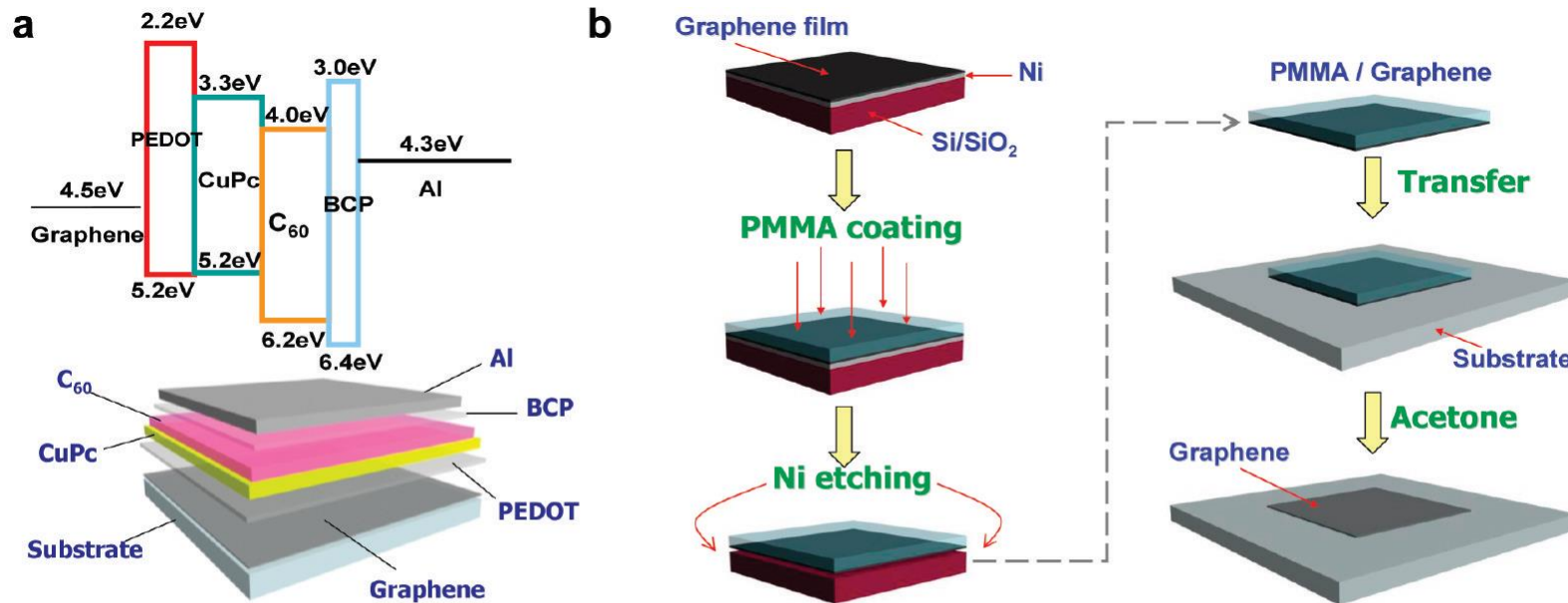


Han et al., *Nat. Photonics* 6, 105 (2012)

Graphene based OPV



Graphene electrodes on glass



GOMEZ DE ARCO ET AL. ACS nano VOL. 4, NO. 5, 2865–2873, 2010

Graphene electrodes on glass

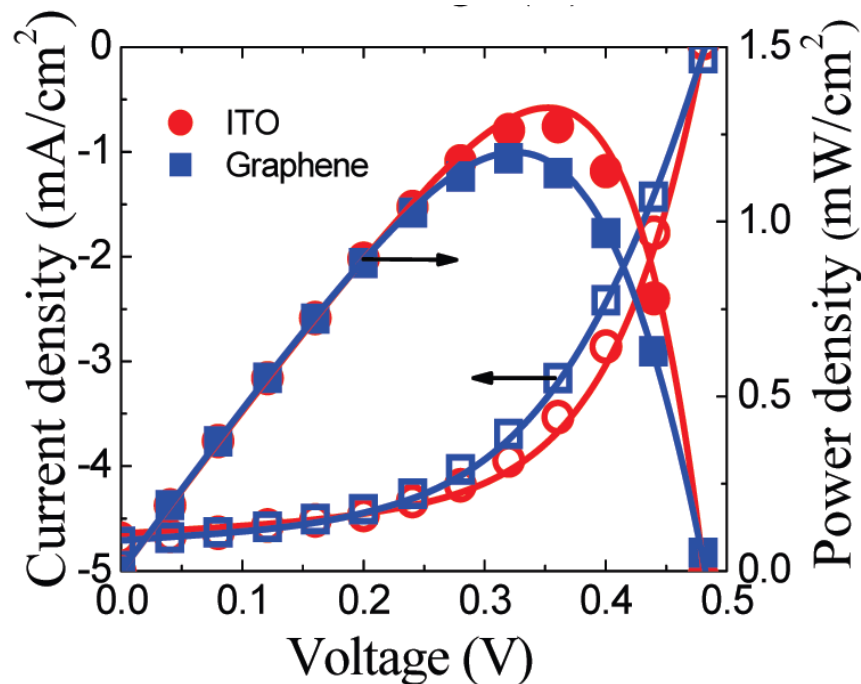
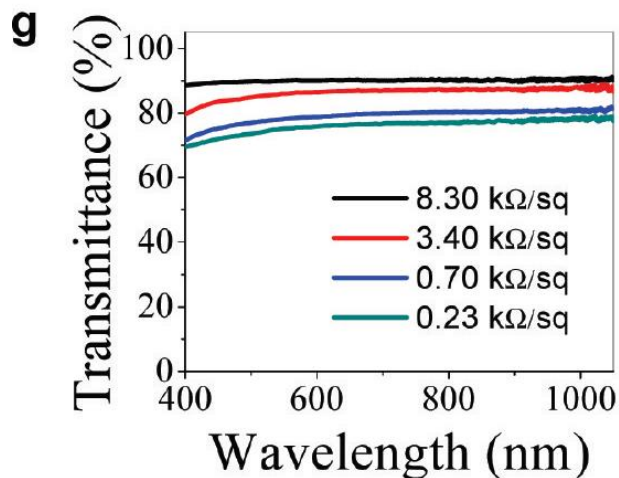


TABLE 1. Performance Details of OPV Cells Built on PET^a

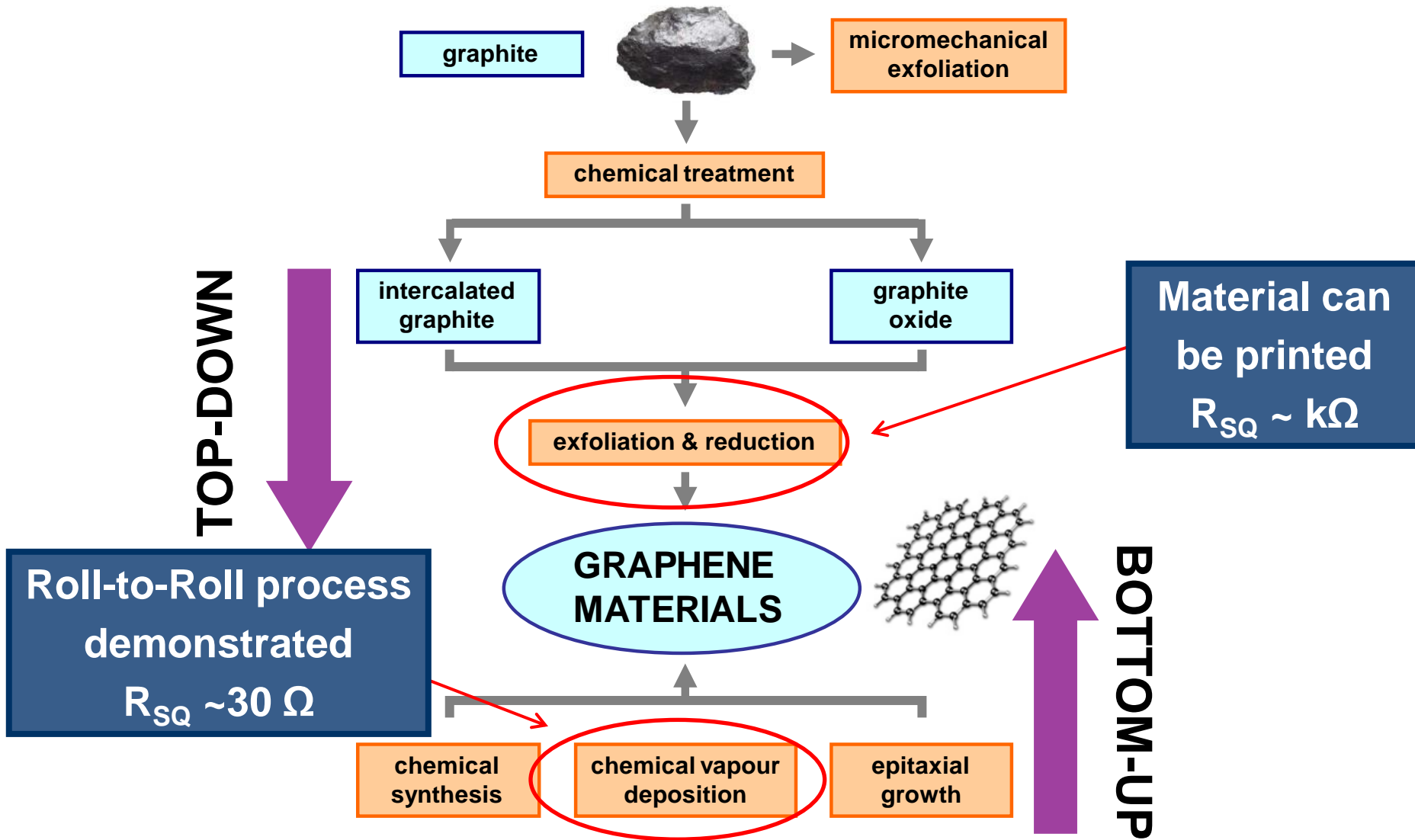
anode	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
CVD graphene	4.73	0.48	0.52	1.18
ITO	4.69	0.48	0.57	1.27

^aThe structure of the devices is given by [CVD graphene/PEDOT/CuPc/C₆₀/BCP/Al] and ITO/PEDOT/CuPc/C₆₀/BCP/Al] for CVD graphene and ITO OPVs, respectively.

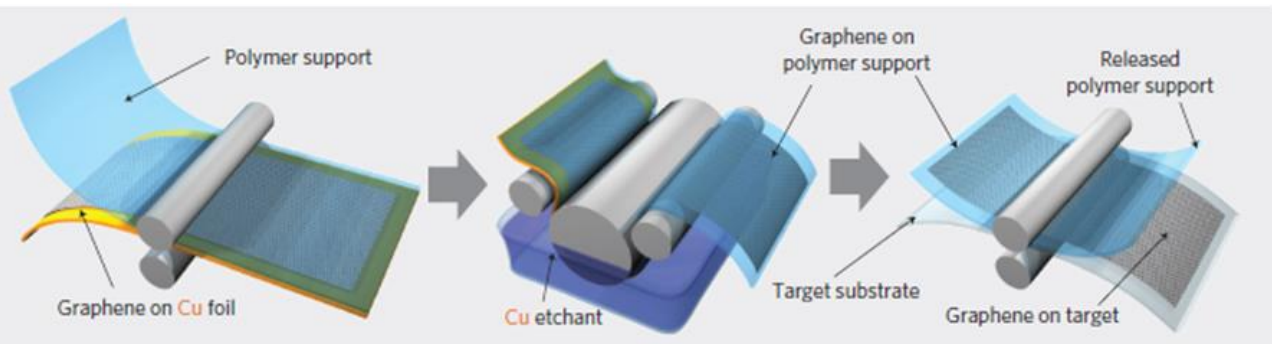
GOMEZ DE ARCO ET AL. ACS nano VOL. 4, NO. 5, 2865–2873, 2010

Is it possible to scale up?

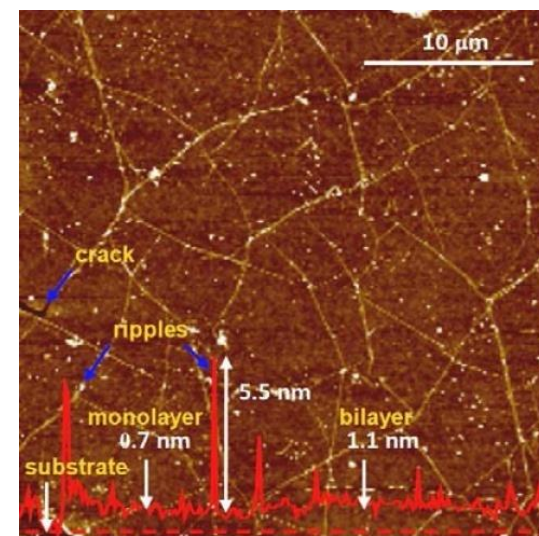
Graphene production



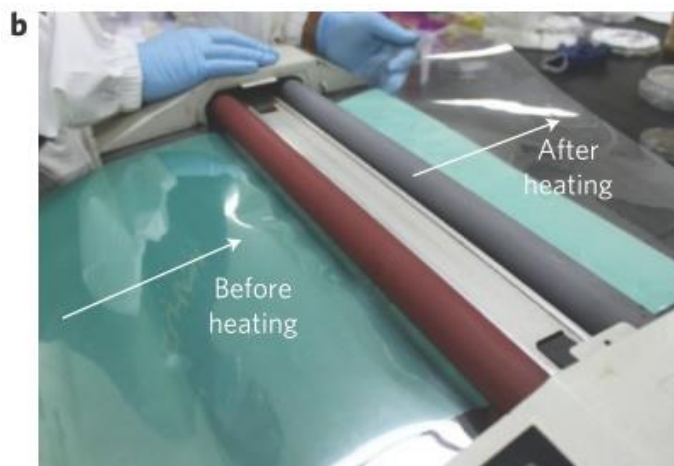
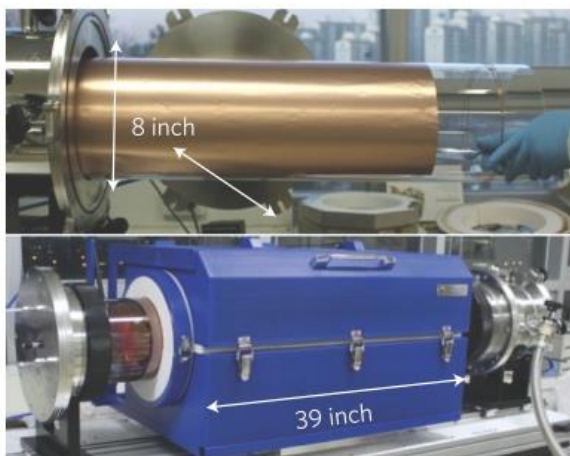
Graphene Roll-to-roll production on copper foil



AFM of graphene on Cu

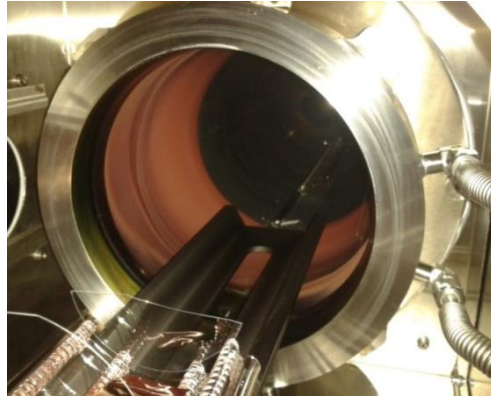
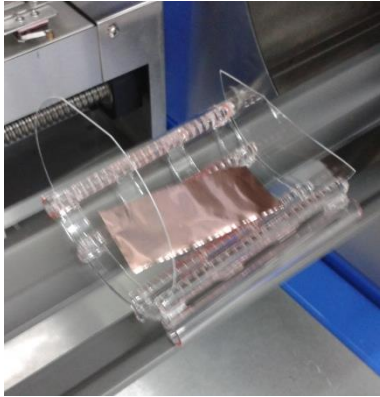


$\mu = 5000 \text{ cm}^2/\text{Vs}$ at RT



S. Bae et al. Nature Nano. 5, 571 (2010)

Perspectives: scaling up the graphene growth



Tyndall CVD:

6" tube

Gas precursor: CH_4

Liquid: toluene (low temperature CVD)

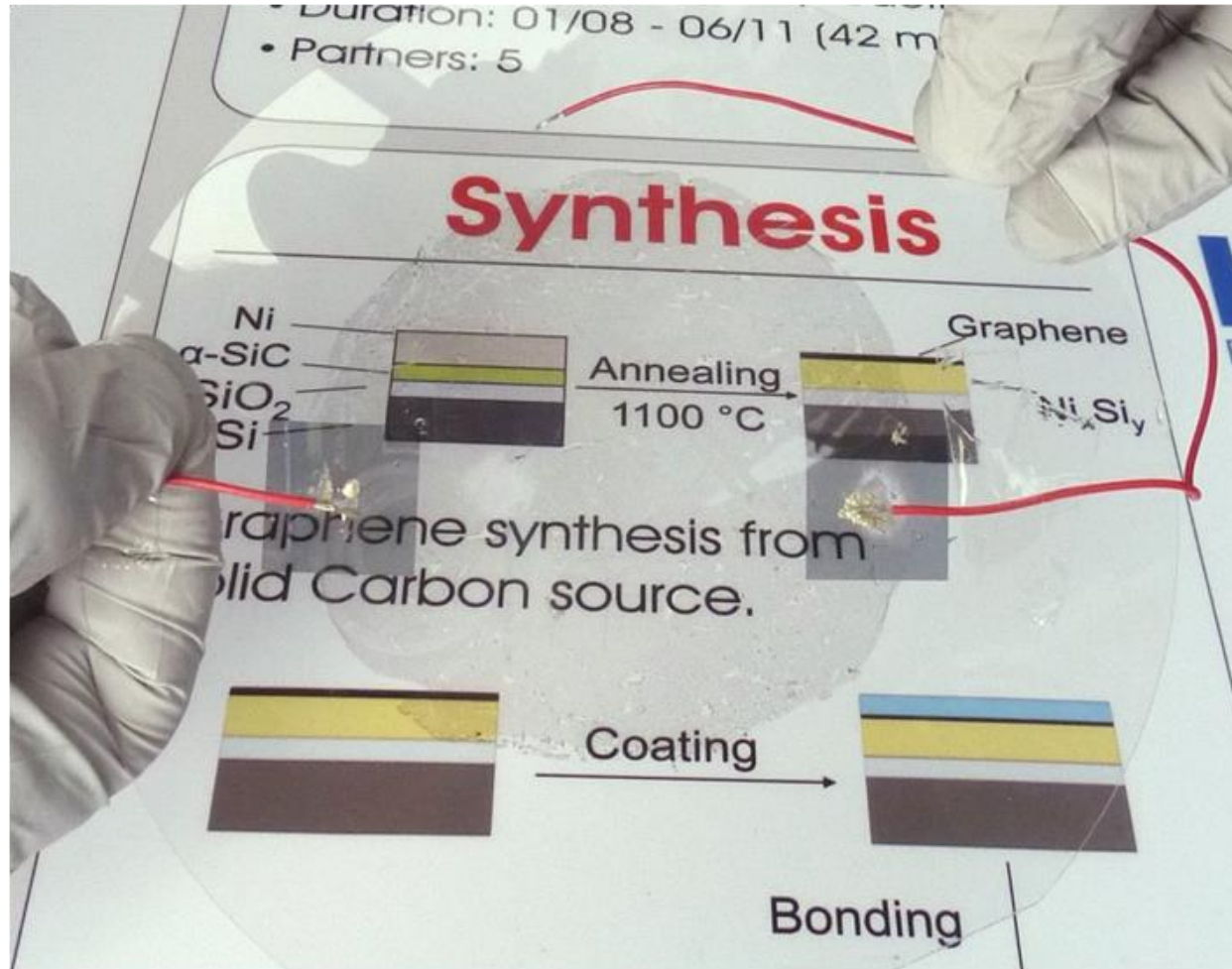
CVD Method

- Cu foil catalyst (25 μm thick) heated in H_2 at 1000 $^\circ\text{C}$ to remove contaminants/oxide and increase grain size
- CVD of CH_4 at 1000 $^\circ\text{C}$, cool down to room temperature
- Spin-on protective polymer layer, wet-etch away Cu foil
- Transfer graphene to transparent substrate and dissolve polymer

Graphene for Transparent Electrodes

- Monolayer graphene transmission: $\sim 97.3\%$ (absorption = π/ehc)
- Intrinsic graphene: $R \sim 6000 \Omega/\text{sq.}$ ($h/4e^2$)
- Heavily-doped graphene:
 $R \sim 100 \Omega/\text{sq.}$ (Bae et al., Nat. Nano 2010)
- Stack of 4 monolayers:
 $R \sim 25 \Omega/\text{sq.}$
- 90% transmission

6 inch wafer scale graphene contact on PET



Acknowledgments

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- Martina Dianetti
- Claudio Ciceroni
- Giacomo Ulisse



Thanks for the attention

Questions?