EnerHarv 2024
PSMA International Workshop | 26-28 June, 2024 | Perugia, Italy

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EnerHarv 2024 Workshop:

Perovskite PV for Flexible & Indoor Applications

Presented By –

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Thursday, June 27, 2024

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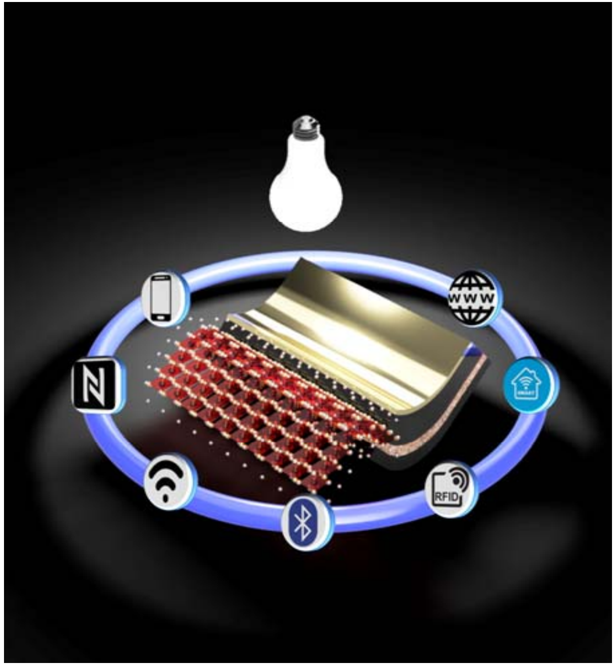
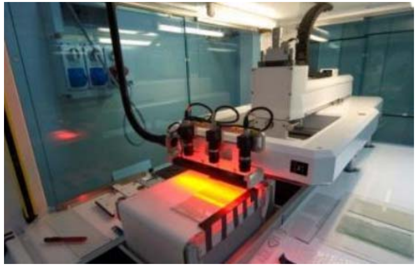
OVERVIEW

- **indoor PV**
- **Test conditions: indoor vs outdoor**
- **Customization of perovskite PV for indoors**
- **Going on flexible plastic substrates**
- **Bandgap engineering**
- **Interface engineering via TBAB**
- **Examples of possible applications**
- **Conclusion**



CHOSE - Center for Hybrid and Organic Solar Energy

- Perovskite Solar Cells
- Polymer Solar Cells
- Dye Solar Cells
- Bio-hybrid devices
- Supercapacitors



http://www.chose.uniroma2.it/

CHOSE Centre for Hybrid and Organic Solar Energy [https://www.linkedin.com/company/19095419/]

Photovoltaics for indoor light harvesting

OUTDOORS

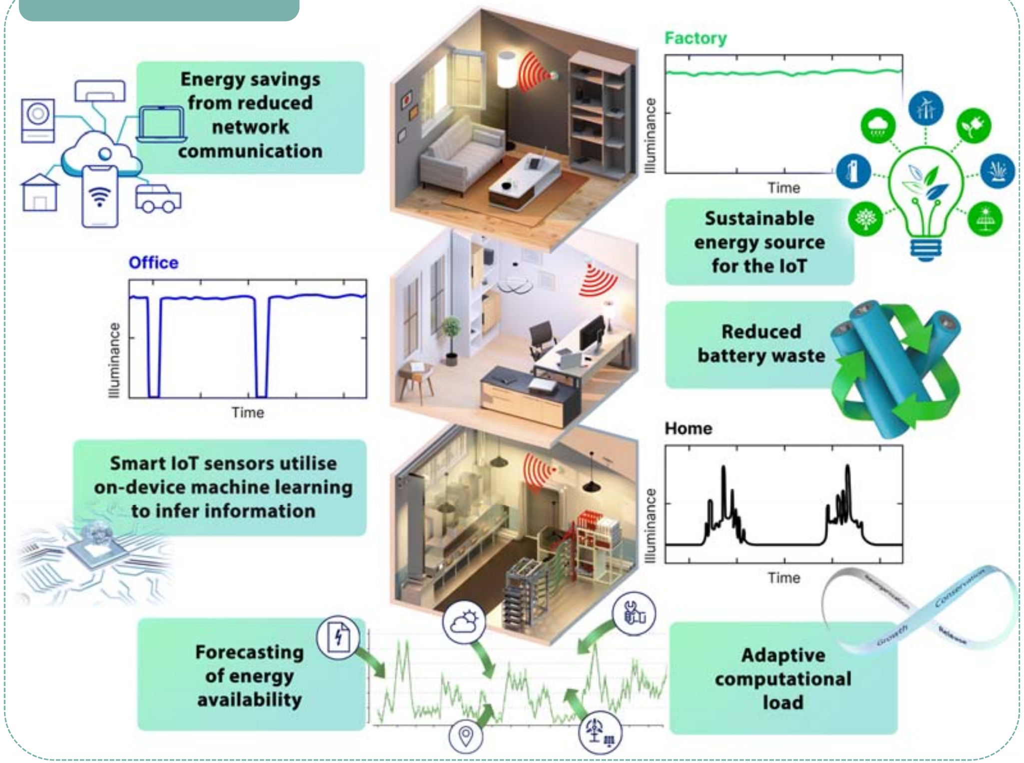
Building-integrated

Solar farms (MWs)

Solar cars

INDOORS

harvesting of artificial light inside buildings



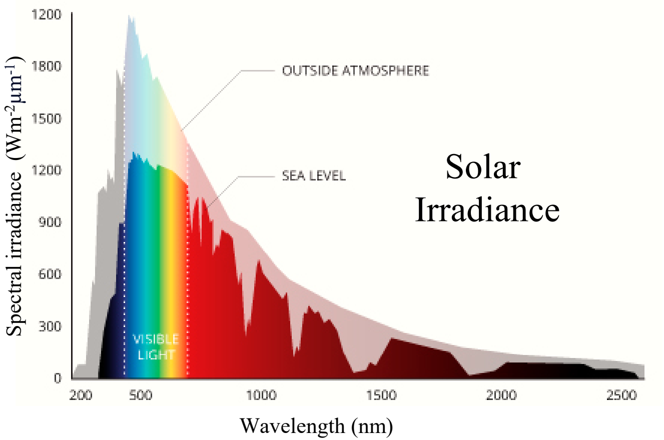
H. Michaels et al., Chemical Science, 2023, 20, 5350-5360.

Outdoor vs Indoor

Standard Test Conditions (irradiance/power)

~100 klx

Temperature	25 °C
Irradiance	1000 W/m^2
Air mass	1.5



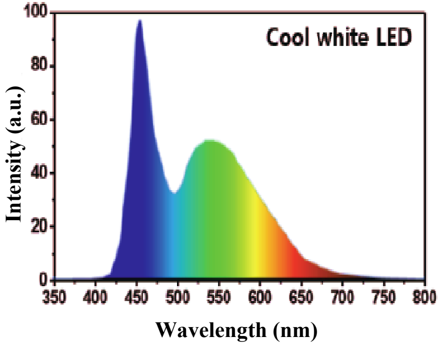
Indoor Illumination (illuminance)

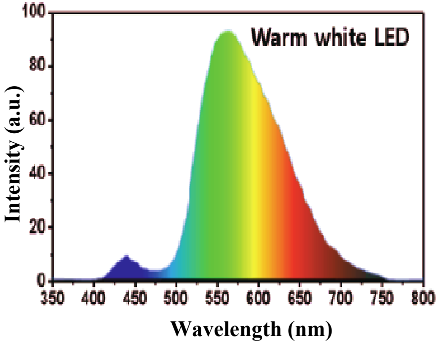
Low light 50 lx

Living room 200 lx

Office 500 lx

Supermarket 1000 lx





100-500 lx optical power densities of ~30 µW/cm^2 - ~160 µW/cm^2

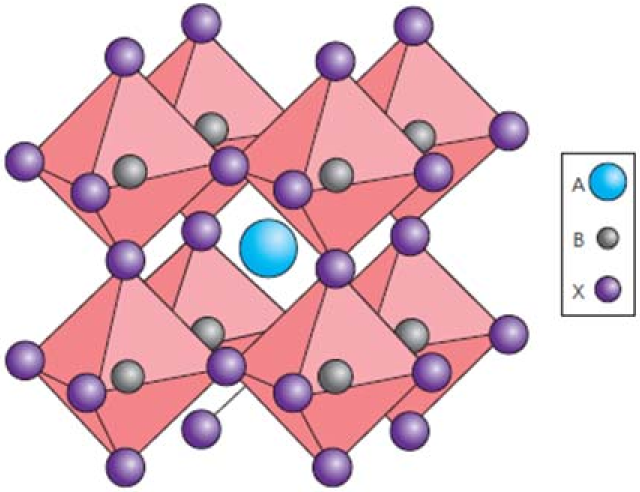
Different optimization of indoor PV compared to outdoor cells!

S. Kim et al., Current Alternative Energy, 2019, 3,1, 3.

Perovskite structure

First discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and named after Russian mineralogist Count Lev A. Perovski.
A perovskite structure is that of calcium titanate ($CaTiO_3$), with general structure ABX_3.

Methylammonium lead halides



A= large cation ($CH_3NH_3^+$ methyl ammonium ion)

B= small cation (Pb^{2+} metal ion)

X= anion (I^-, Br^-, halogen ion)

BX_6 octahedra (central B-atom) and A cation in the interstices

M.A. Green et al,NAT. PHOT.,VOL 8, 2014

Perovskite films for solar cells

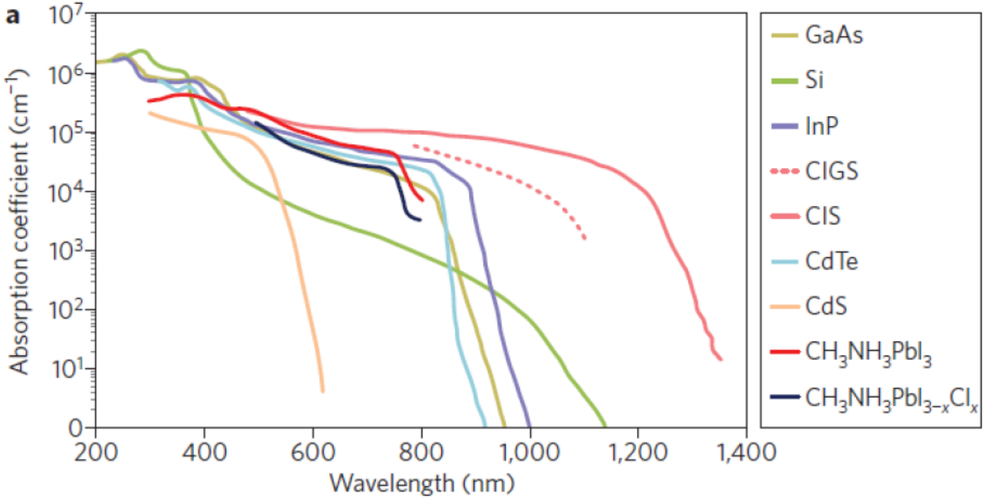
$CH_3NH_3PbI_3$ or $CH_3NH_3PbI_{3-x}Cl_x$ metalorganic lead halide perovskite films

- direct E_G of 1.55 eV (OK for PV)
- $n_i = 10^9$ cm^{-3} (similar i-Si)
- $\alpha = 10^4$-10^5 cm^{-1} (thin films OK)

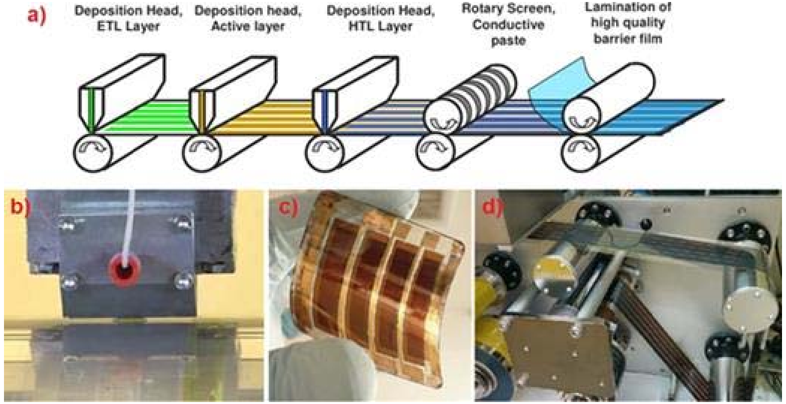
- μ_n=66 cm^2/Vs
- Binding energy: < 30-50meV
- Carrier Diffusion L ~100nm-1μm

- Processable in **solution** or by **vapor deposition**

Green, Martin A., Anita Ho-Baillie, and Henry J. Snaith. "The emergence of perovskite solar cells." *Nature Photonics* 8.7 (2014): 506-514.

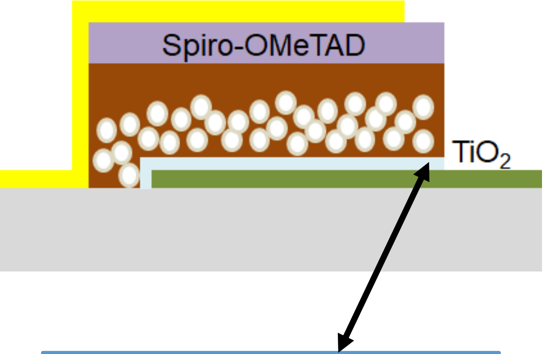


Princeton Cava's Lab https://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html

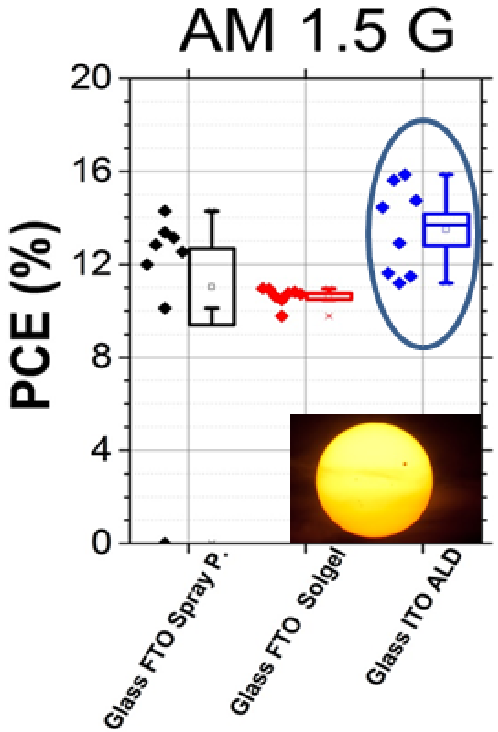


Razze et al., APL Materials, 4, 091508 (2016)

Perovskite Photovoltaic Cells for Indoors



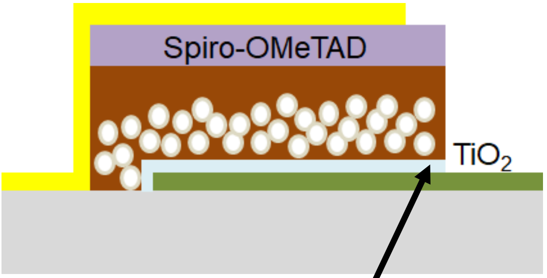
- Spray Pyrolysis (450ºC)
- SolGel spin coating (500ºC)
- ALD (150ºC)



- Much higher efficiency indoors
- Performance indoors more sensitive to film & interface quality

F. Di Giacomo, Nano Energy 30, 460 (2016)

Perovskite Photovoltaic Cells for Indoors



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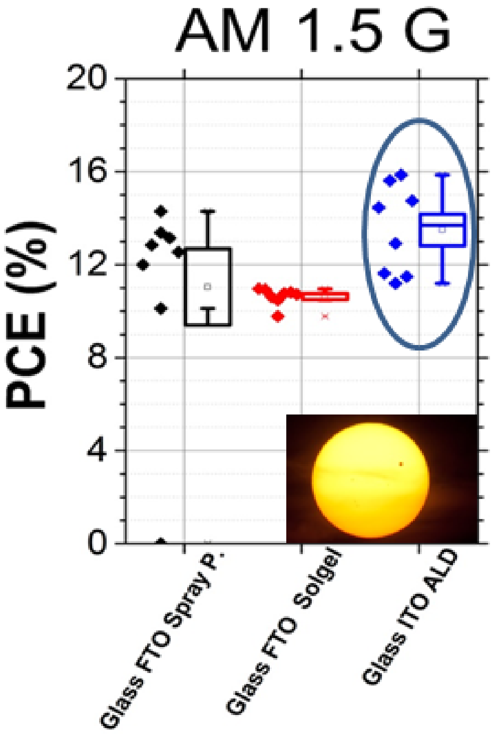

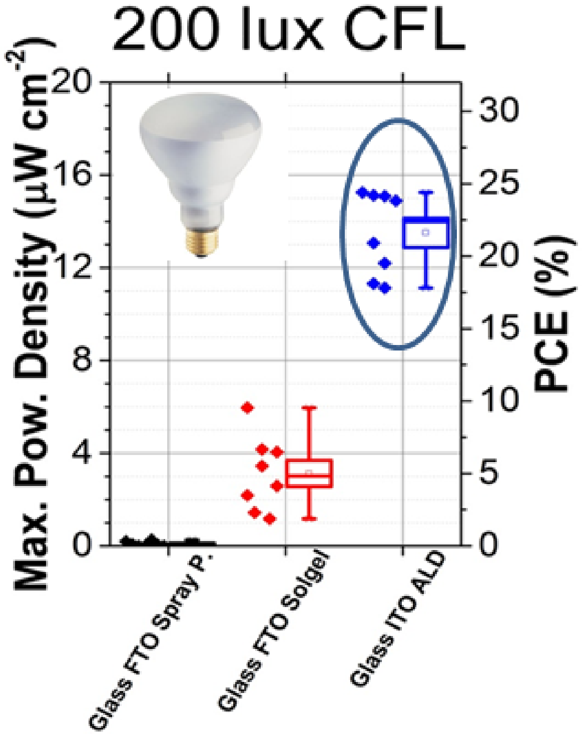

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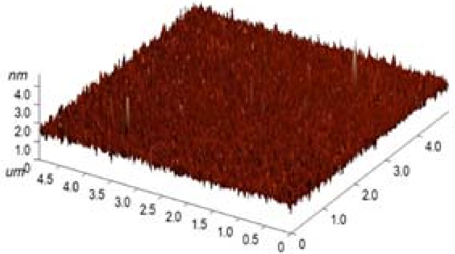
F. Di Giacomo, Nano Energy 30, 460 (2016)

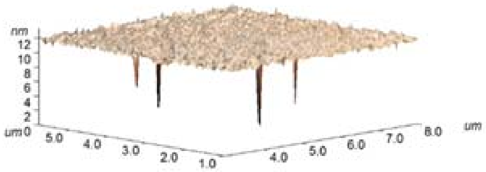
Efficiency as a result of low recomb. compact layers

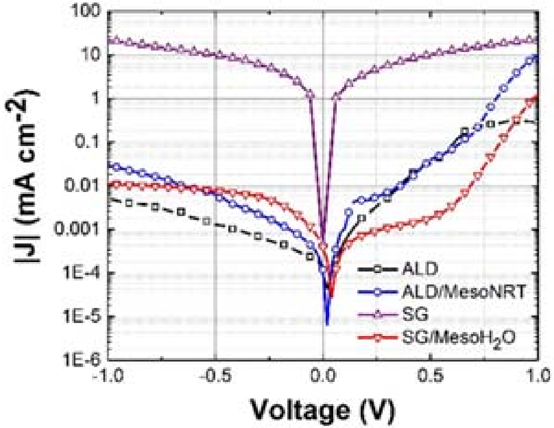
AFM morphology

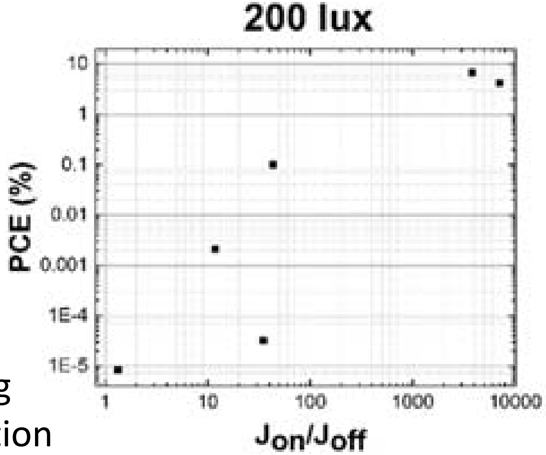
b
- ALD ETL

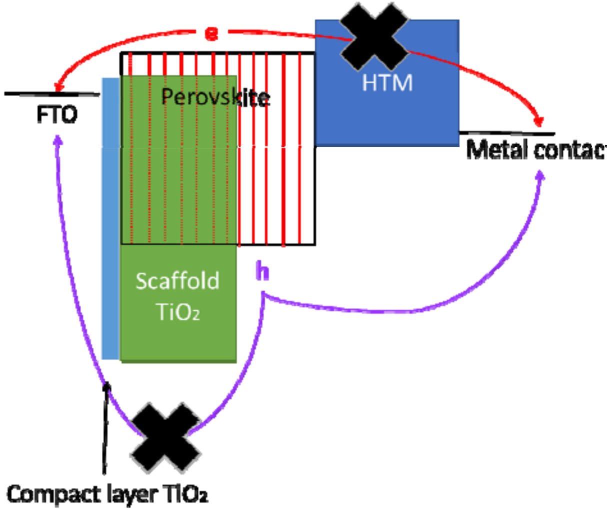


d
- sol-gel with pin-holes









- High quality compact electron extracting layers crucial to achieve low recombination
- Recombination currents need to be << photogenerated currents

G. Lucarelli et al., Nano Research **10**, 2130 (2017)

Powering the future

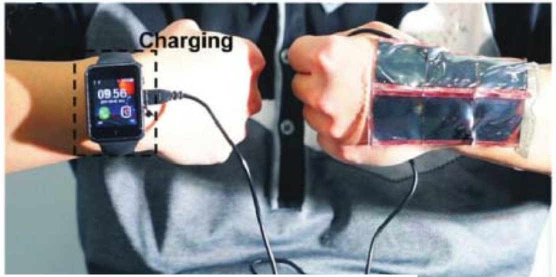
with Flexible Perovskite Solar Cells

Solar powered outdoor flight

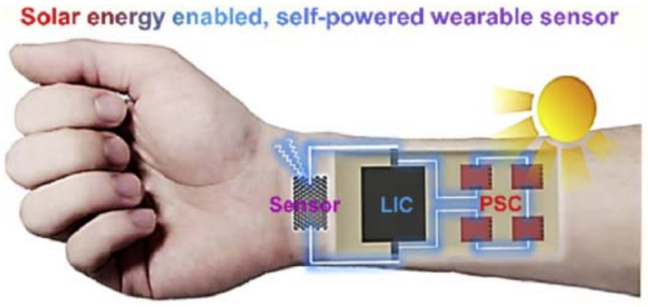
Solar powered tents

Smart integrated building

Solar powered jacket



Wearable PSCs as a power source

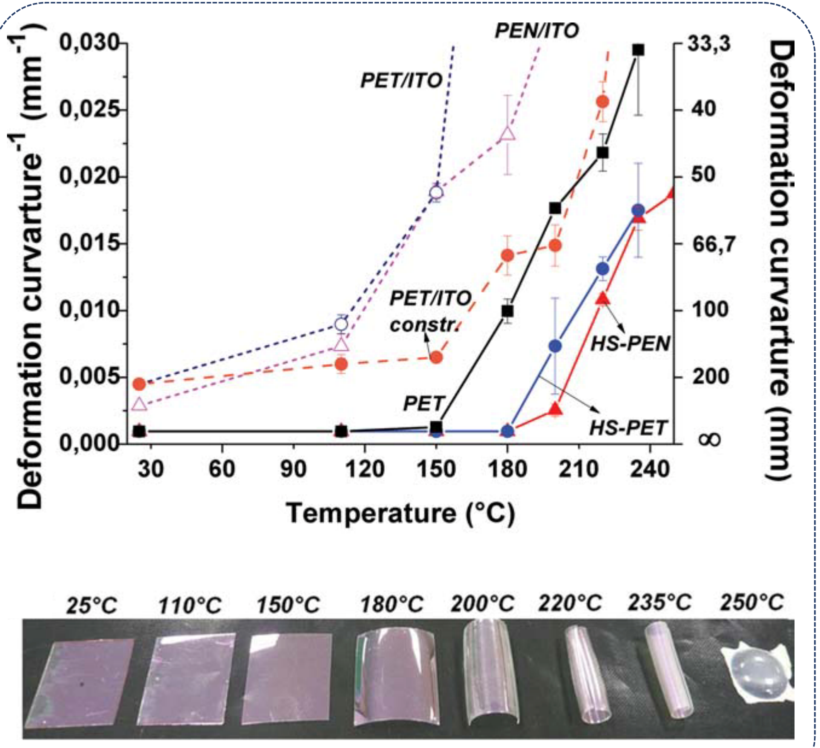


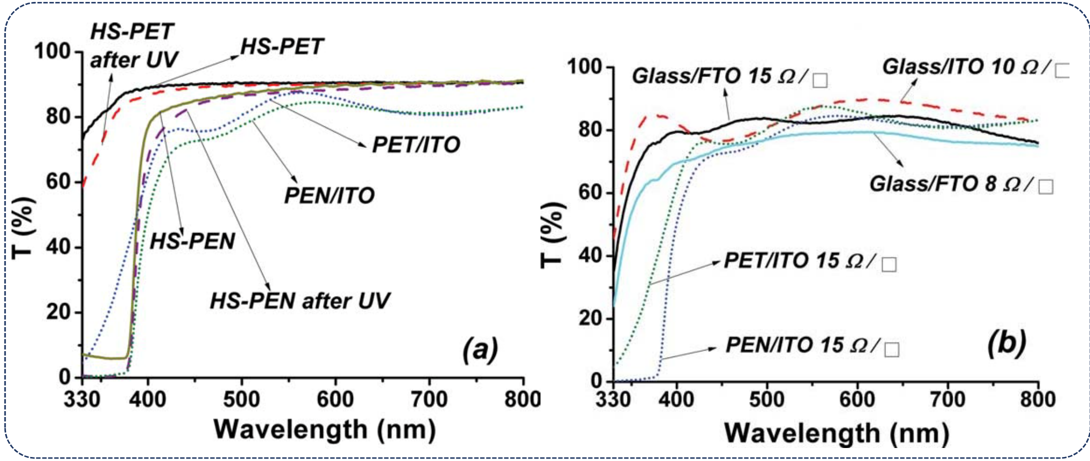
Solar powered backpack

- Ultrathin and lightweight substrates meet the demands of the emerging flexible electronics market
- Applications that can not be achieved with conventional photovoltaic devices

G. Tang, and F. Yan, Nano Today, 2021, 39, 101155. *S. A. Hashemi et al., Energy and Environment Science, 2020, 13, 685–743.*

PET film is a substrate of choice in PV technology

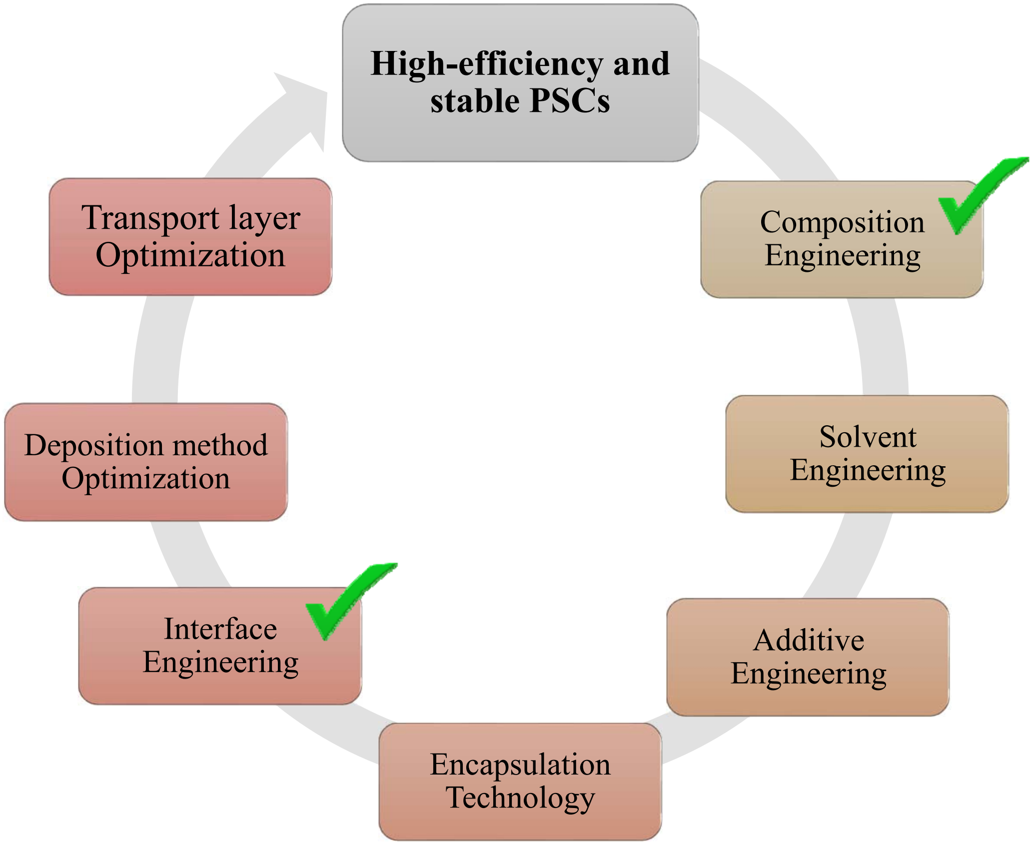




- PET films bent to a radius of curvature of 1 m **at 115 °C**
- PET is **more transparent** than PEN
- PEN turns yellow due to **UV degradation**
- PET **does not show any color change** from UV exposure

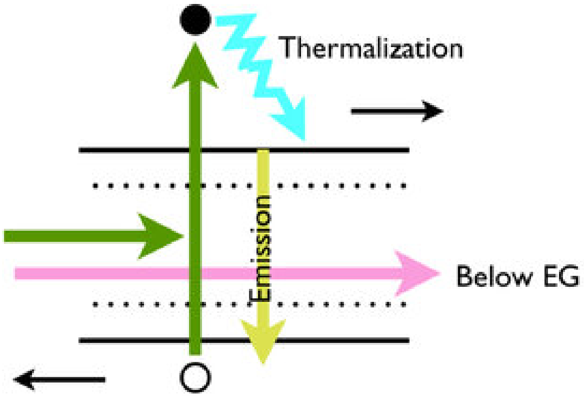
V. Zardetto et al., Polymer Science Part B: Polymer Physics, 2011, 49, 9, 638-648.

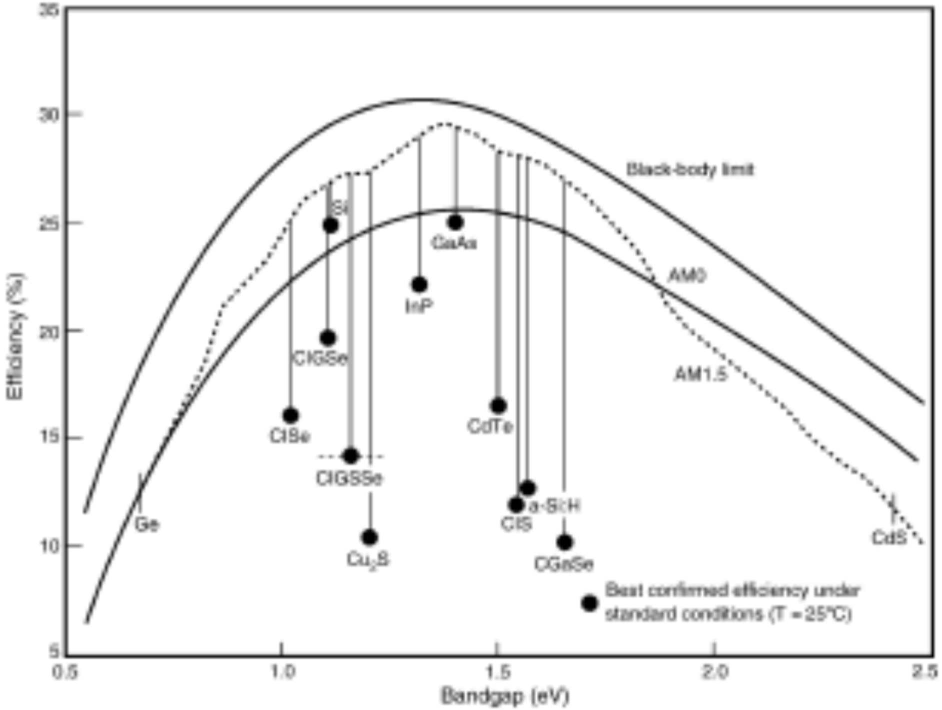
High-efficiency and stable Perovskite solar cells for indoor PV



Y. Huang et al., Applied Materials Today, 2022 28, 101550.

Detailed balanced limit: maximum PCE vs Eg at 1 sun





Taking count of basic (radiative) losses the

maximum attainable efficiency at STC is ≅ 30%

Best Eg in 1.1-1.5 eV range

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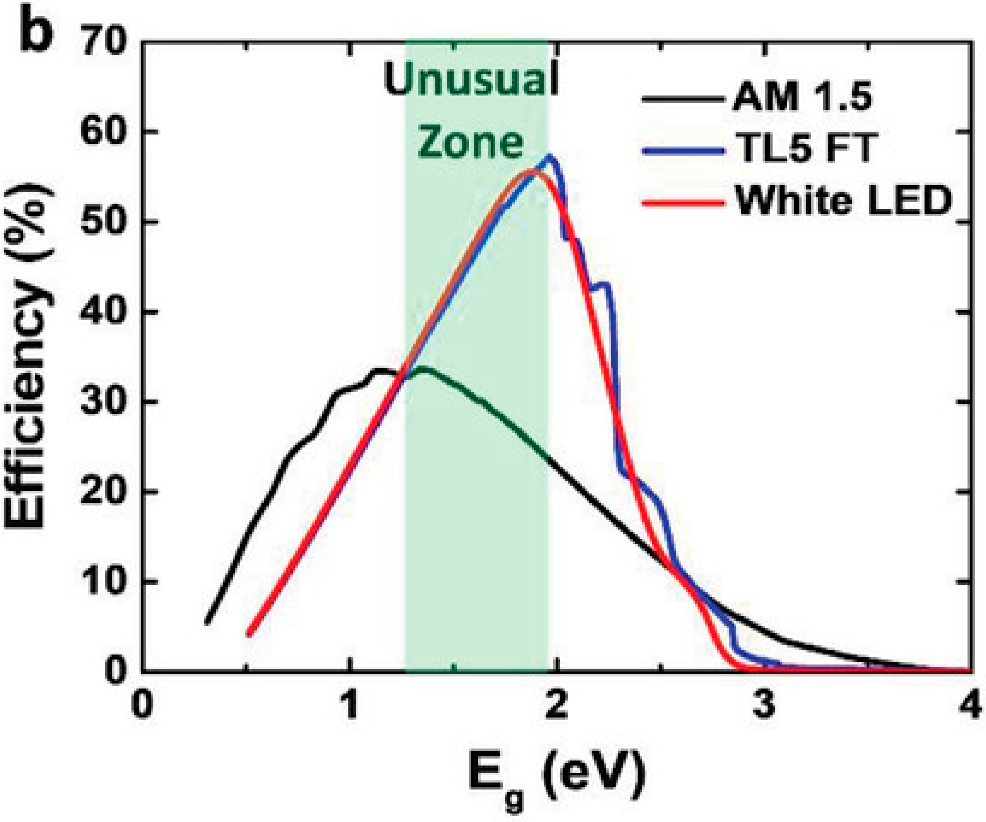
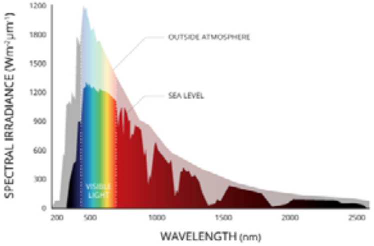
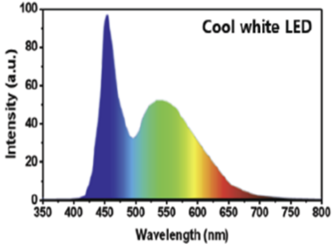
Journal of Physics D: Applied Physics 46(26):264007

L.L. Kazmerski / Journal of Electron Spectroscopy and Related Phenomena 150 (2006)

Detailed Balanced limit under indoor on





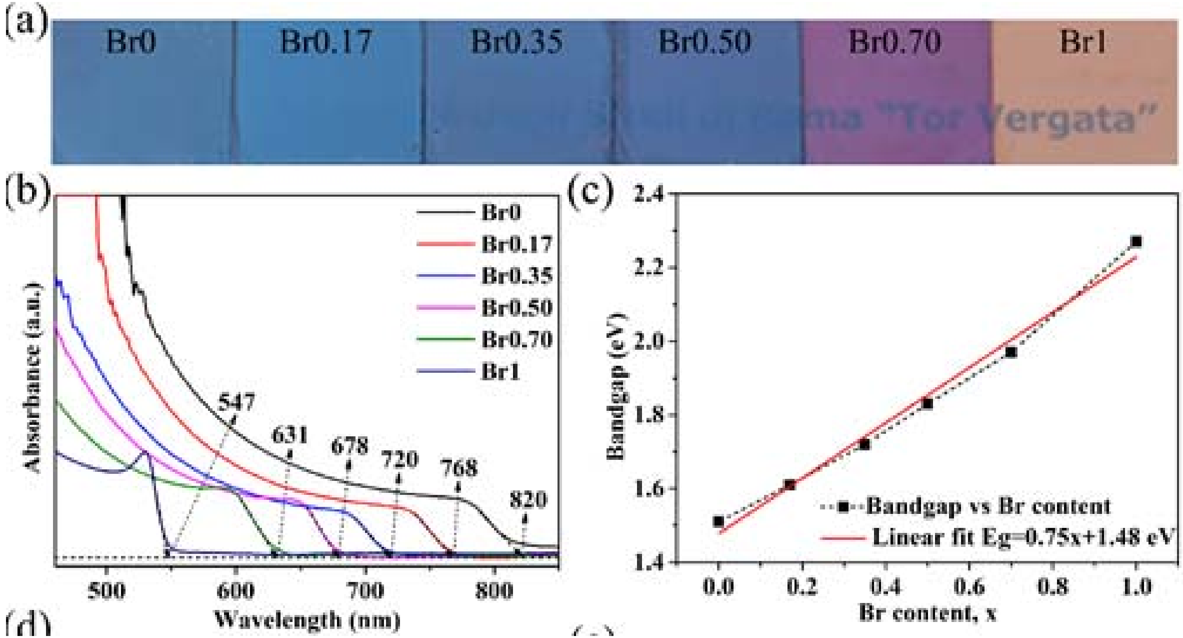


Upon LED illumination

- **Optimal Eg is at 1.9 eV**
- **Theoretical PCE above 50%**

Wu M. et al. (2019) Adv. En. Mat. 9, 37, 1901863

Band Gap Engineering via Br addition



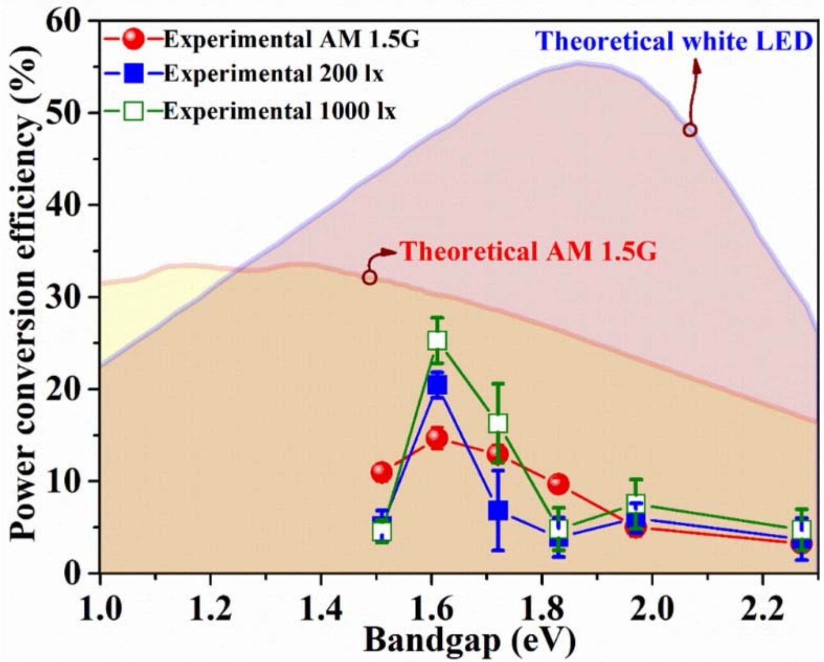
Compositional tuning of perovskite from $MAPbI_3$ to $MAPbI_2Br$:

- Eg increase 1.5 eV -> 2.3 eV

J. Xu et al., ACS Applied Energy Materials, 2023, https://doi.org/10.1021/acsaem.2c03394.

Perovskite Solar Cells under Indoor LED Illumination

Photovoltaic parameters for the PSCs on glass with different Br^- contents, measured under LED at 1000 lx.



- **Indoor PCE improves by increasing band gap of perovskite semiconductor but** values do **not** show the same **trend as theoretical expectactions**
- Other important figures to be understood

J. Xu et al., ACS Applied Energy Materials, 2023, https://doi.org/10.1021/acsaem.2c03394.

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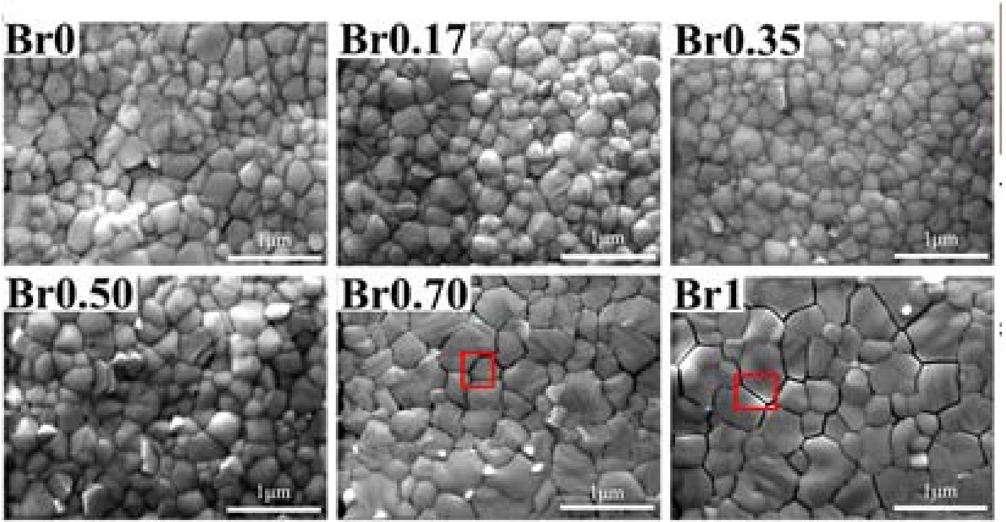
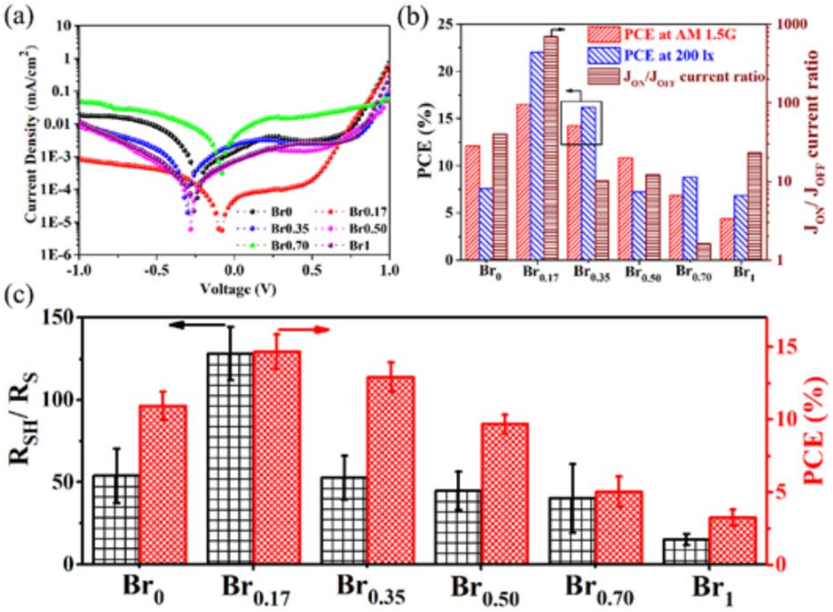
Key parameters to achieve PCE > 25%





Key parameters	J_{ON}/J_{OFF} current ratios	R_{SH}/R_S resistance ratios	Average grain sizes	Inter-grain spacing
Threshold values	> 100	> 100	> 300 nm	<< 10 nm

J. Xu et al., ACS Applied Energy Materials, 2023, https://doi.org/10.1021/acsaem.2c03394.

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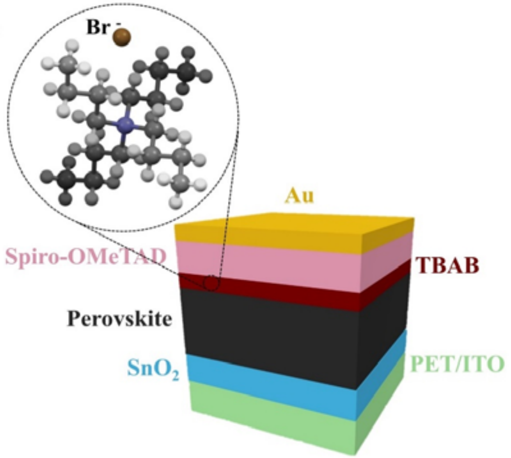
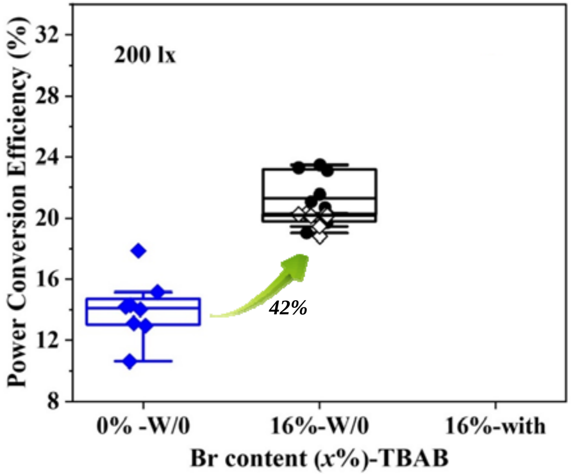
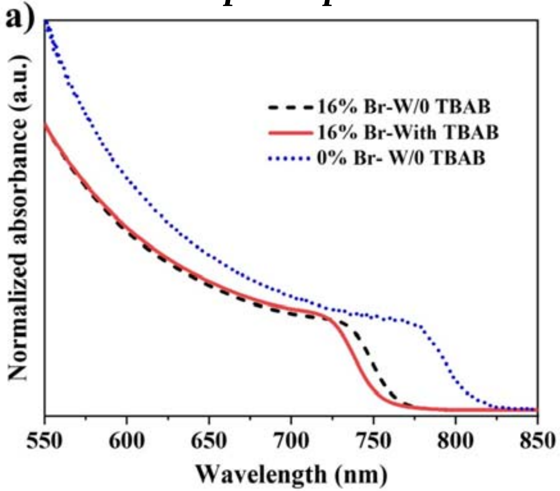
Compositional engineering + interface engineering



Compositional test results

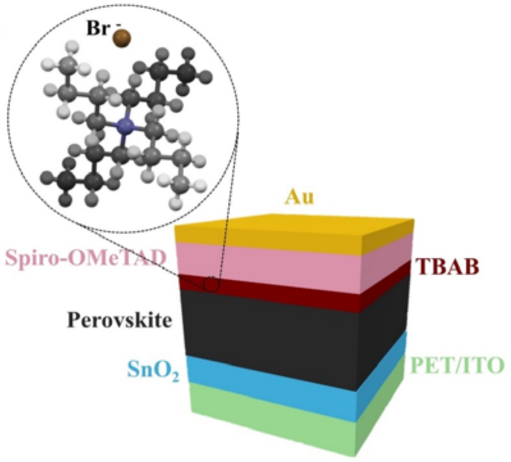


Absorption spectra

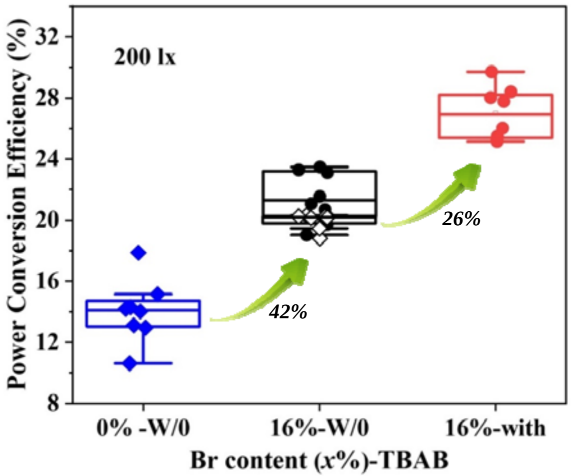


- **Increasing Br** content from **0%** to **16%** boosted PCE considerably from **(14.0 ± 1.9)%** to **(20.7 ± 1.4)%**
- The **higher E_g** determined for the **16%** composition **(1.637 eV)** compared to the **0%** one **(1.531 eV)**
- **Improved morphology**, leads to a **higher V_{OC}** and **fill factor (FF)** without compromising currents
- The optical spectrum spans the **visible spectrum** only (no IR) as in the case of **LED illumination**

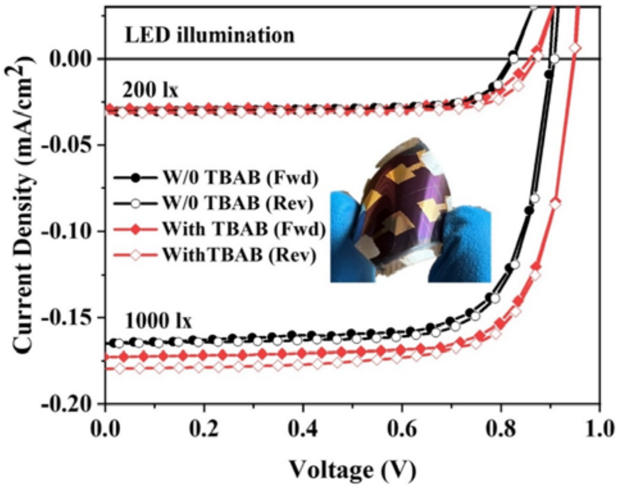
Compositional engineering + **interface engineering**



Compositional test results



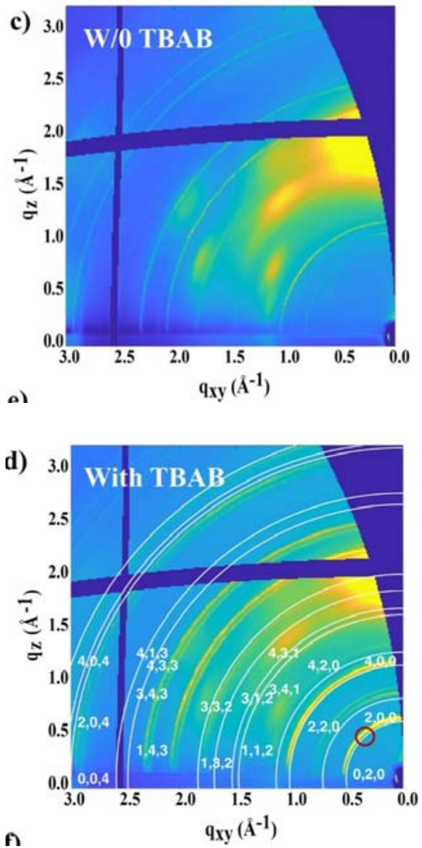
J-V Curves

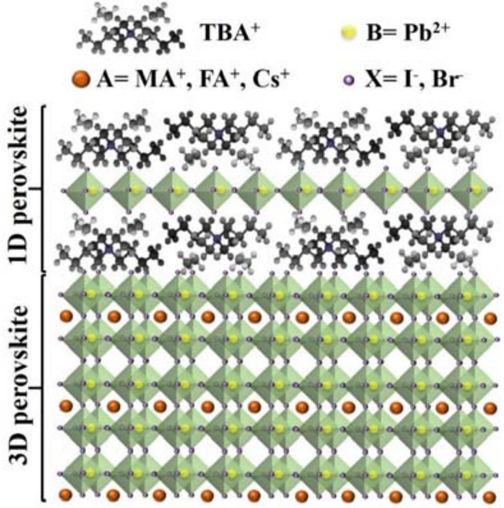


- Large enhancement in PCE by **26%** at **200 lx** after **tetrabutylammonium bromide TBAB incorporation**
- **Best-performing** flexible device **modified with TBAB** was **32.5% at 1000 lx** (with Maximum Power Density **(MPD) of 127.8 µW/cm^2**) and **28.9% at 200 lx** (**MPD = 23.3 µW/cm^2**)

Perovskite layer characterization

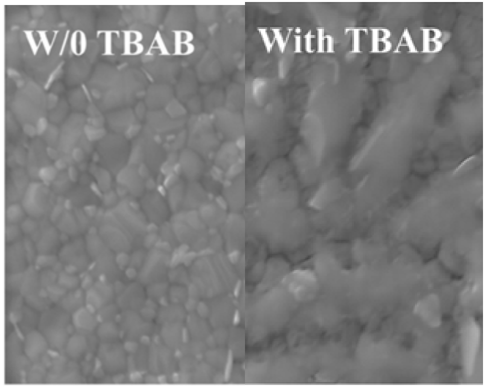
2D GIWAXS patterns



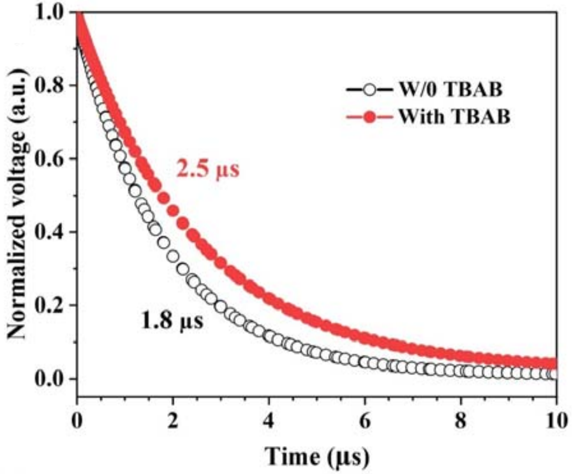


- TBA$^+$ cations are much larger than FA$^+$ and MA$^+$
- **TBA$^+$ cations** can **substitute FA$^+$** and form **a low-dimensional 1D perovskite** layer **at the perovskite/TBAB interface**
- This low-dimensional phase with **larger structures** is visible via SEM images
- Lower defect density!

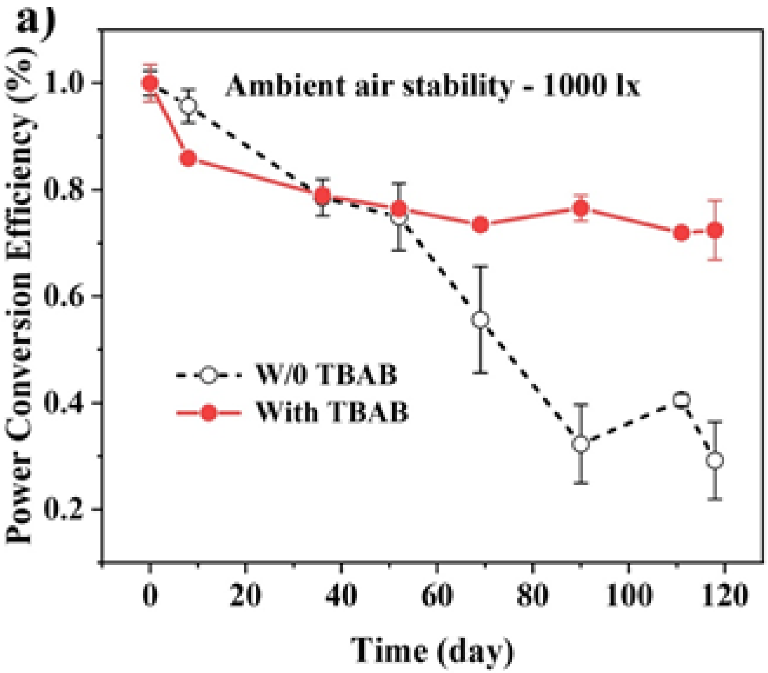
SEM



TPV decay

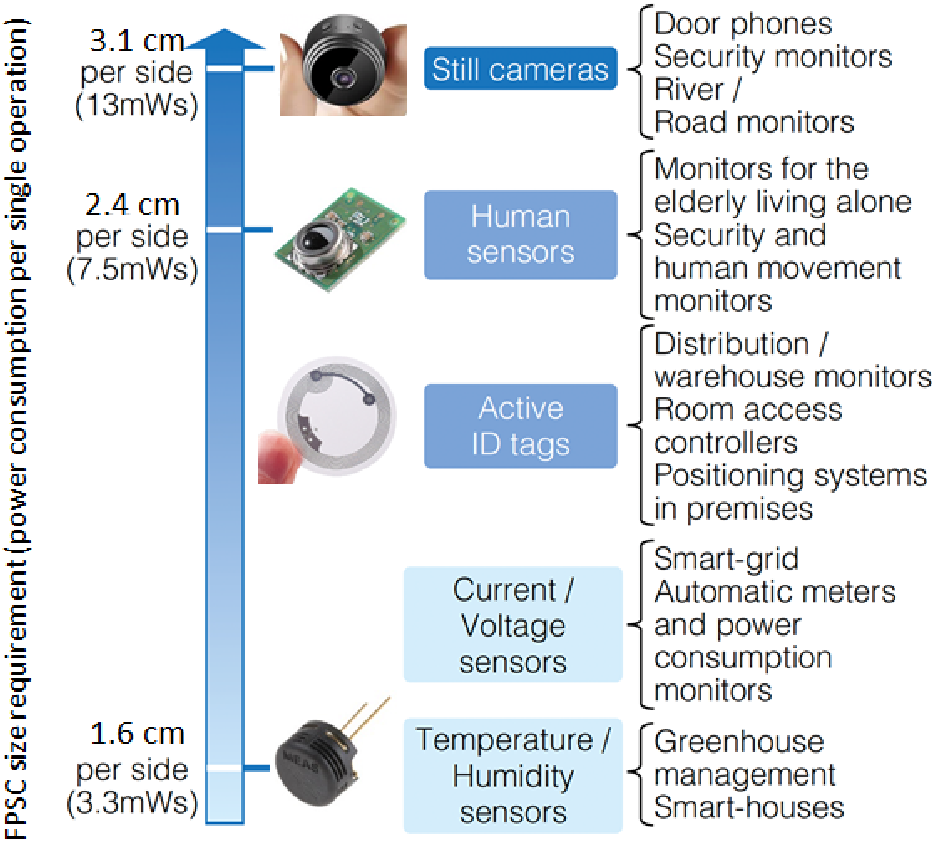


Device stability



- **Ambient air stability improvement** (ISOS-D1) **more than doubled** with TBAB treatment
- Enhanced **durability of PV-active perovskite phase** with TBAB treatment

III–V compound semiconductors for indoor photovoltaics



Calculation conditions:

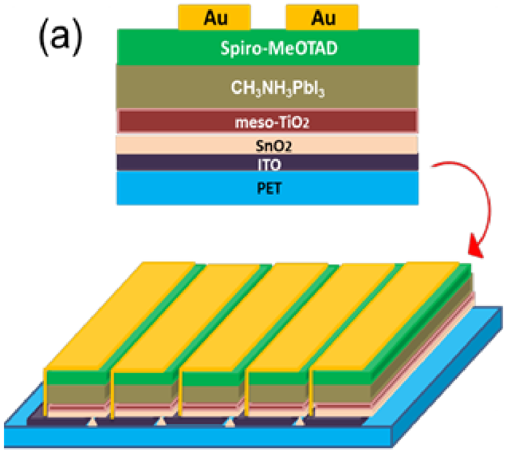
1000 lux illumination

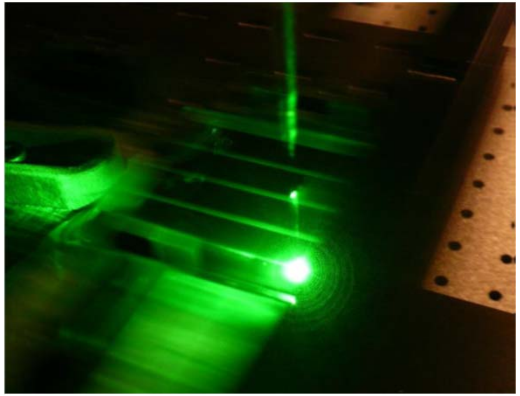
Power output of PV:
127.8 μW/cm^2 for cells with ~30% PCE at 1000 lx

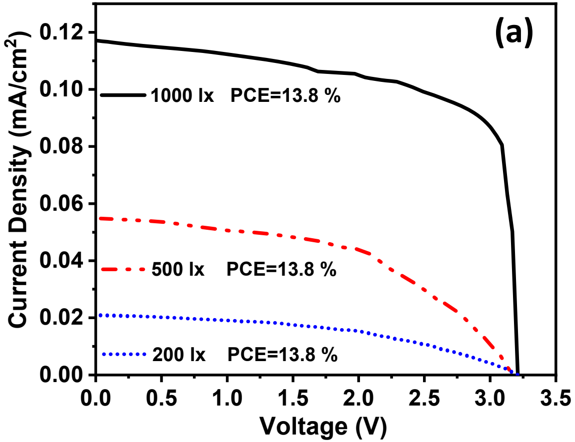
Operation cycle:
every 10s

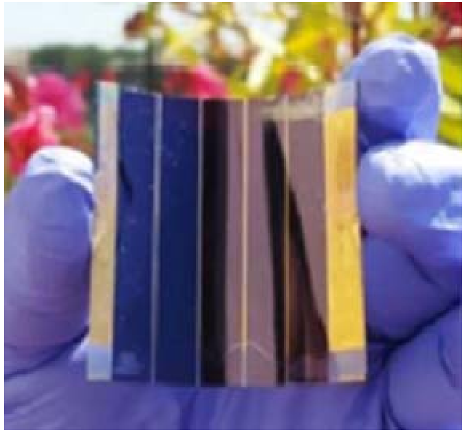
Fujikura Technical Review, 2013. *F. De Rossi et al., Applied Energy, 2015, 156, 413.*

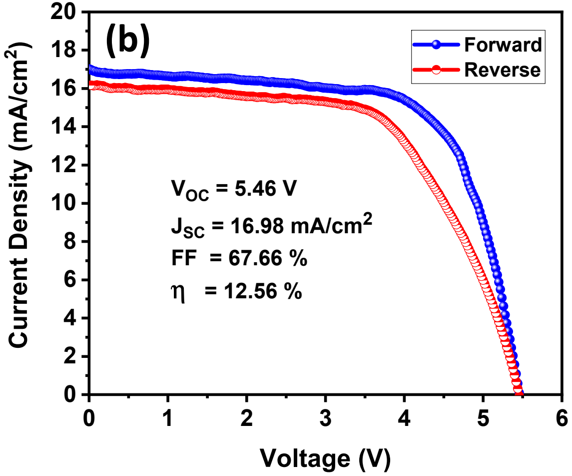
Flexible Mini module performance







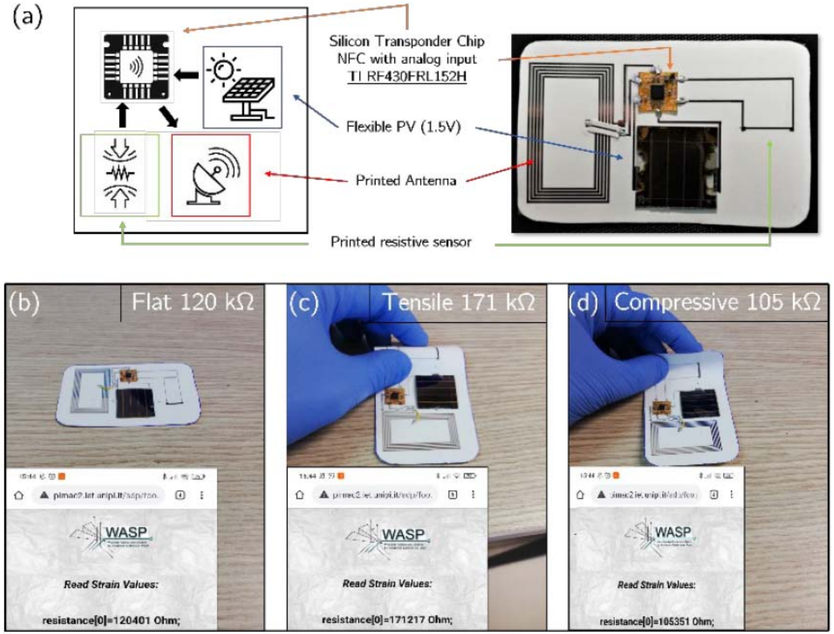




J. Dagar et al Nano Research 11, 2669 (2018)

H. Javanbakht, De Rossi, F. Brunetti et al, under review

Flexible Perovskite Module powering a hybrid flexible electronic system

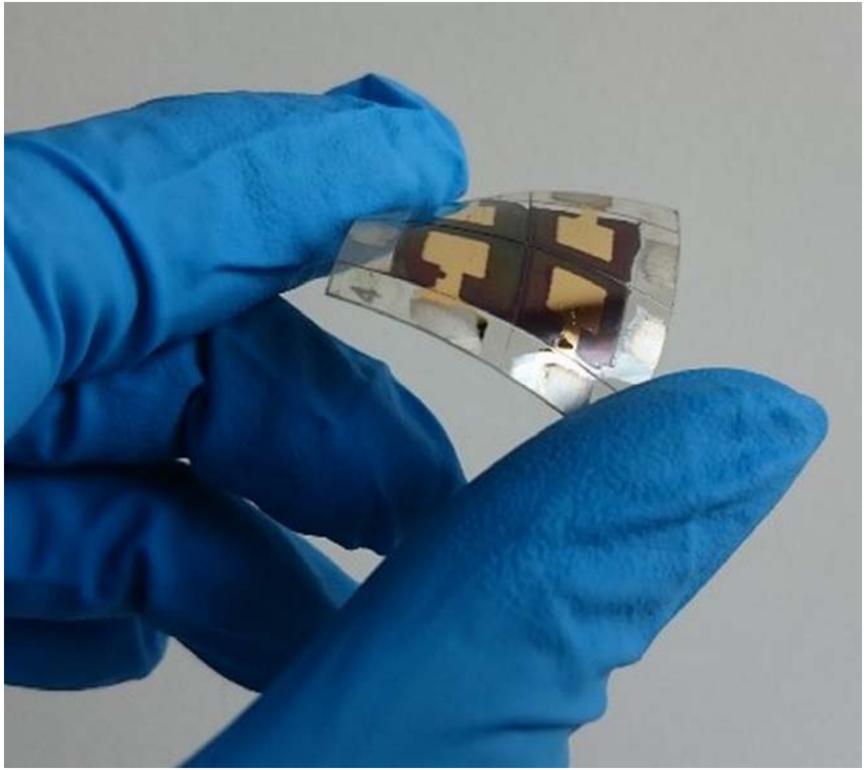


WASP
Wearable Applications enabled by electronics Systems on Paper

S. Conti et al., "Hybrid Flexible NFC Sensor on Paper", IEEE Journal on Flexible Electronics, 2, 4 (2023).

Summary

- dual low-temperature (≤100 °C) approach,
- first by anion mixing (replacing I with Br) (42% improvement),
- interfacial engineering with TBAB
- The TBA^+ cation intercalates substituting formamidinium cations inducing large-sized, 1-D structures.
- efficiencies between 28.9% at 200 lx and 32.5% at 200-1000 lx on PET.



More details are described in:
Z. Skafi, J, Xu et al., "*Highly Efficient Flexible Perovskite Solar Cells on PET films via Dual Halide and Low-Dimensional Interface Engineering for Indoor Photovoltaics.*"
Solar RRL, 7, 2300324 2023.
DOI: 10.1002/solr.202300324

Zeynab Skafi

Jie Xu

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Ministero degli Affari Esteri e della Cooperazione Internazionale

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Chose Polo Solare Organico

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Q & A

EnerHarv 2024

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Thanks very much for your time and attention!

Questions/comments???

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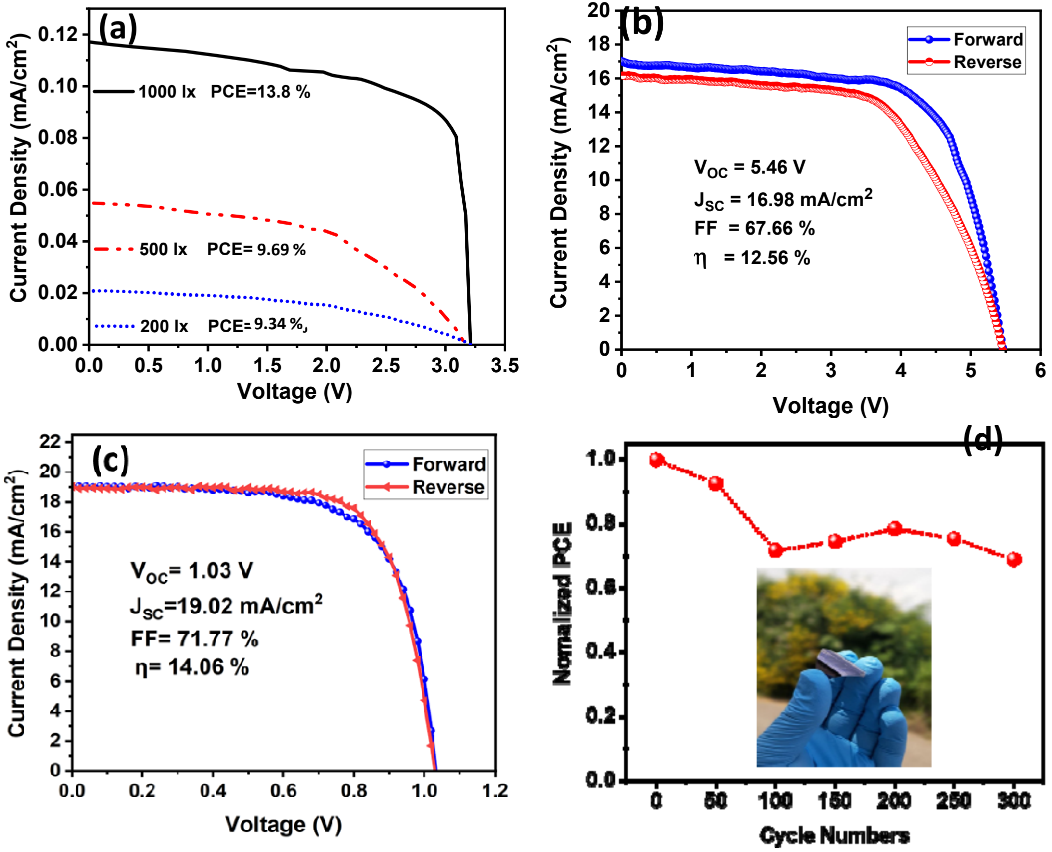
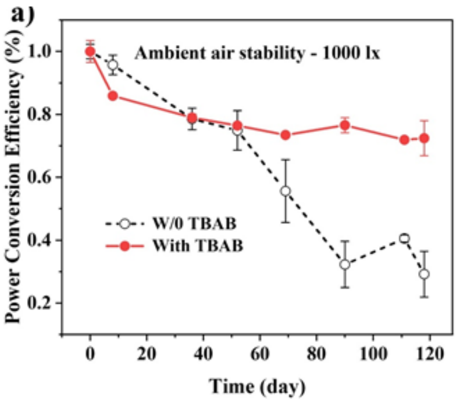
Perovskite modules indoors vs outdoor

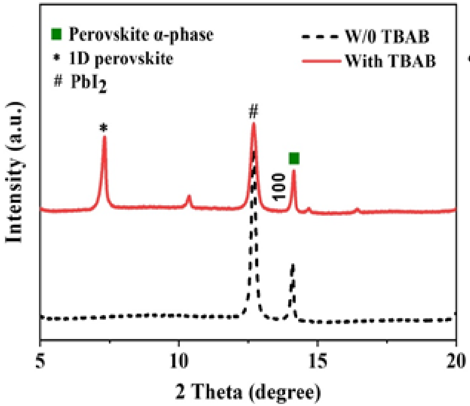


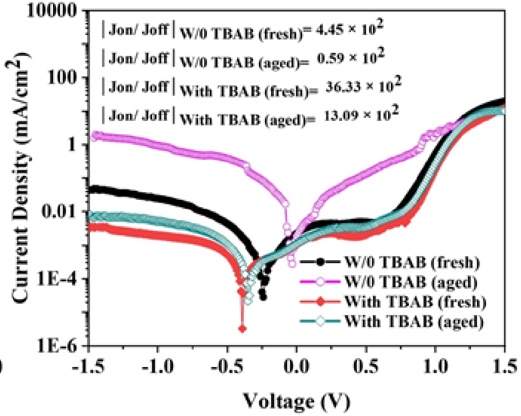
Performance of the mini modules; (a) J-V curve with variation in light intensity, (b) J-V curve under 1 sun illumination, (c) J-V curve of the module after 1 day and (d) tracking of voltage and current with respect to time, (d) bending angle test

H. Javanbakht, under review

Device stability

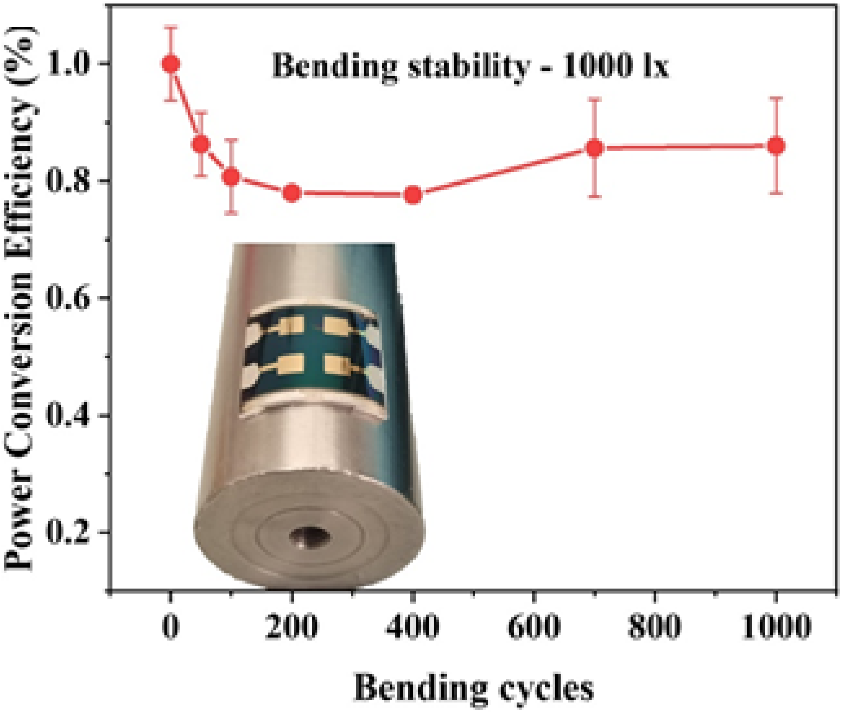






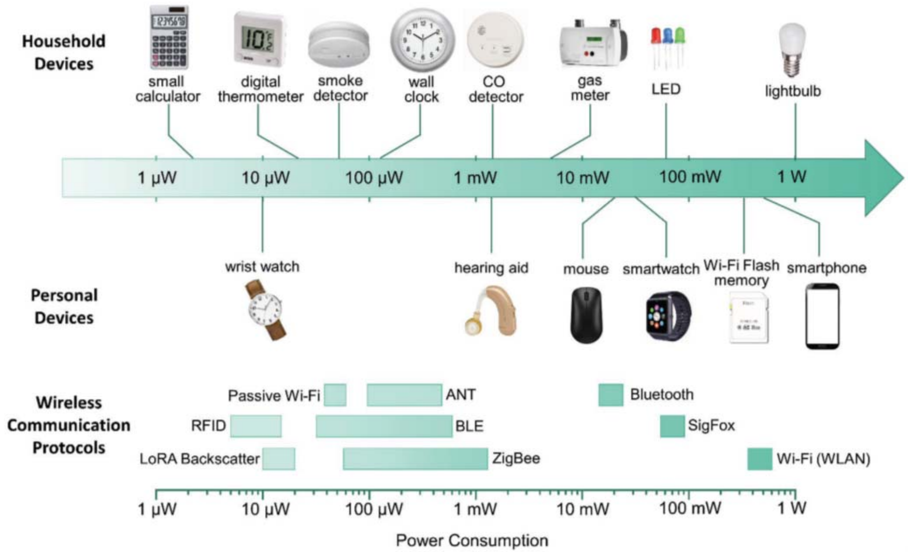
- **Ambient air stability** (ISOS-D1) **more than doubled** with TBAB
- Enhanced **durability of PV-active perovskite phase** with TBAB treatment
- **Less inactive PbI_2 with TBAB** in time
- **Higher J_{ON}/J_{OFF} ratios** and **lower leakage current** in TBAB-passivated devices ($J_{OFF} = 3.44 \times 10^{-3}$ mA/cm^2 vs 3.57×10^{-2} mA/cm^2)

Device stability

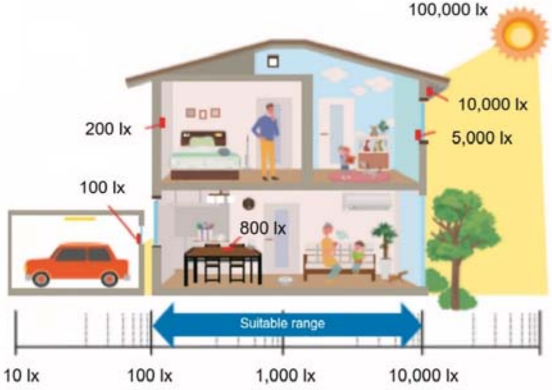


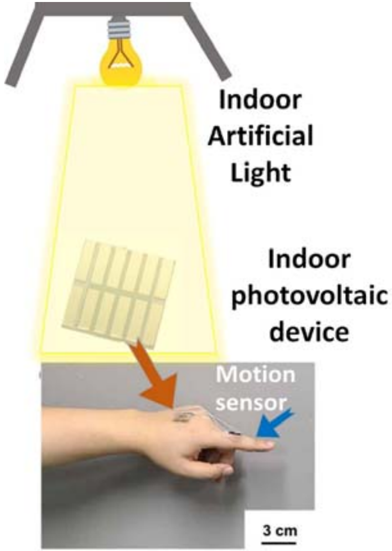
- TBAB-passivated device maintains **over 80%** initial PCE after **1000 bending cycles** at 1.8 cm bending radius

Applications of indoor PV



- Consumer electronics
- Portable and wearable electronics
- Healthcare and biomedical devices
- Building-integrated and indoor appliances
- Communication technologies
- WSN and RFID
- Sensors for the Internet of Things



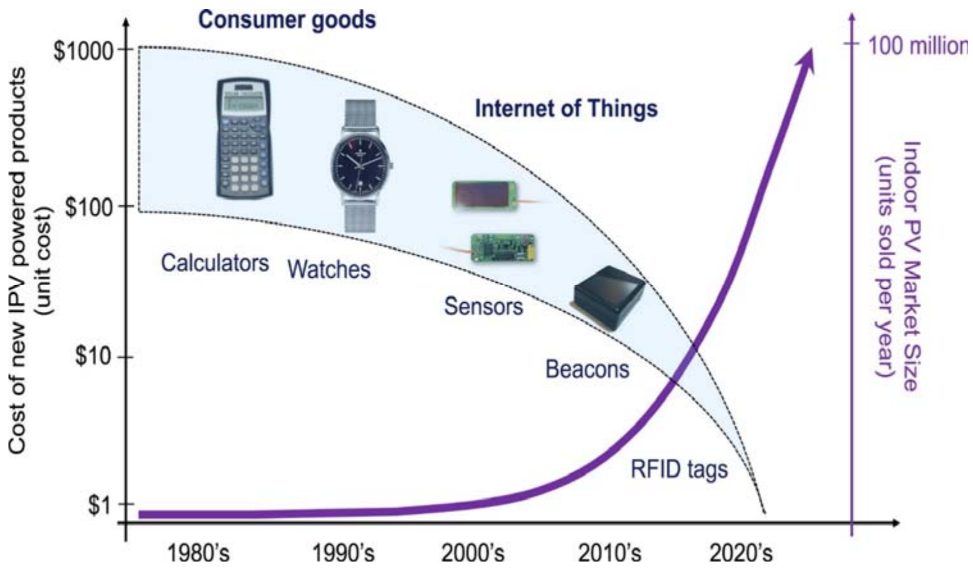


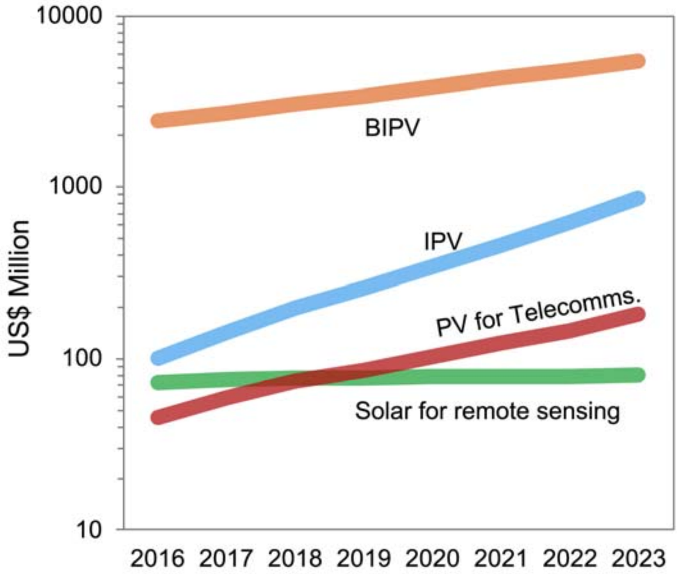
Perovskite electronic shelf labels

V. Pecunia. et al., Adv. En. Mat, 2021, 11, 2100698.

W., Shaoyang et al., Journal of Physics: Materials, 2023, 6, 2, 024004.

Applications and markets of indoor photovoltaics (PV)





- Market rise associated with **lowering of consumers products' cost**
- **Fastest growth** among alternative small volume PV markets

I. Mathews et al., Joule, 2019, 3, 6, 1415-1426.

PET film is a substrate of choice in PV technology

Characteristics	PP Polypropylene	PET Polyethylene Terephthalate	PPS Polyphenylene Sulfide	PEN Polyethylene Naphtholate
Melting temperature (°C)	160 –170	254	285	266
Max. operating temperature (°C)	105 -125	125 -150	160 -190	150 -170
Dielectric constant	2.2	3.25	3	3.05
Density (g/cm³)	0.91	1.36	1.35	1.36
Dielectric strength film V/µm at 25°C	300 -400	240	200	260
Dissipation factor Tgδ 1÷10 kHz	2×10^{-4}	50×10^{-4}	20×10^{-4}	40×10^{-4}
Cost ratio	90	100	750	370
Energy Density (nF x V/ mm³)	50	400	140	250
Self-Healing property	++	+	o	-

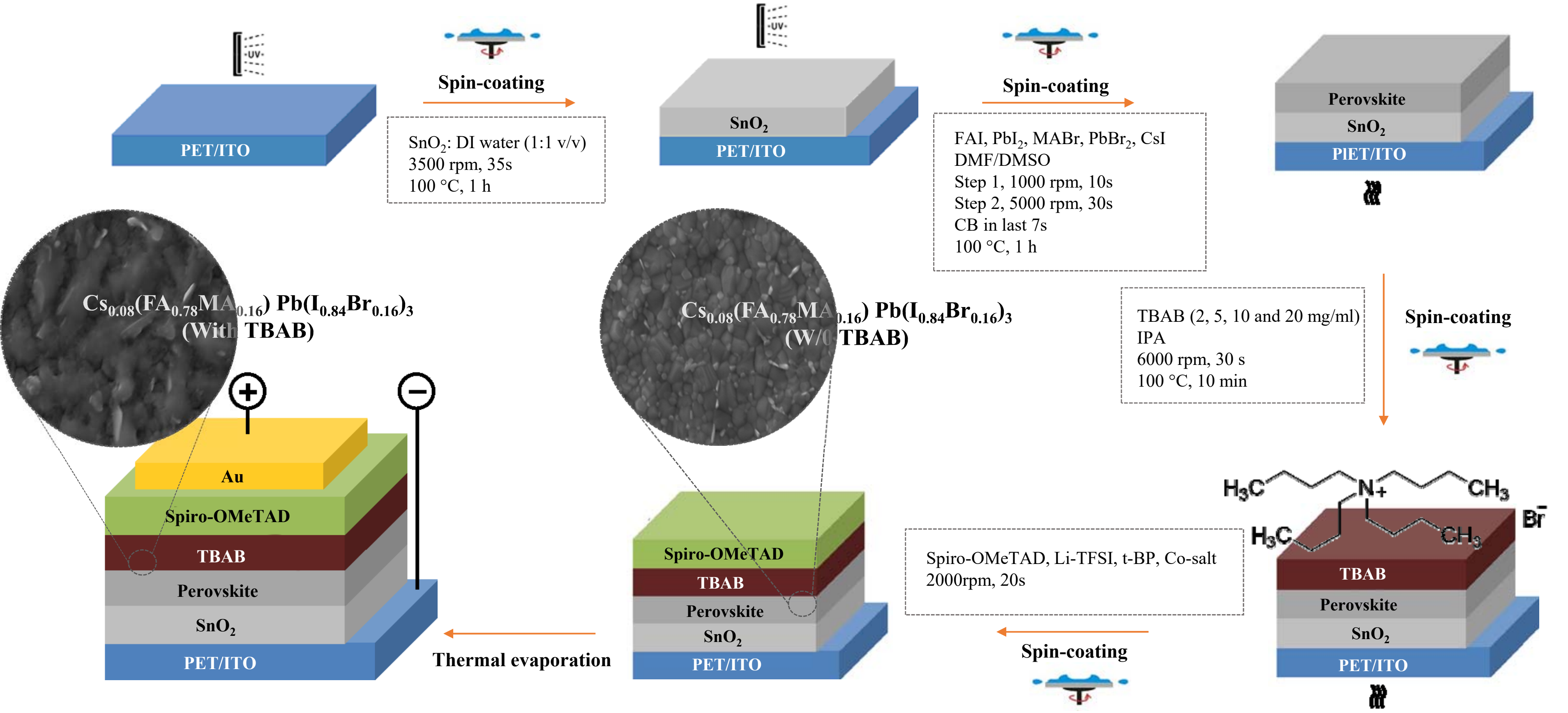
- PET is **6 times cheaper** than PEN
- PET has a **cost ratio*** **4 times lower** than PEN

*the proportion of the cost of goods available to the retail price of those goods

S. Heusing et al., in Proc.SPIE, 2008, p. 69992I.

W. Bruno et al., "5.1. New KEMET Miniaturized EMI-Suppression and DC-Link Power Box Unique Designs for Harsh Environment in Energy, Industrial and Automotive Application."

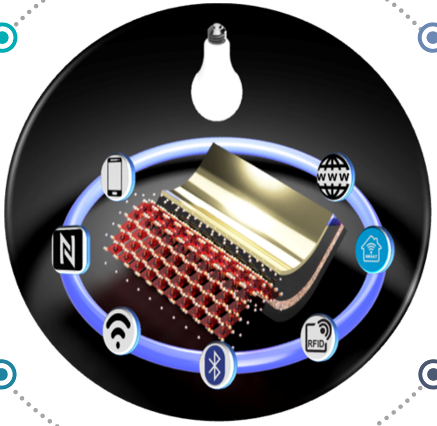
Device fabrication



Parameters to consider for a PV Technology

Functionality
(transparency, colour, flexibility, weight, easy integration)

Efficiency
(STC, indoor low lighting e.g. CFL and LED lamps, 200-1000 lx)



Stability and environmental impact
(toxic elements content, green solvents, lifetime in indoors)

Cost and commercialization
(market readiness, production volumes, cost of raw materials and processes)

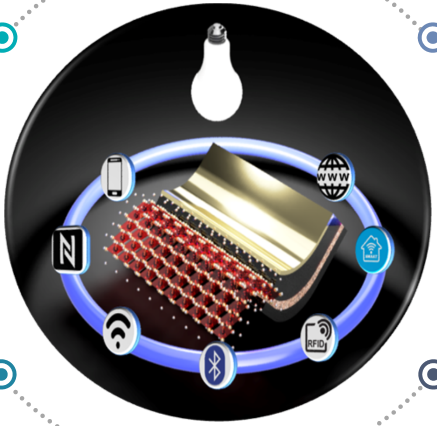
G. Lucarelli, T.M. Brown, NanoInnovation 2020.

Parameters to consider for a PV Technology

Functionality
(transparency, colour, flexibility, weight, easy integration)

Flexible Perovskite Solar Cells

Efficiency
(STC, indoor low lighting e.g. CFL and LED lamps, 200-1000 lx)



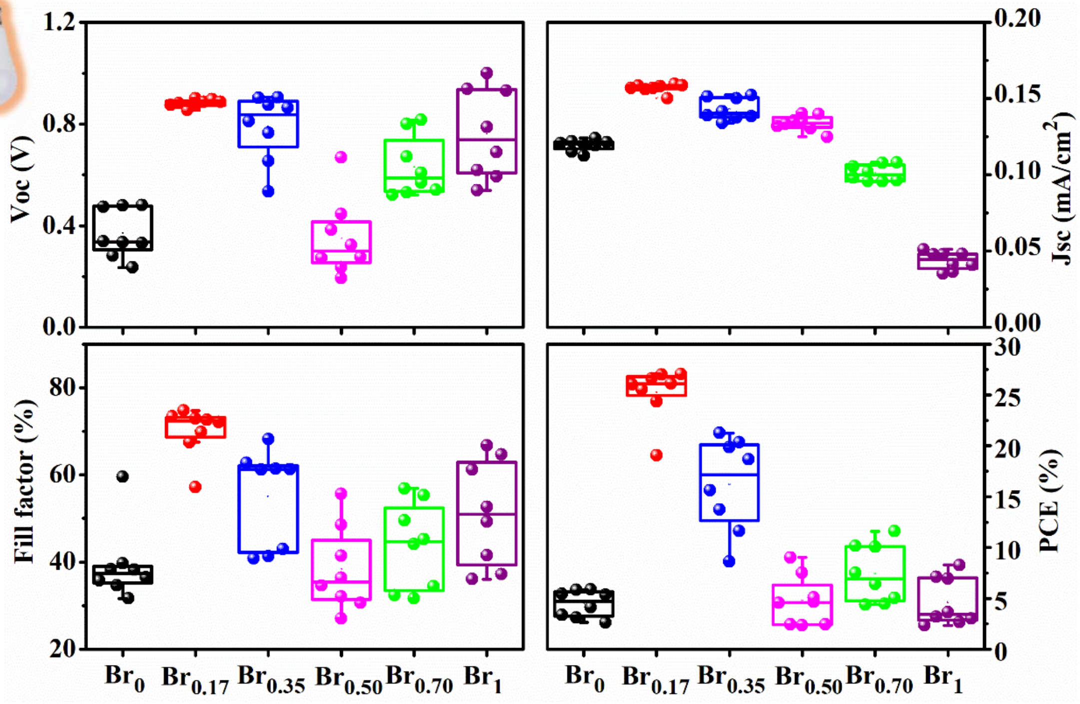
Stability and environmental impact
(toxic elements content, green solvents, lifetime in indoors)

Cost and commercialization
(market readiness, production volumes, cost of raw materials and processes)

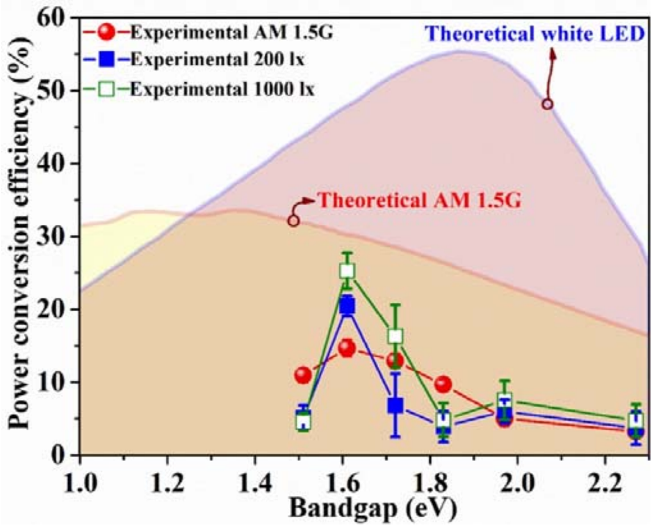
G. Lucarelli, T.M. Brown, NanoInnovation 2020.

Perovskite Solar Cells under Indoor LED Illumination on Glass

Photovoltaic parameters for the PSCs with different Br^- contents, measured under LED at 1000 lx.



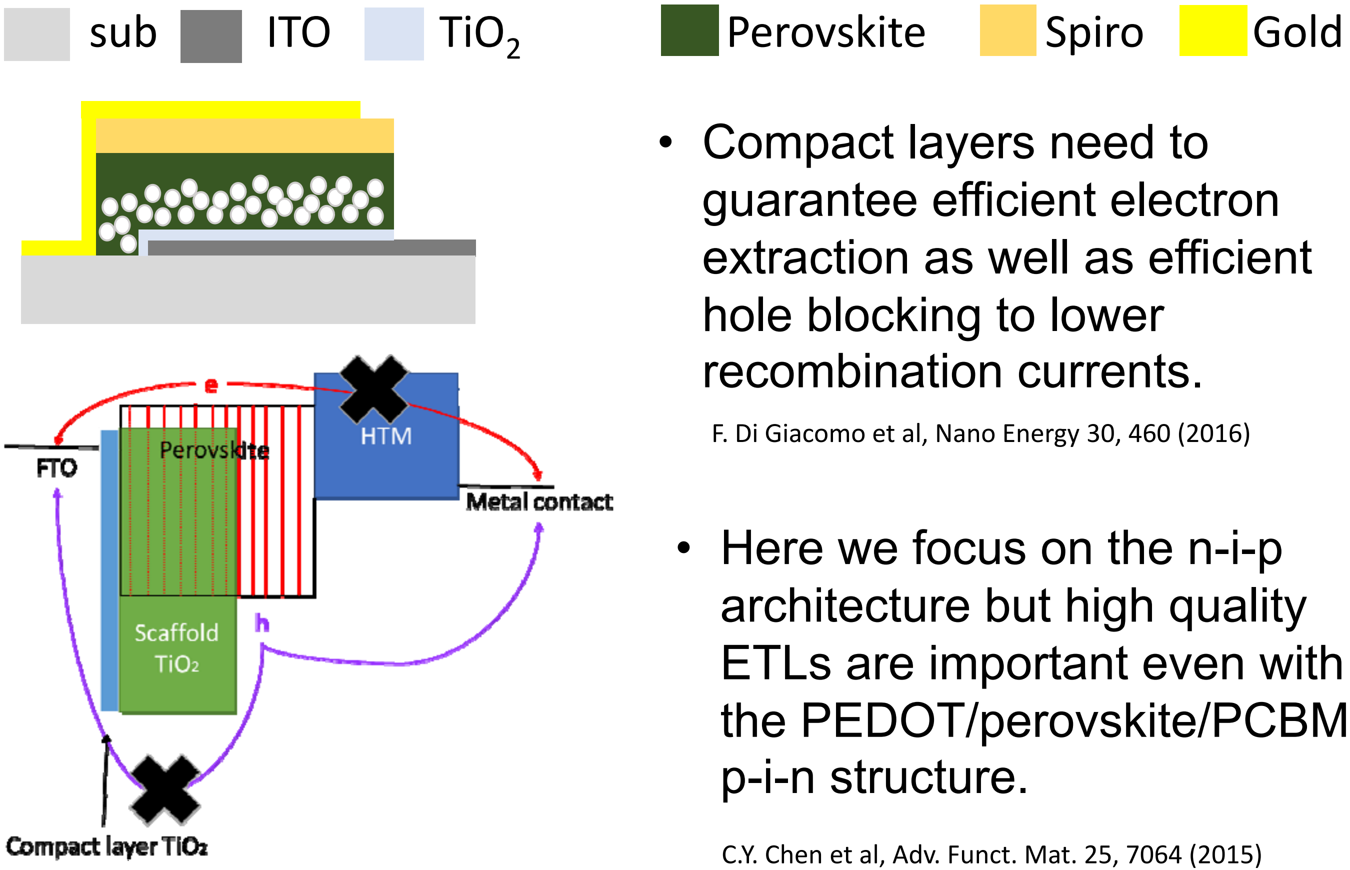
- The **indoor V_{OC} and J_{SC}** values do **not** show the same **monotonic trends**
- The average PCE for Br0.17 devices was **at least 50% higher** than at others Br^-



J. Xu et al., ACS Applied Energy Materials, 2023, https://doi.org/10.1021/acsaem.2c03394.

Thomas Brown

$CH_3NH_3PbI_3$ Perovskites solar cells



Sum, *Energy Environ. Sci.*, 2014,7, 2518

- Compact layers need to guarantee efficient electron extraction as well as efficient hole blocking to lower recombination currents.

F. Di Giacomo et al, Nano Energy 30, 460 (2016)

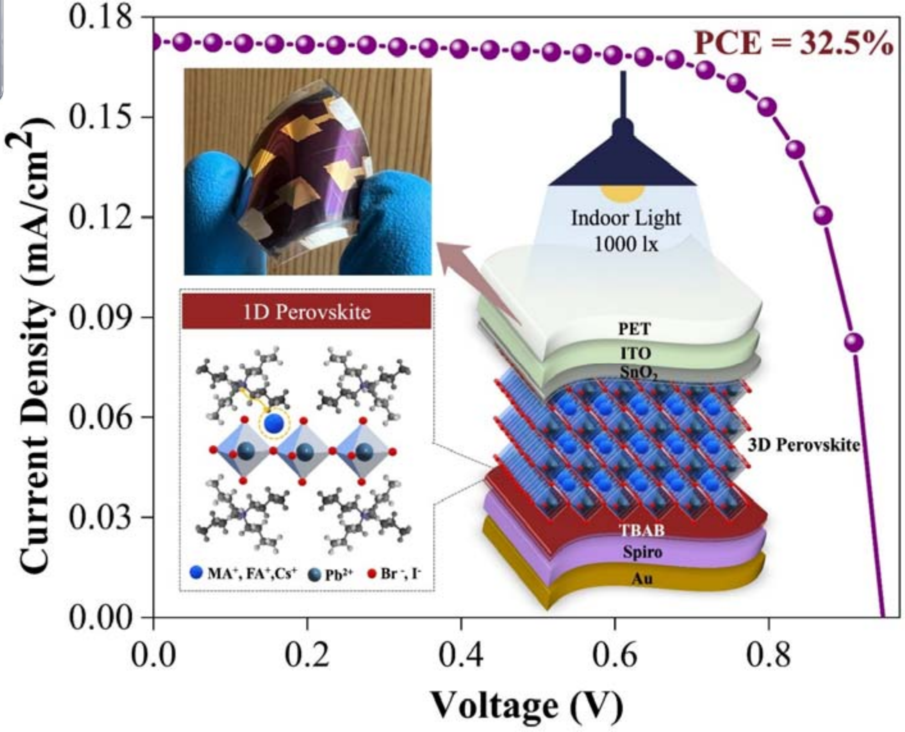
- Here we focus on the n-i-p architecture but high quality ETLs are important even with the PEDOT/perovskite/PCBM p-i-n structure.

C.Y. Chen et al, Adv. Funct. Mat. 25, 7064 (2015)

High-efficiency indoor perovskite solar cells on PET film

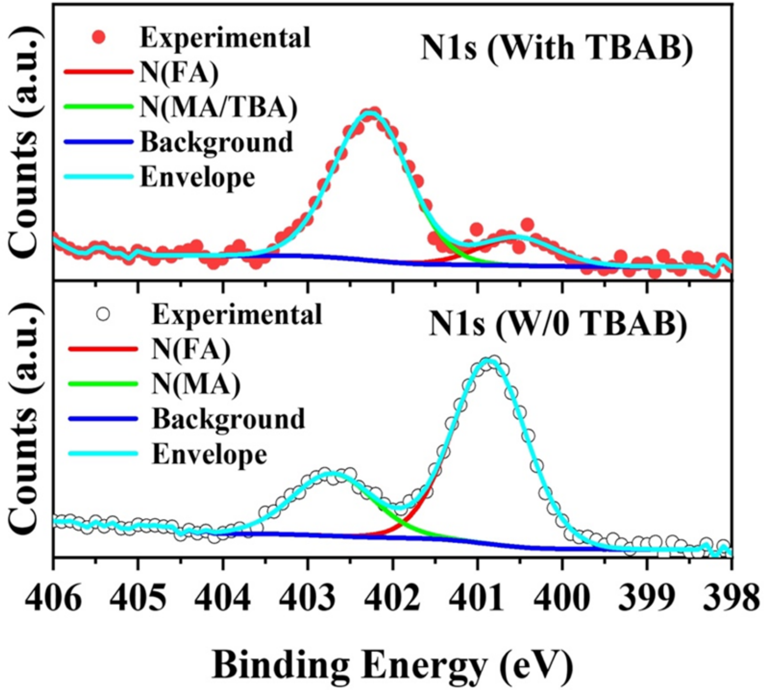
Halide mixing → Interfacial engineering → > 30% efficiency

- Dual low-temperature (≤100 °C) approach
- Halide mixing (replacing I with Br) to increase band gap
- interface modification using tetrabutylammonium bromide (TBAB) to create a low-dimensional perovskite
- Reaching 28.9% at 200 lx and 32.5% efficiency at 1000 lx under indoor illumination
- TBAB treatment reduces defect densities, charge-carrier recombination, and improves ambient air stability considerably



Z. Skafi et al., Solar RRL, 2023.

Perovskite layer characterization - XPS analysis



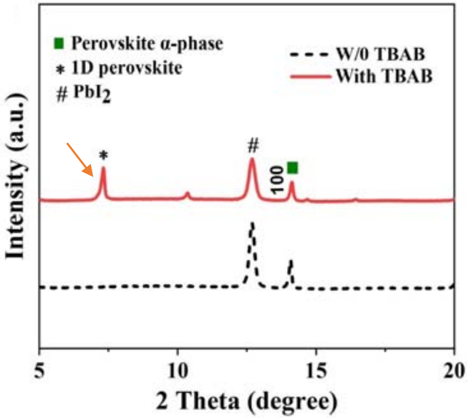
- **Aftere TBAB treatment**, the 400.8 eV **N1s peak** assigned to **nitrogen in FA^+** was severely **weakened**
- Emergence of N1s peak signal at **402.2 eV**, attributed to **nitrogen** in the **TBA^+ cation within the perovskite**

V. Valenzano et al., Sol. RRL 2022, 6, 2200909.

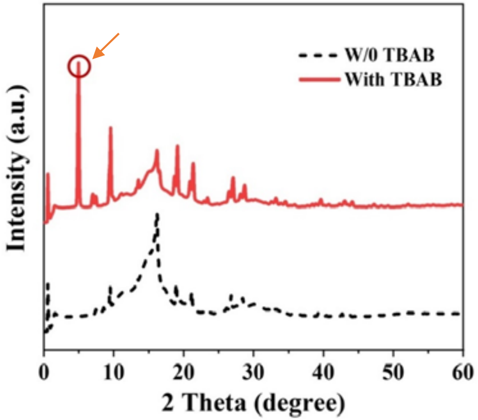
J. Mi et al., J. Energy Chem, 2022, 68, 387.

Perovskite layer characterization - XRD and GIWAX analyses

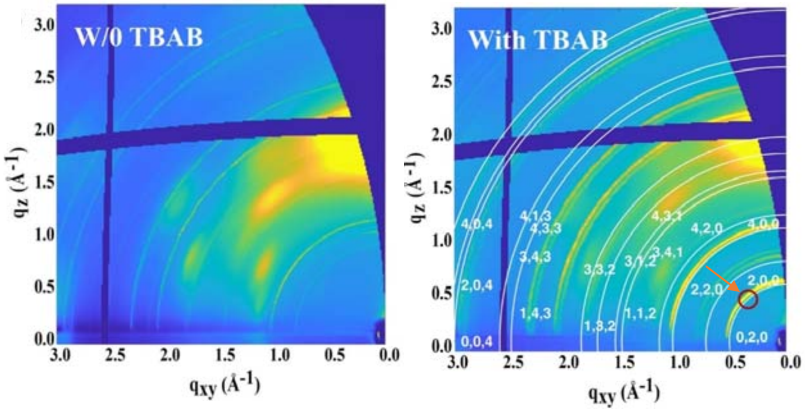
XRD patterns



1D GIWAXS patterns



2D GIWAXS patterns

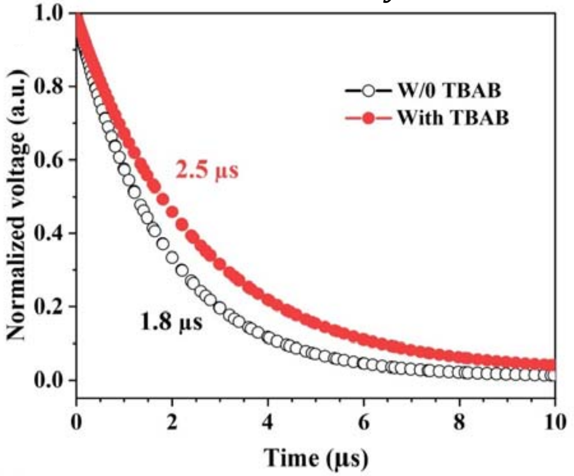


- A **new peak in XRD** pattern at **7.3° after TBAB treatment**
- A **new diffraction ring in 1D and 2D GIWAXS** patterns at smaller q values **(0.54 $Å^{-1}$) after TBAB treatment**
- **TBA^+ cations** have **strong intercalation ability**
- Formation of **a low dimensional perovskite**, in particular **1D TBA-PbI_3-like phase** at the interface between the deposited perovskite material and the TBAB overlayer

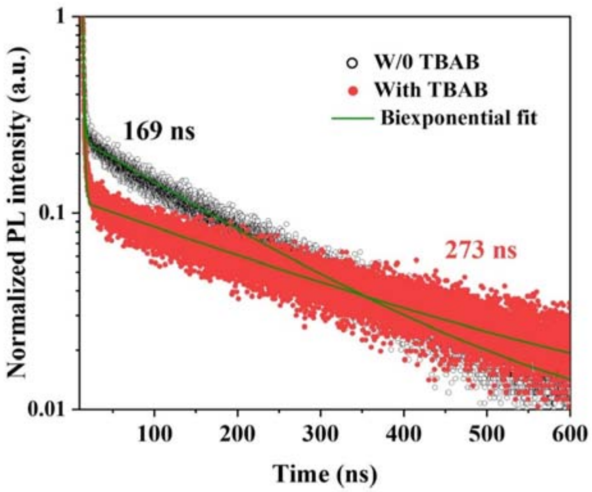
X. Liu et al., Angew. Chemie Int. Ed. 2021, 60, 12351. J. Mi et al., J. Energy Chem. 2022, 68, 387. Y.-J. She et al., Inorg. Chem. Commun. 2014, 46, 29.

Device optoelectrochemical characterization

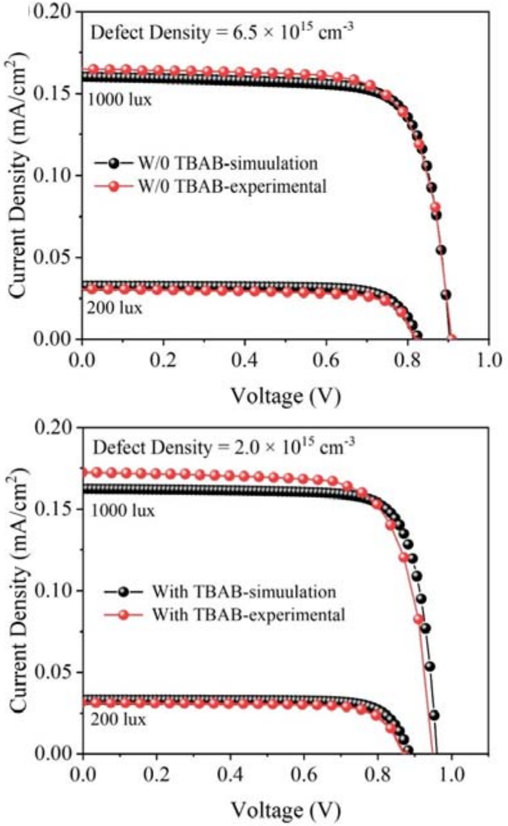
TPV decay



TRPL

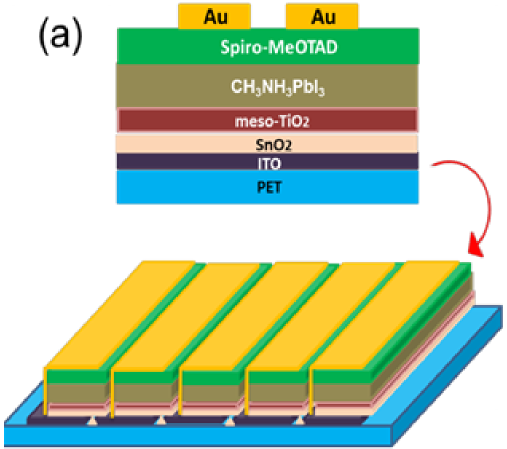


J-V simulations

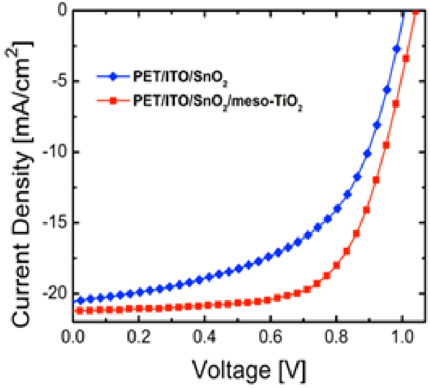


- **Lower density of non-radiative traps** after TBAB treatment
- Carrier fall time of **2.5 µs (with TBAB)** vs **1.8 µs (without TBAB)**
- Longer PL lifetimes of **273 ns (with TBAB)** and **169 ns (without TBAB)**
- Simulations show that TBAB-treated films have lower trap density **6.5×10^{15} cm^{-3}** vs **2×10^{15} cm^{-3}**

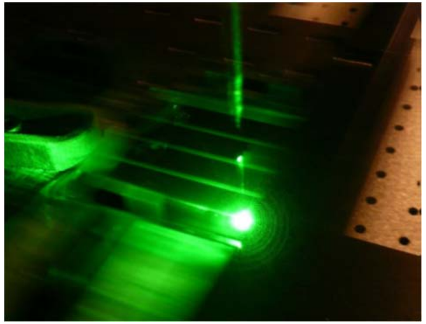
Flexible Solar Cell and fully laser patterned Modules



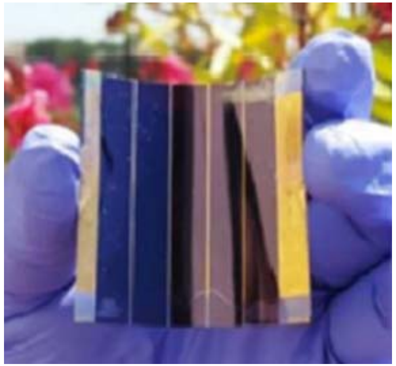
Cell



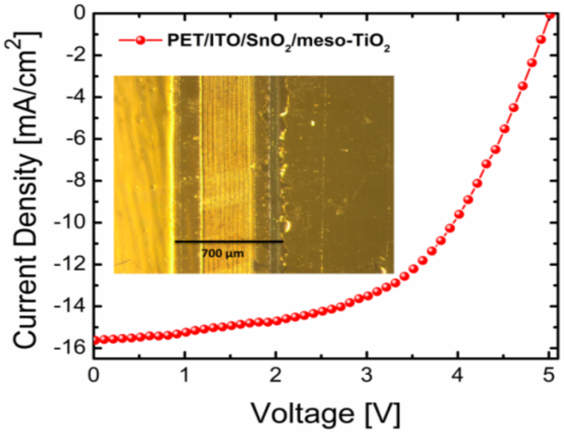
Laser patterning



Module

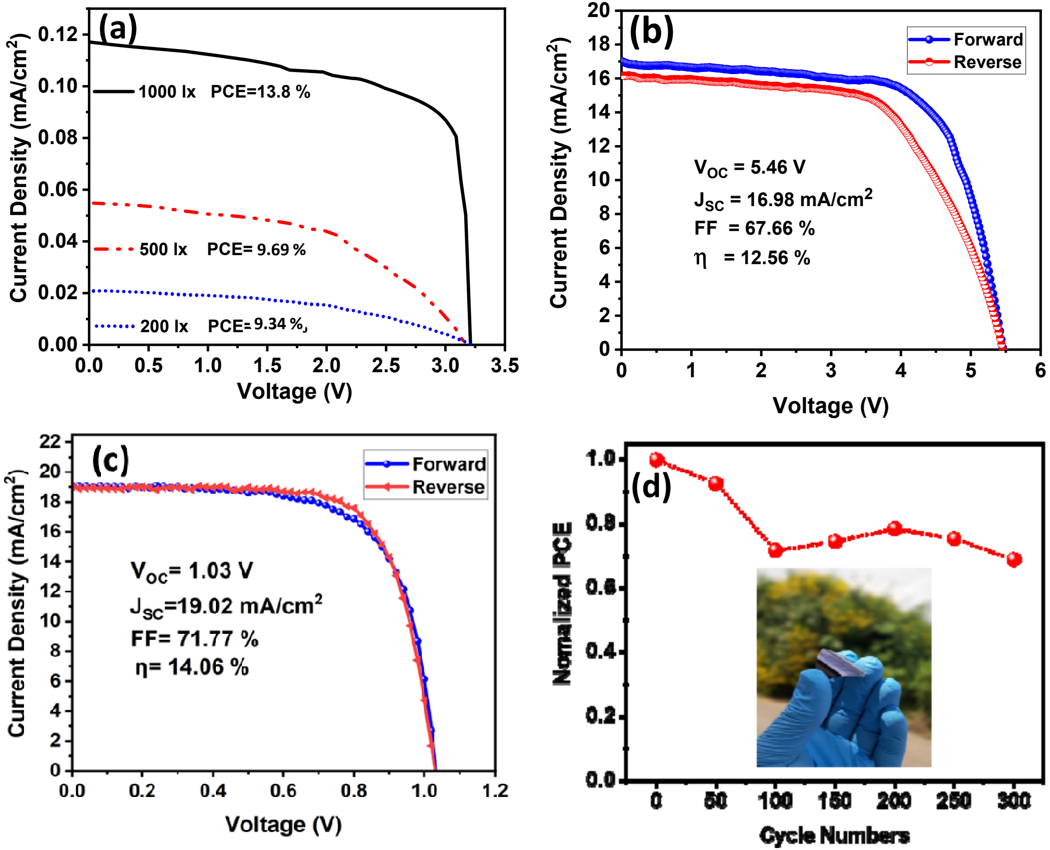


On plastic PET films:
Efficiency of cell = 14.8 %
Efficiency of module = 8.8 %



J. Dagar et al Nano Research 11, 2669 (2018)

Flexible Mini module performance



Performance of the mini modules; (a) J-V curve with variation in light intensity indoors, (b) J-V curve under 1 sun illumination, (c) J-V curve of the module after 1 day and (d) bending test

H. Javanbakht, De Rossi, F. Brunetti et al, under review