FROM PEROVSKITE SOLAR CELLS TO MODULES AND PANELS

(with the help of 2D materials)

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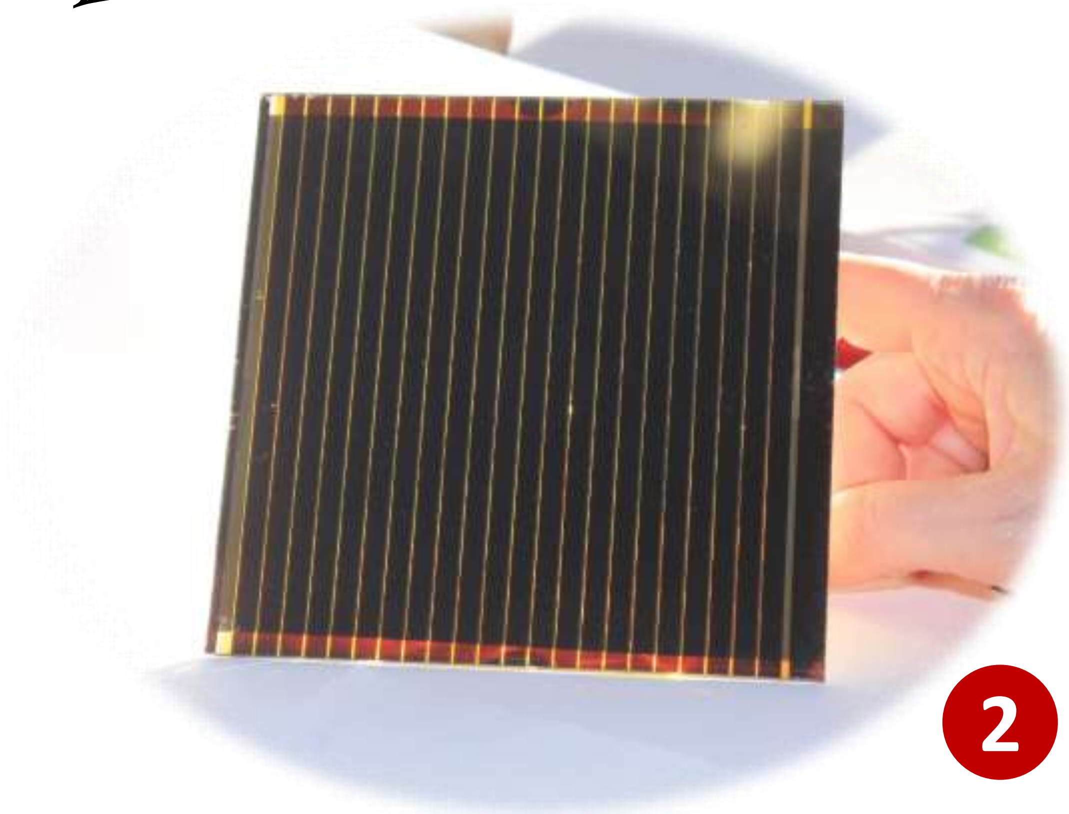
- TEI Crete (Greece): **E. Kymakis** Group
- LENS-Florence (Italy): **A. Vinattieri** group
- University of Namur (Belgium): **Y. Busby** group

Scaling up to large area modules

Let's get power from the sun !



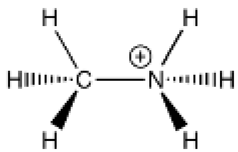
1. Small area
   The impact of 2D materials

2. Scaling up to module/panels size

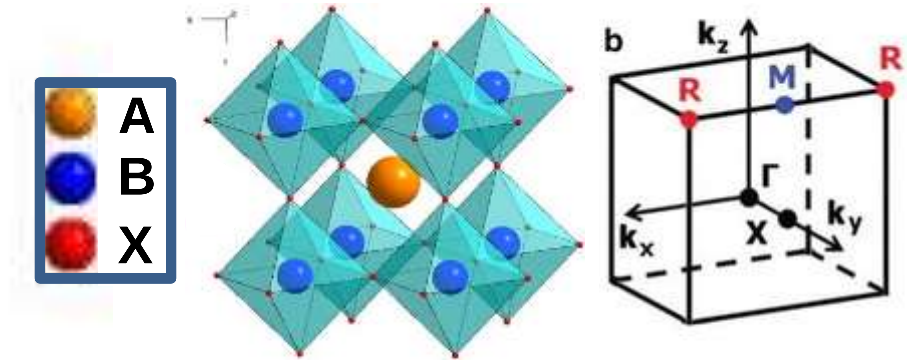
Organometal Halide Perovskite

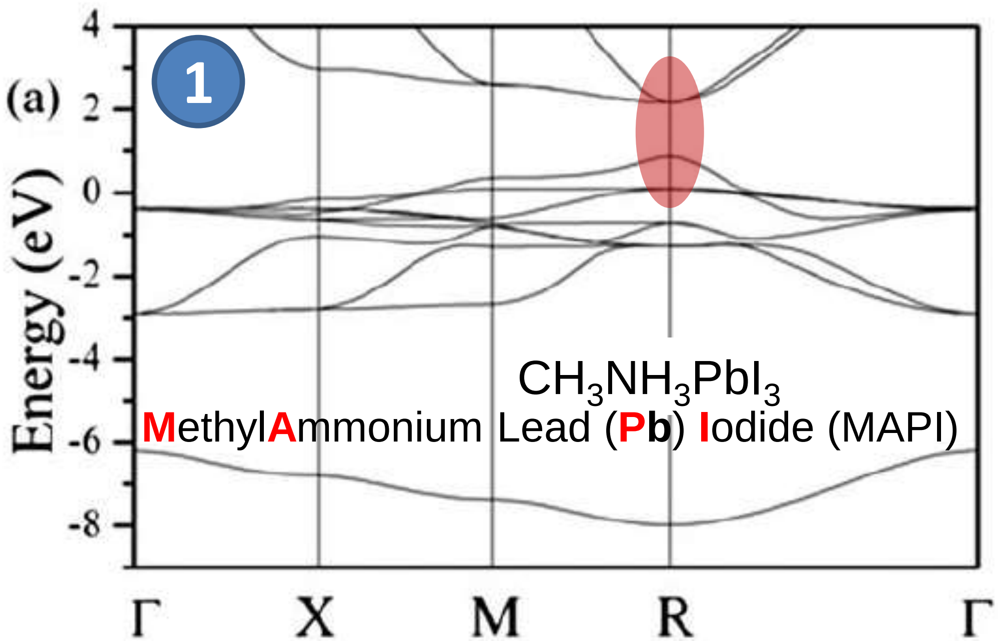
Methyl**A**mmonium Lead (**P**b) **I**odide (MAPI)

A=$CH_3NH_3^{(+)}$; **B**= $Pb^{(+)}$ **X**= $I^{(-)}$



methylammonium ion





Direct band gap of 1.51 eV for $CH_3NH_3PbI_3$

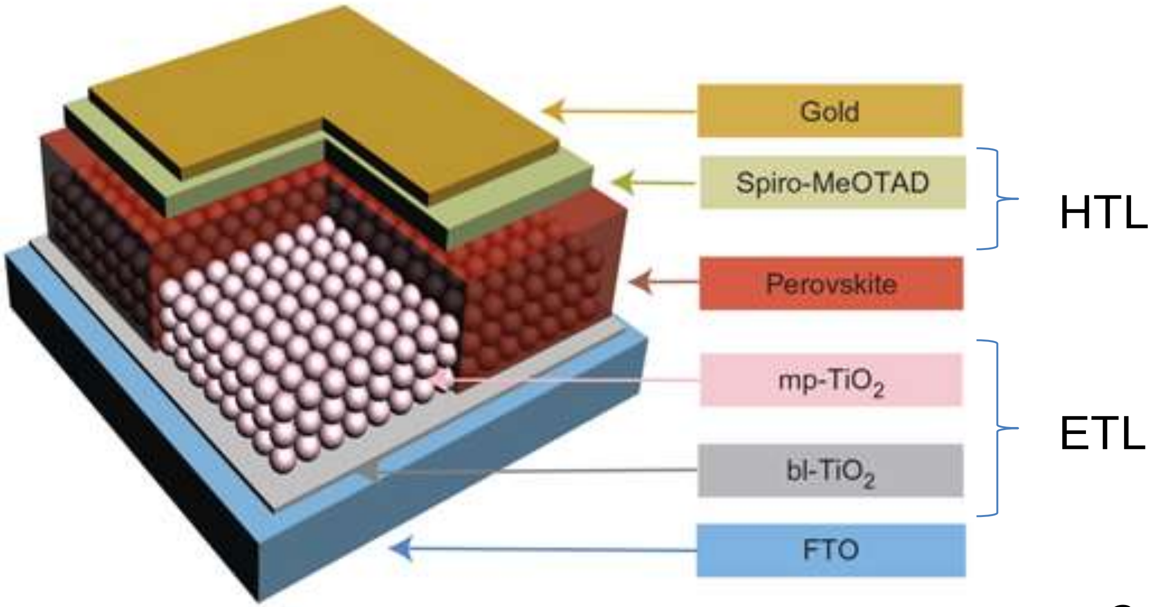
Good hole and electron diffusion lengths from 100 nm to 1 μm **2**

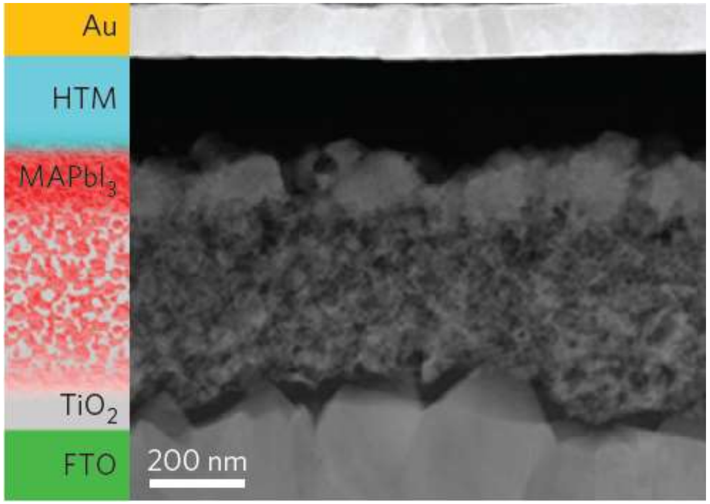
Solution process **3**

MAPI is ideal for optoelectronics

Baikie et al. J. Mater. Chem. A, 2013, 1, 5628

Typical (mesoscopic) PSC





G. Divitini et al., Nature Energy (2016) 1, 15012

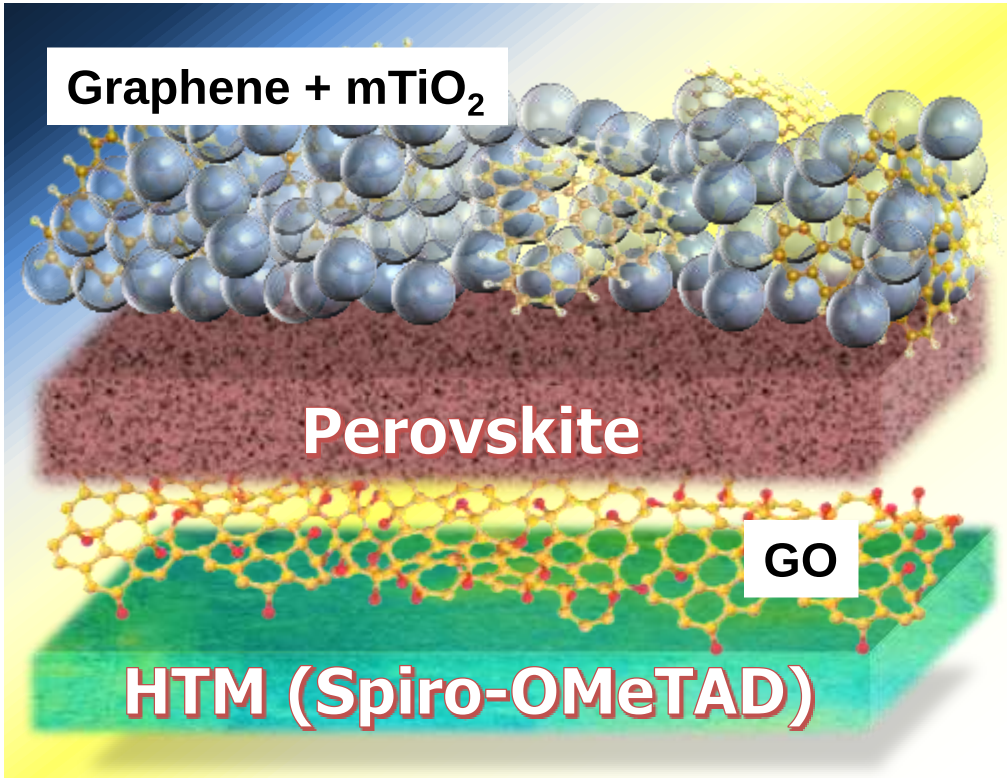
“Efficiency and stability are controlled by the interfaces

E. Palomares* et al. Chem Mat (2015) DOI: 10.1021/acs.chemmater.5b03902

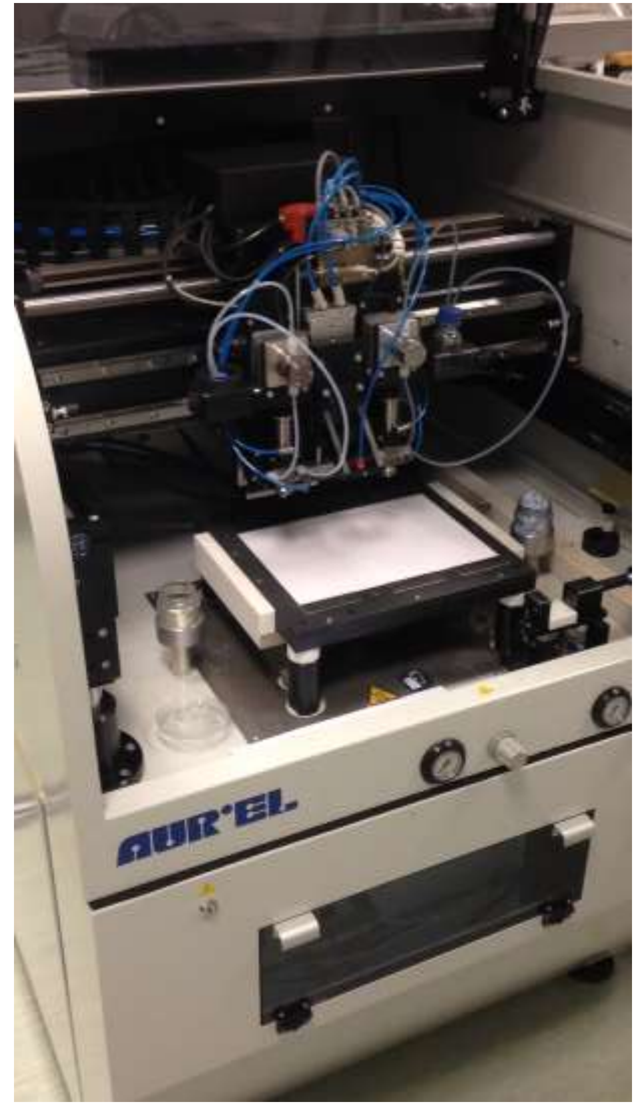
Several strategies can be used to tune interface properties. Both chemical and physical methods have been applied so far

Can we use **Graphene and Related 2D Materials** to properly change interface properties ?

Anode and Cathode with Graphene



G in $mTiO_2$ improve charge-transport dynamics



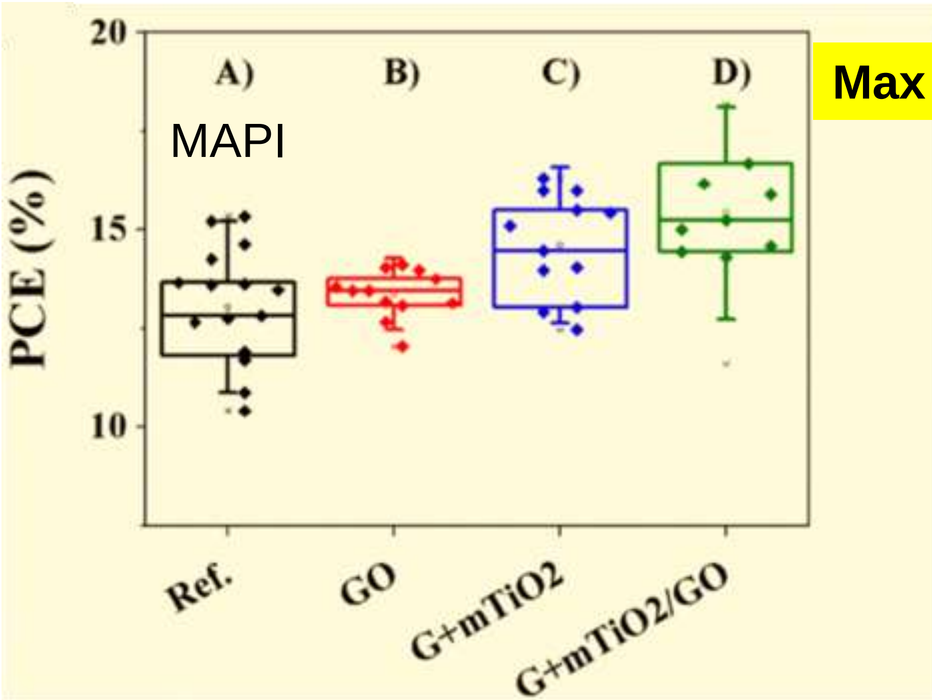
GO interlayer:

- increase wettability of PSK
- Improve the interconnection between perovskite and spiro-OMeTAD film, by enhancing the charge-collection efficiency

W. Li, et al. J. Mater. Chem. A 2014, 2, 20105.

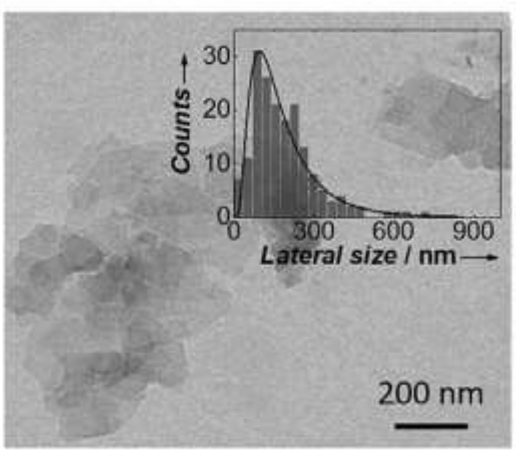
A. Agresti et al. ChemSusChem (2016) 9, 2516

Interface Engineering with G and GO

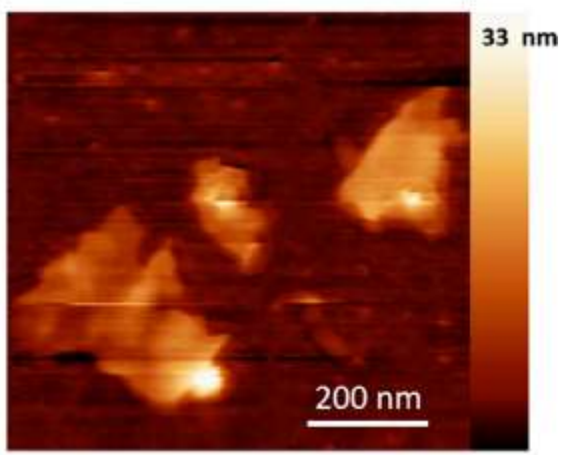


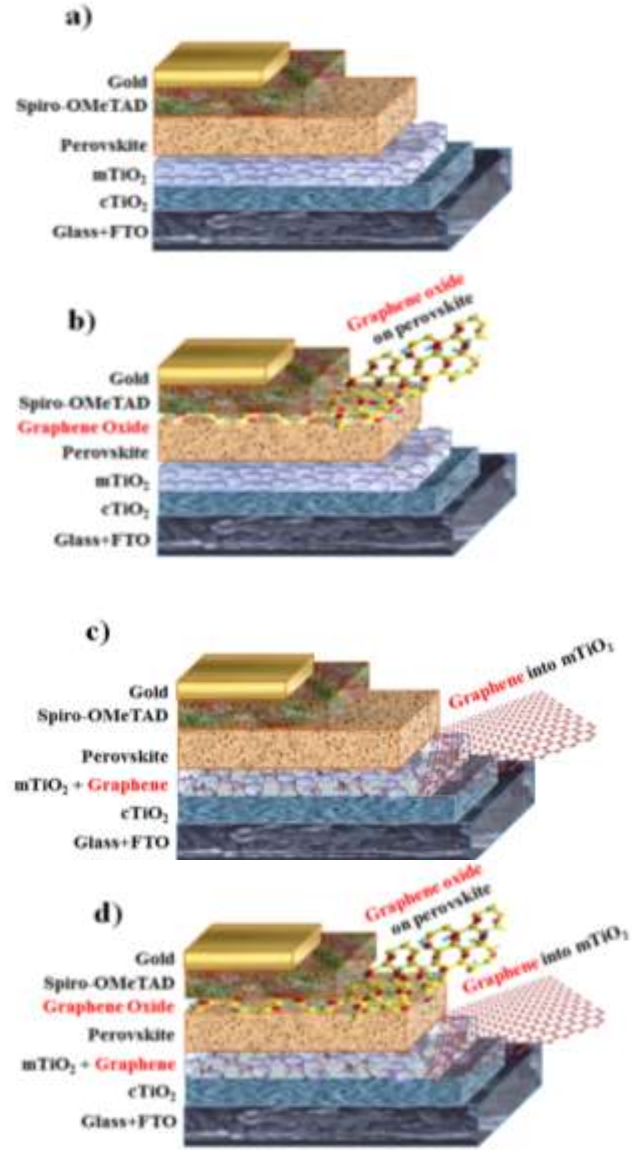
Max 18.2%

a)



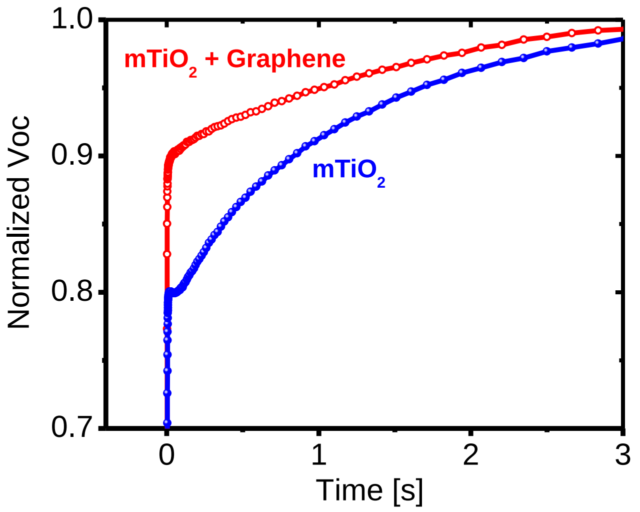
b)





A. Agresti et al. ChemSusChem (2016) 9, 2516

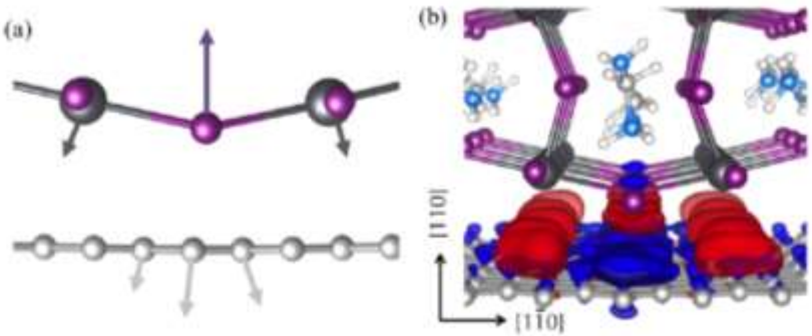
Graphene and perovskite: why?

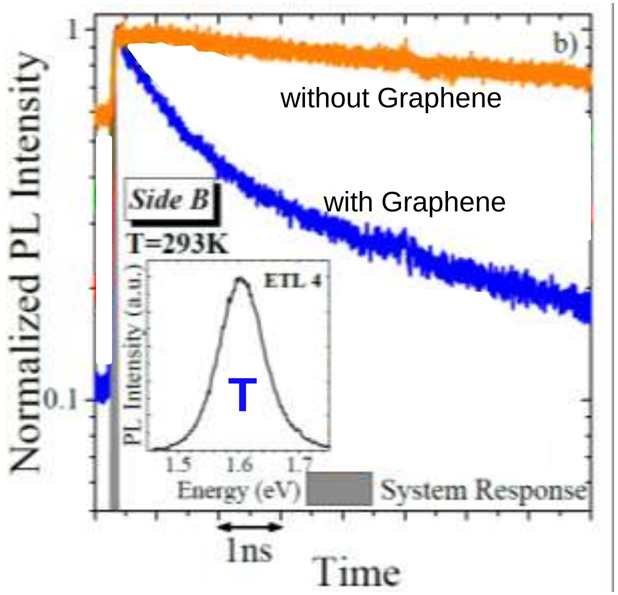


PSC with Graphene has faster rise-time than Ref. PSC.
V_{OC} rise time is correlated to:

- the charge transfer from the active to transport layer
- the active layer regeneration

Graphene stabilize permanent ferrorelectric dipole improving charge injection
Volonakis and Giustino JPCL, 2015, 6, 2496,



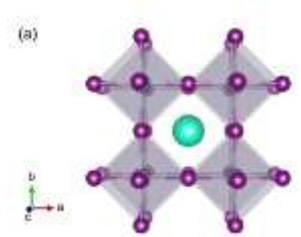


This result has been confirmed by Time-Resolved Photoluminescence experiments

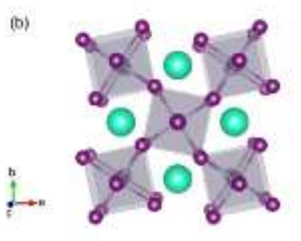
PL measurements: impact of Graphene

Perovskite crystalline structure

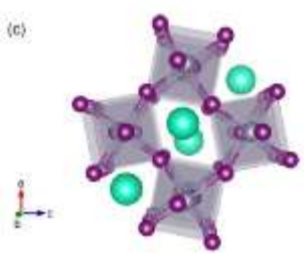
C- Cubic (T>300K)



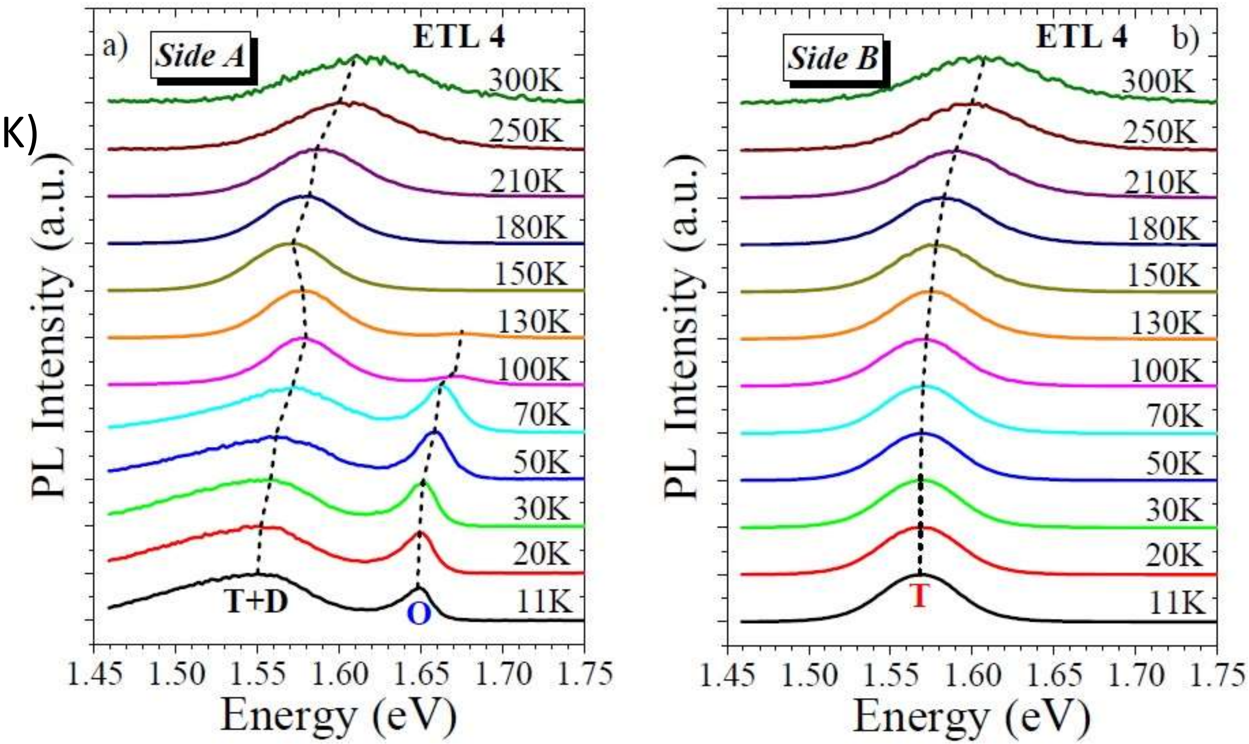
T- Tetragonal (150K<T<300K)



O- Orthorhombic (T<150K)



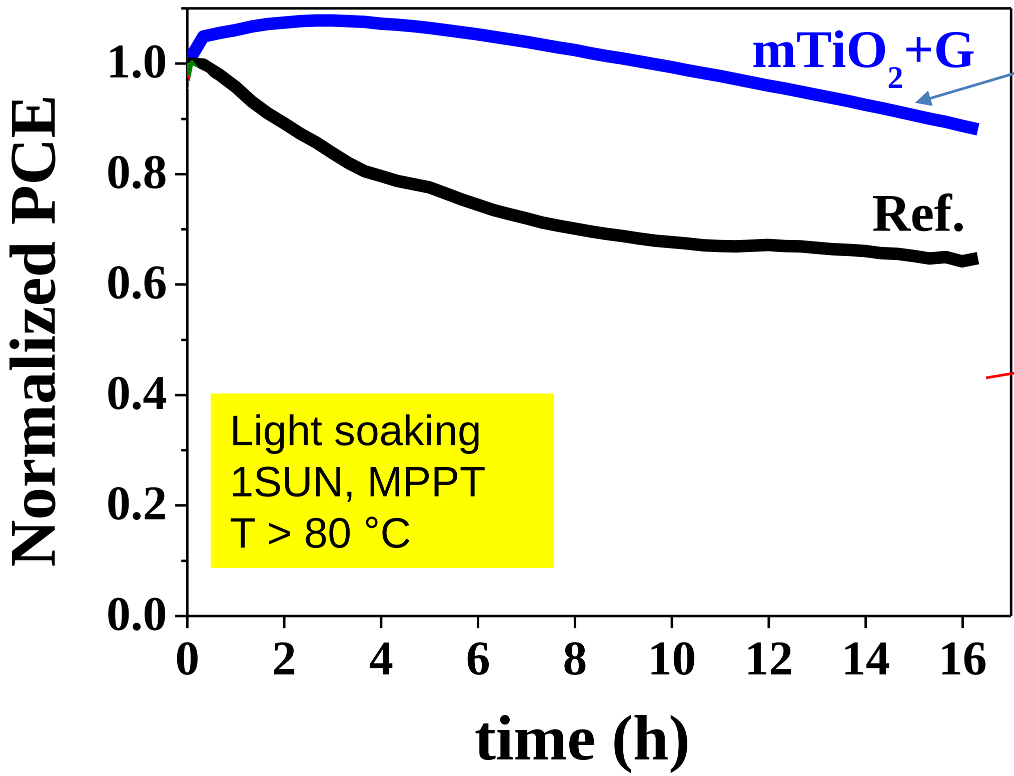
Temperature-dependent PL



Crystallinity of MAPI at low temperature: the presence of graphene inhibits phase change into the orthorhombic form.

Biccari et al., Adv. En. Mater. 2017, 22,1701349

Light soaking stability



Light soaking reveal better stability of PSC with graphene doped mTiO2 with respect to reference cells.

On the other hand all the cells with GO interlayer show a worse performance

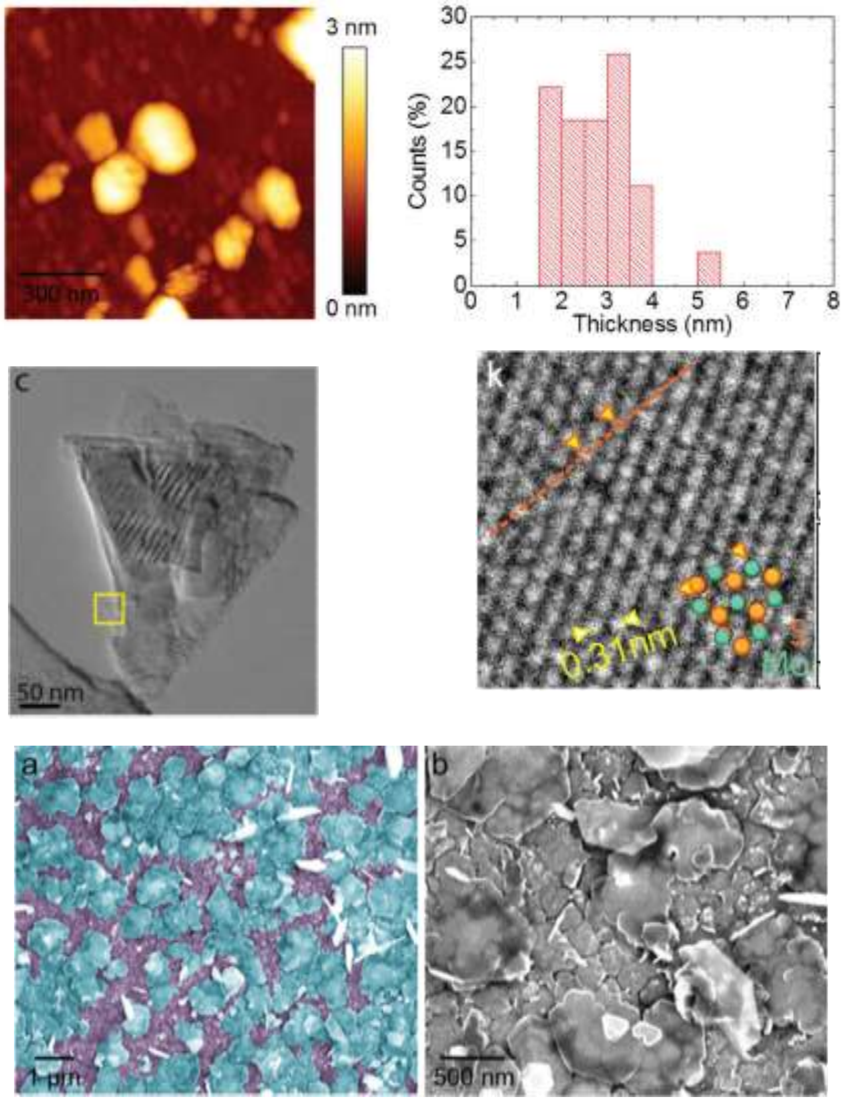
- **G in mTiO2 reduces the trapping of the charges** improving the stability of the cell (Ann et al arXiv:1604.07912)

- MAPI crystals can undergo a **hydration reaction** triggered by prolonged illumination. (Kamat et al. JACS 2016, 137, 1530) This can produce **hydrogen iodine (HI) which can reduce the GO** (S. Pei et al. Carbon 2010, 48, 4466, Z. Fan et al. Joule 1, 548–562 (2017).;).

…. But there are 2000 bidimensional materials !!

A. Agresti et al. ChemSusChem (2016) 9, 2516

From GO to MoS_2 interlayer

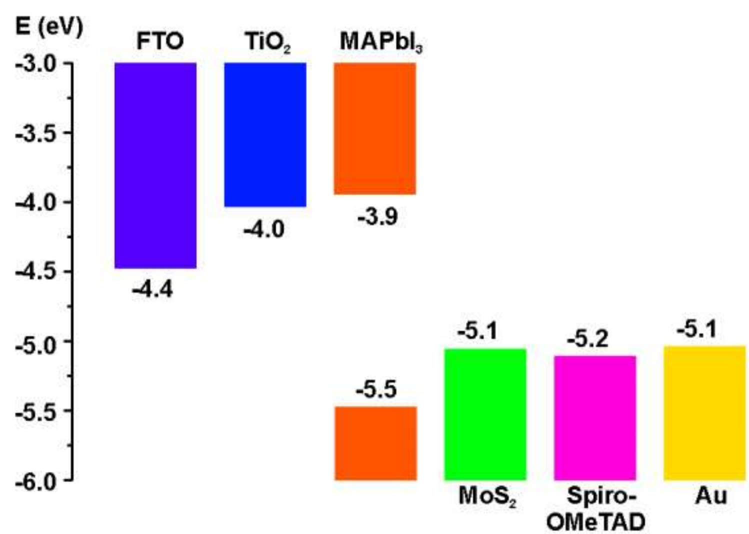


MoS_2: High mobility, chemical inertness

Liquid-phase exfoliation (LPE) of MoS_2 in NMP

Solvent exchange with IPA (compatible with perovskites)

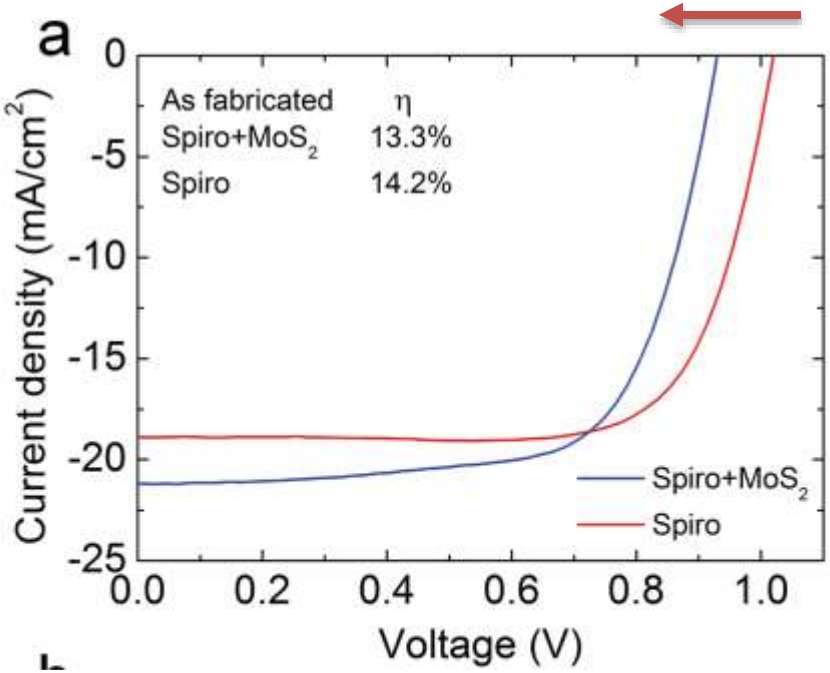
MoS_2 flakes are deposited by spin-coating on perovskite



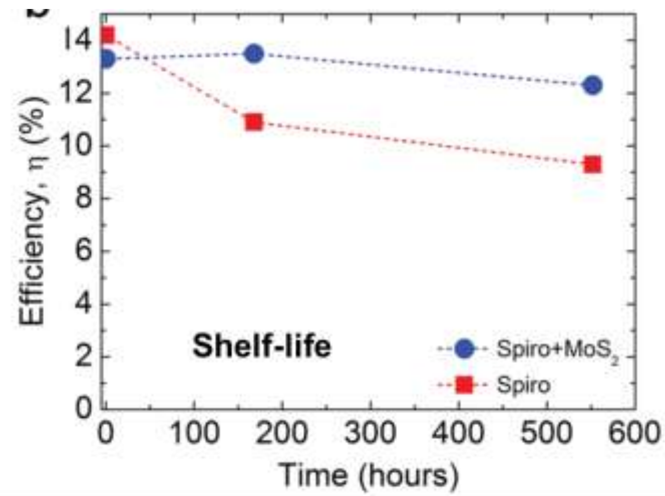
Efficiency and Stability of PSK/MoS_2

Stability increases with MoS_2

Voc reduction

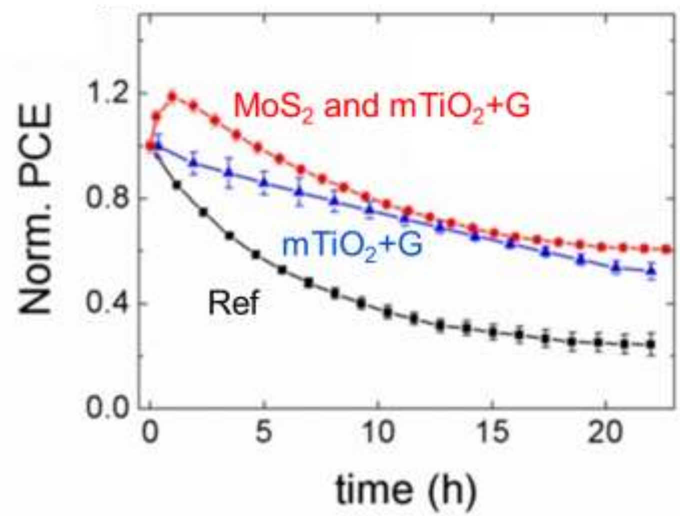


Efficiency doesn’t increase with MoS_2



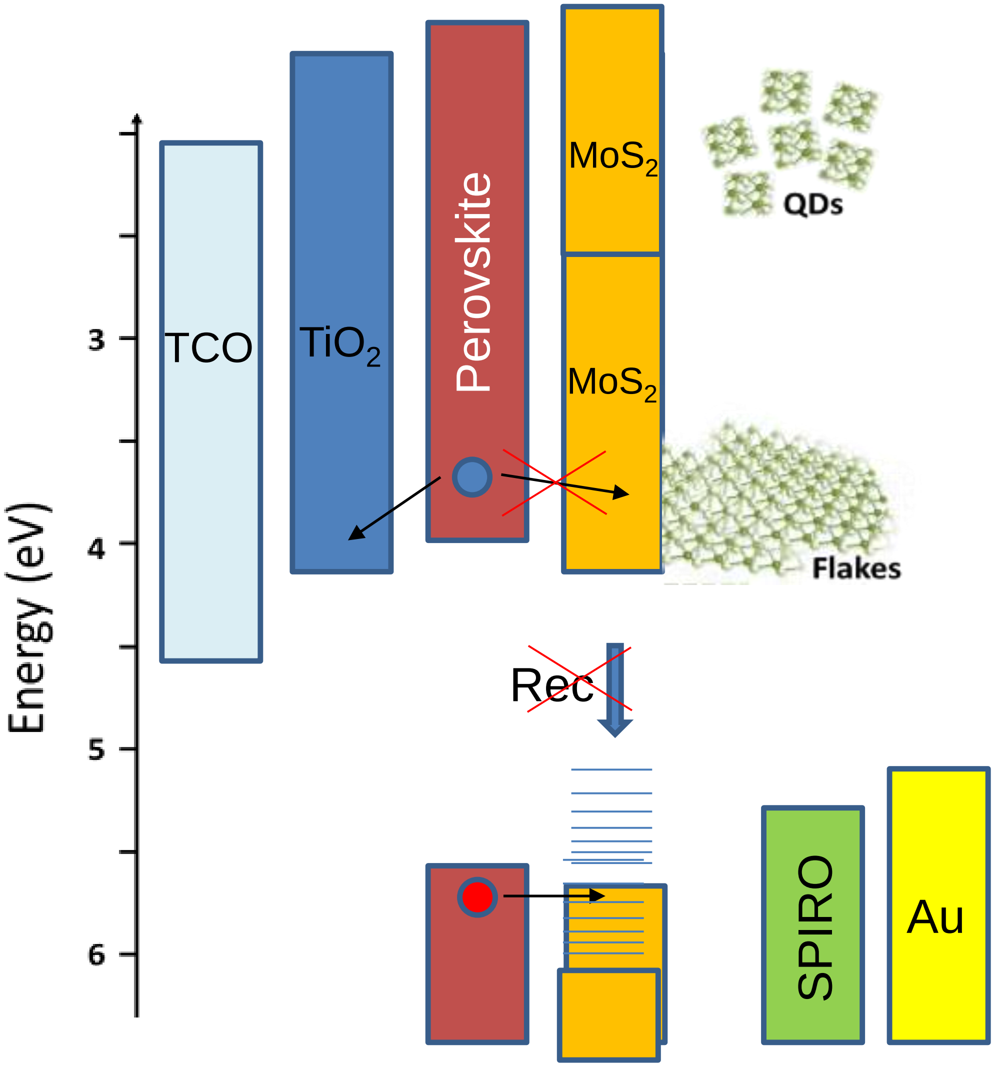
Stress condition:

- 1 SUN light soaking @ ≈ 90C

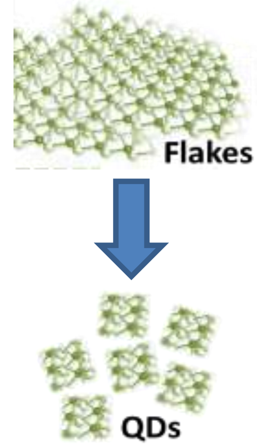


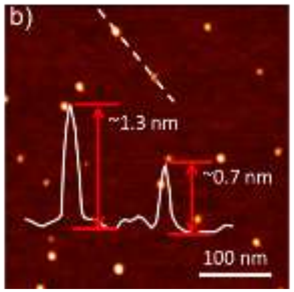
A. Capasso et al. Adv. Energy Mat. (2016) 6, 1600920; Y. Busby et al, Materials Today Energy 2018, 9, 1

Where is the problem of MoS_2 ?

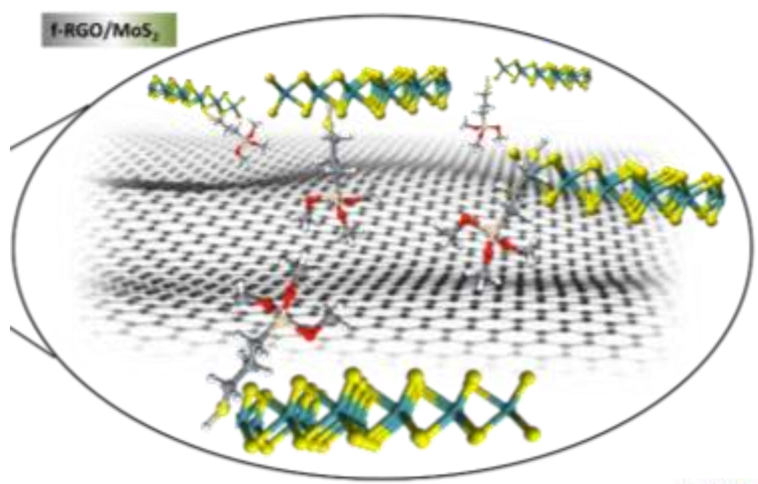


From MoS_2 flakes (Eg =1.4 eV)





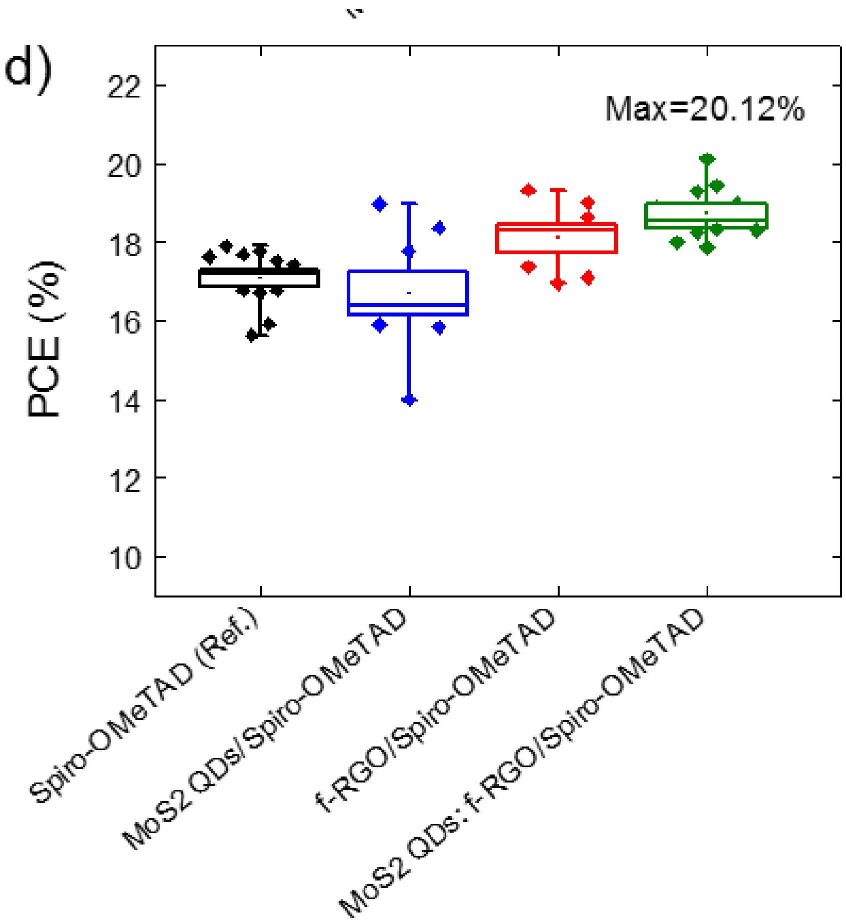
MoS_2 Quantum Dots (Eg = 3.2 eV)

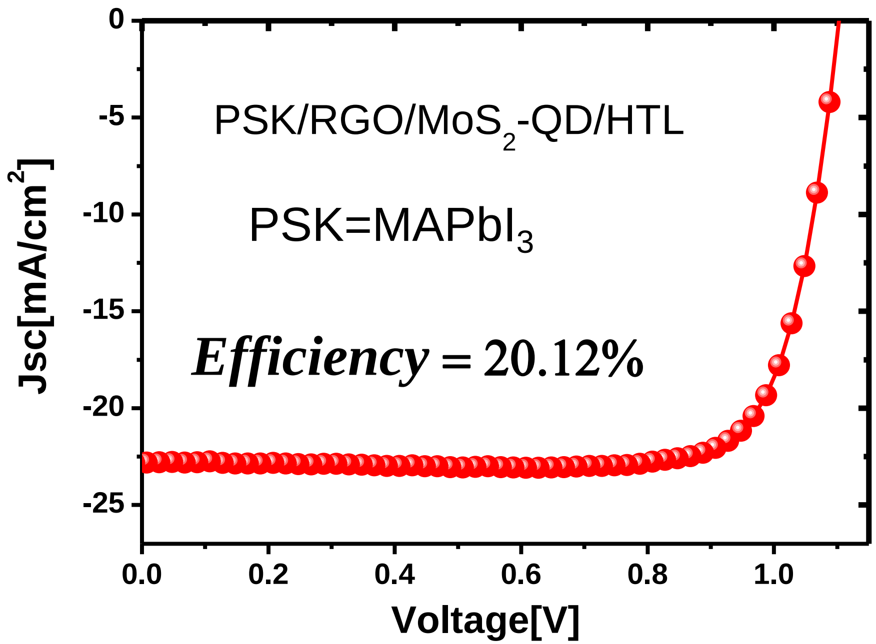


L. Najafi et al, ACS Nano 2018, 12, 11, 10736

Graphene Interface Engineering 2.0

2D materials can be properly combined to boost further the efficiency of the cell and to properly protect the interface from degradation

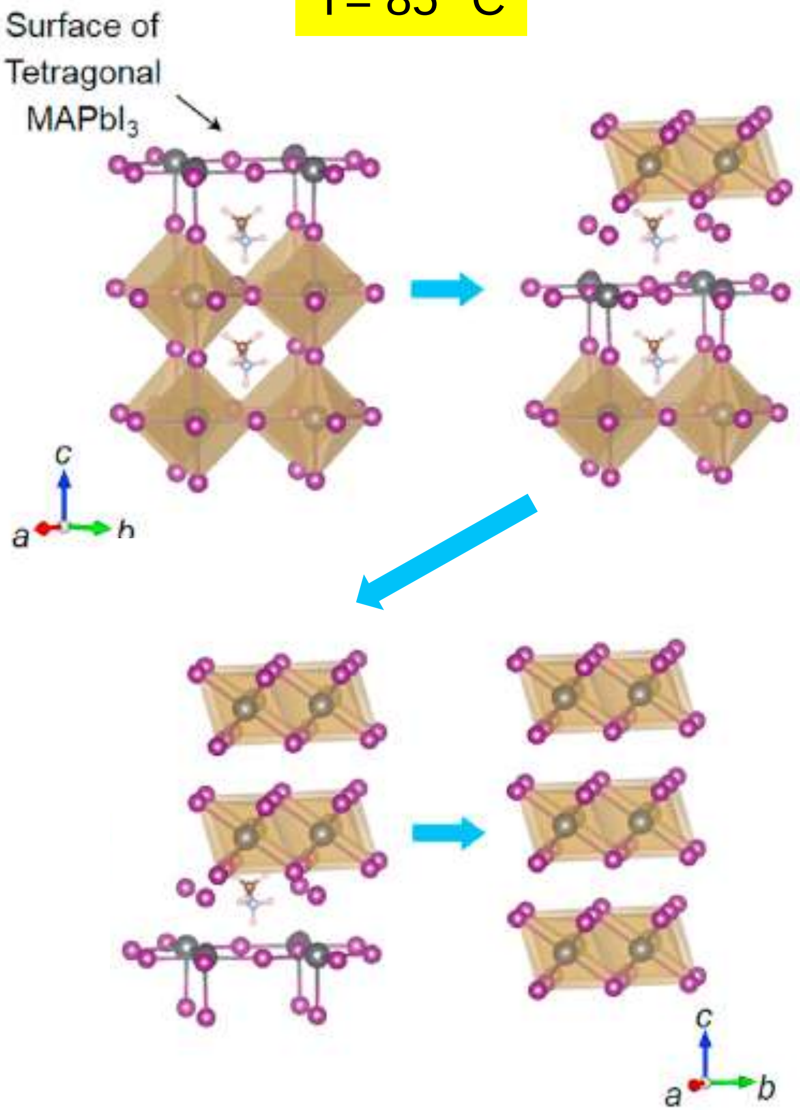


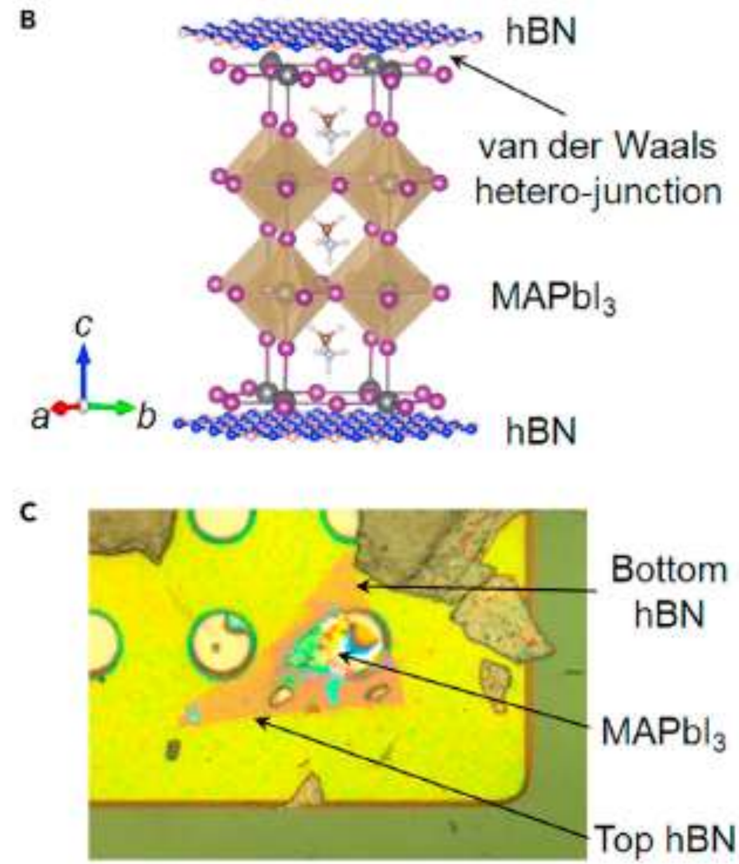


The control of the interface with 2D materials can boost the charge transfer and the simple MAPI perovskite could lead to an efficiency exceeding 20%

MAPI degradation at 85°C: Exfoliation

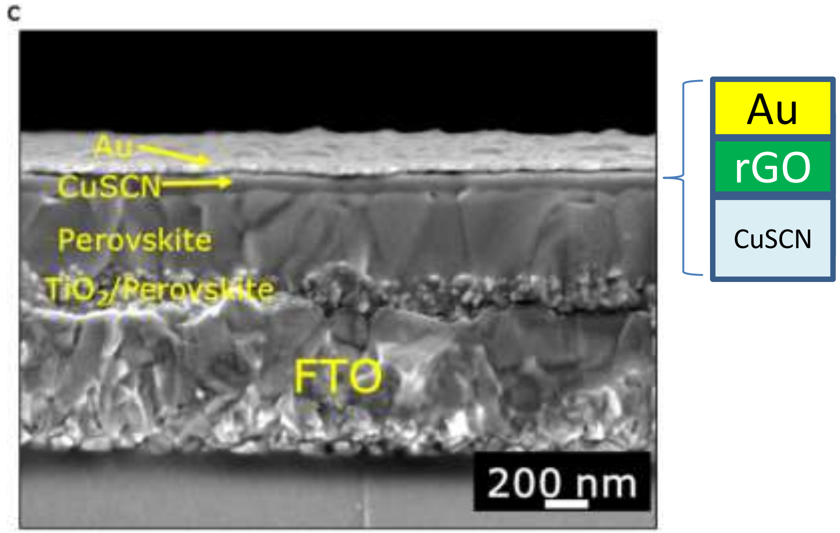
T= 85 °C

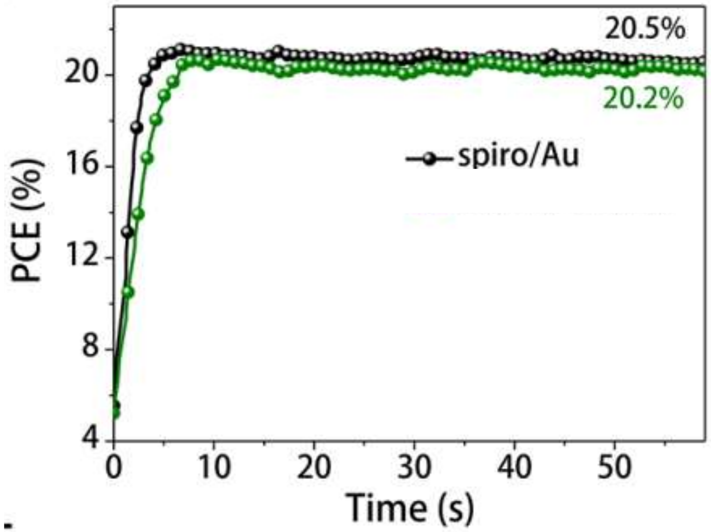


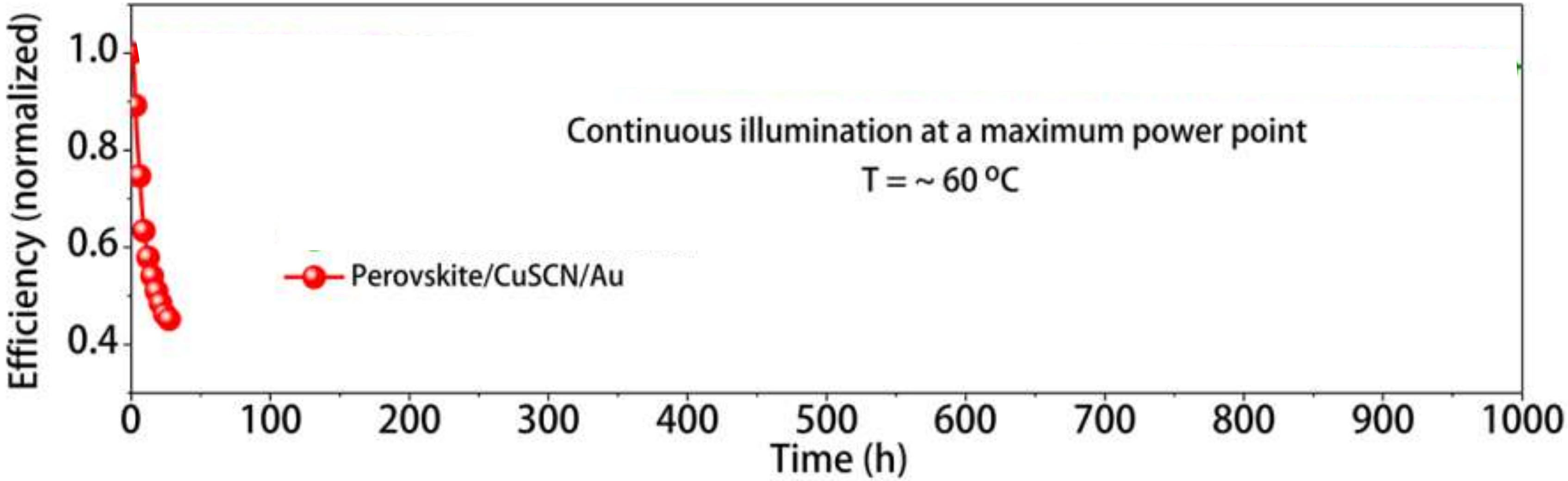


No exfoliation with 2D-BN

Stable high-efficiency PSC is with 2D materials !







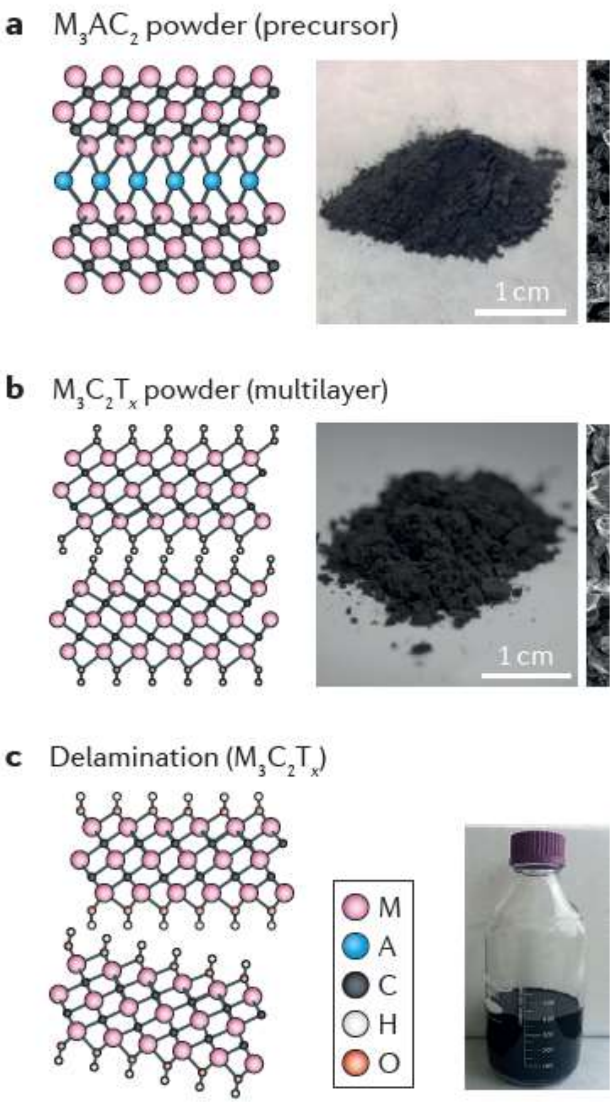
Arora, Graetzel et al., Science (2017);

A new 2D material strategy: MXenes

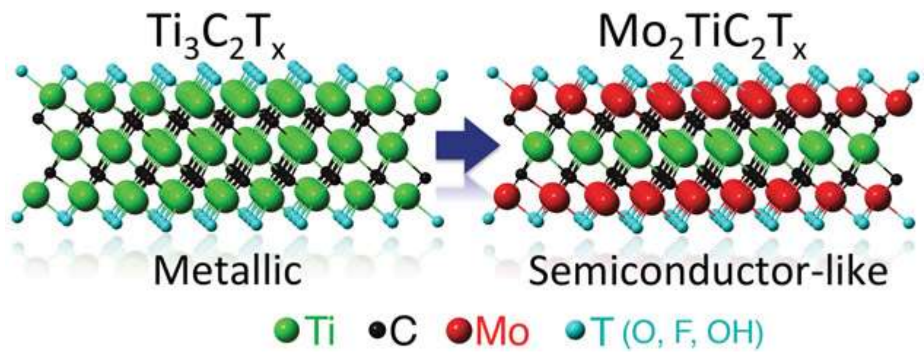
MAX phase

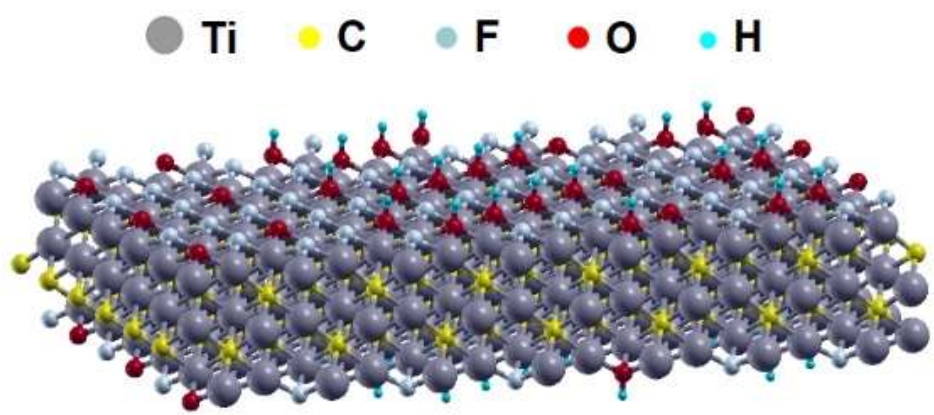
HF etching

Exfoliation



MXenes consist of few atoms thick layers of transition metal carbides, nitrides , or carbonitrides.

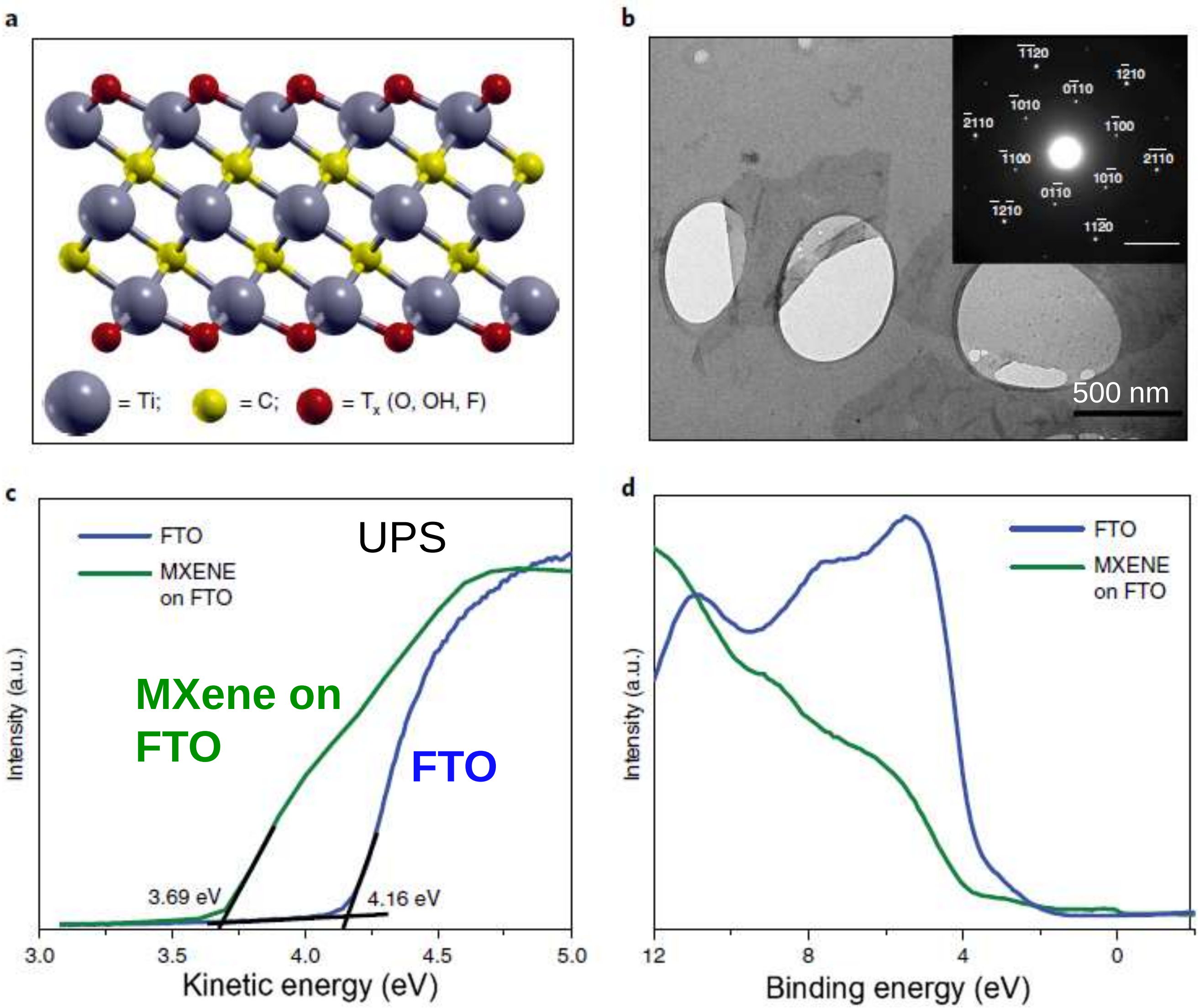




Surface terminations

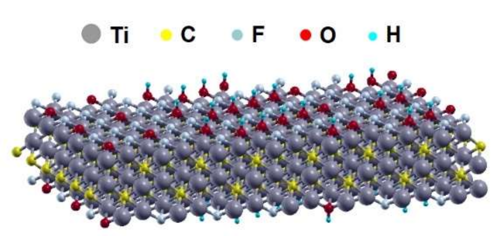
Y. Gogotsi et al Nature Review Materials (2017)

Ti_3C_2Tx MXene: Experimental Work function



XPS measurements:

F:OH:O = 62:25:13

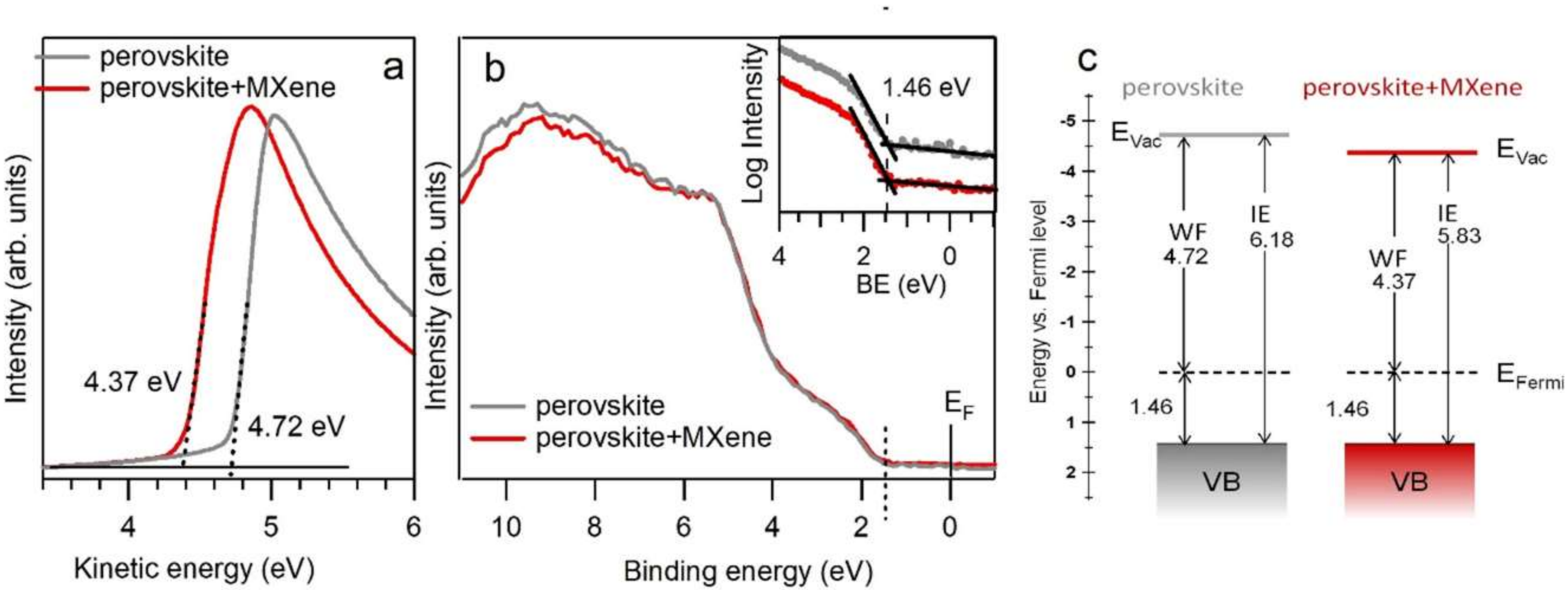


DFT -> WF=3.75 eV

In good agreement with experimental data

A. Agresti et al. Nature Materials (2019) DOI: 10.1038/s41563-019-0478-1

Perovskite WF shift induced by MXenes

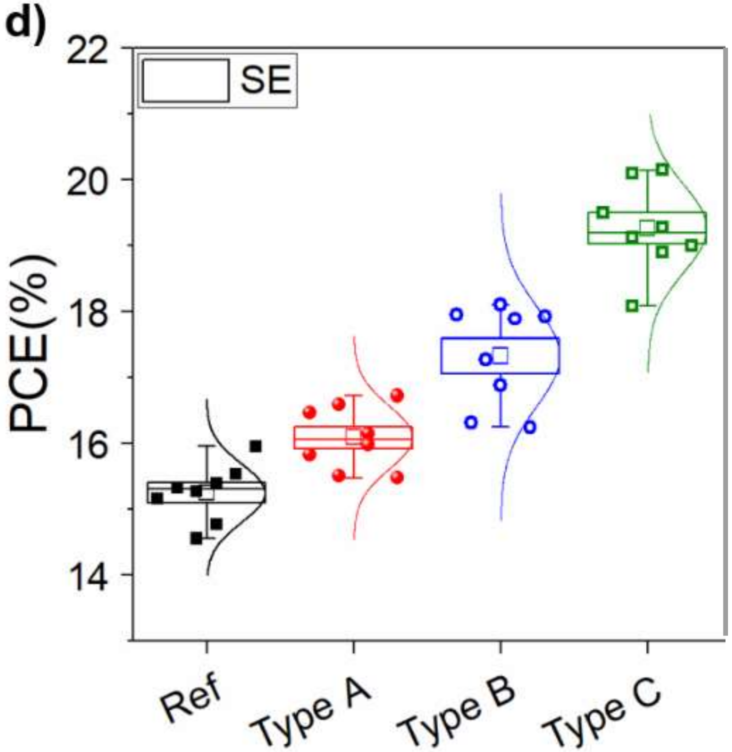


A 0.35 eV reduction of the multication perovskite WF is observed by "doping" perovskite with MXenes (0.014 mg/ml)

A. Agresti et al. Nature Materials (2019) DOI: 10.1038/s41563-019-0478-1

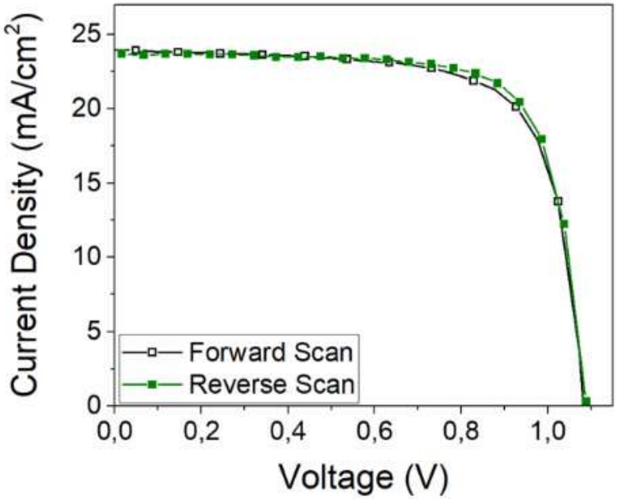
Perovskite/MXene solar cells

Name	Device Structure
Reference	$cTiO_2/mTiO_2$/perov/spiro-OMeTAD/Au
Type A	$cTiO_2/mTiO_2$/perov+**MX**/spiro-OMeTAD/Au
Type B	$cTiO_2$+**MX**/$mTiO_2$+**MX**/perov+**MX**/spiro-OMeTAD/Au
Type C	$cTiO_2$+**MX**/$mTiO_2$+**MX**/**MX**/perov+**MX**/spiro-OMeTAD/Au



Max Efficiency 20.14%

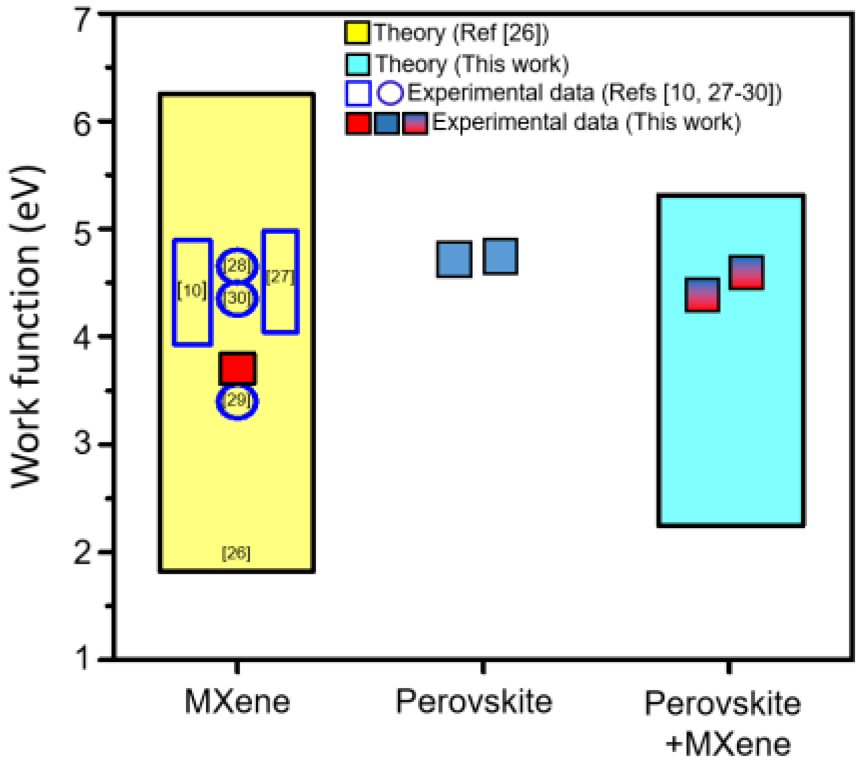
Negligible hysteresis



Better alignment improves Voc and charge transfer

A. Agresti et al. Nature Materials (2019) DOI: 10.1038/s41563-019-0478-1

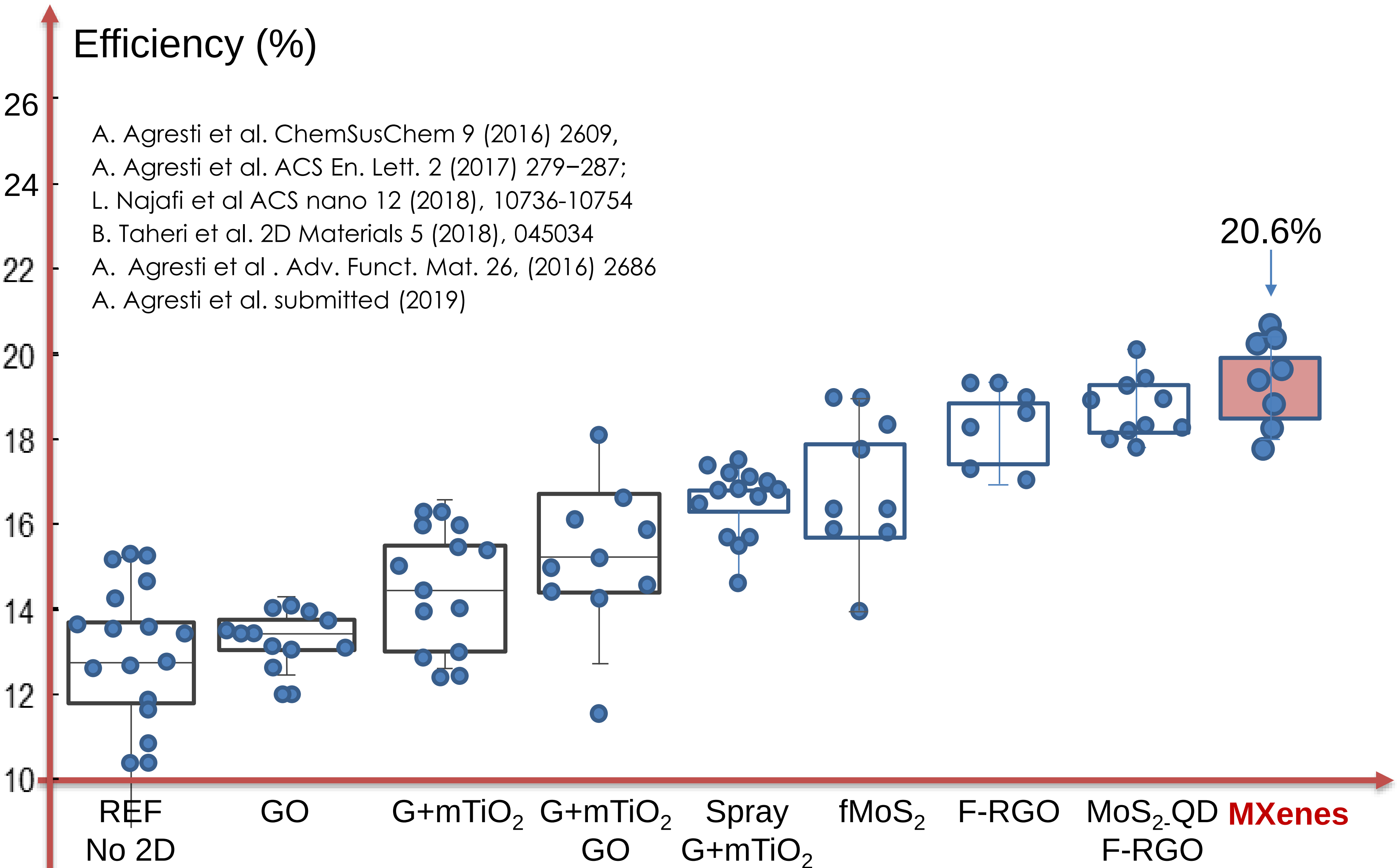
MXenes in perovskite: Work Funcion engineering



WF tuning can be use to align perovskite with other charge transport layer beside conventional ones

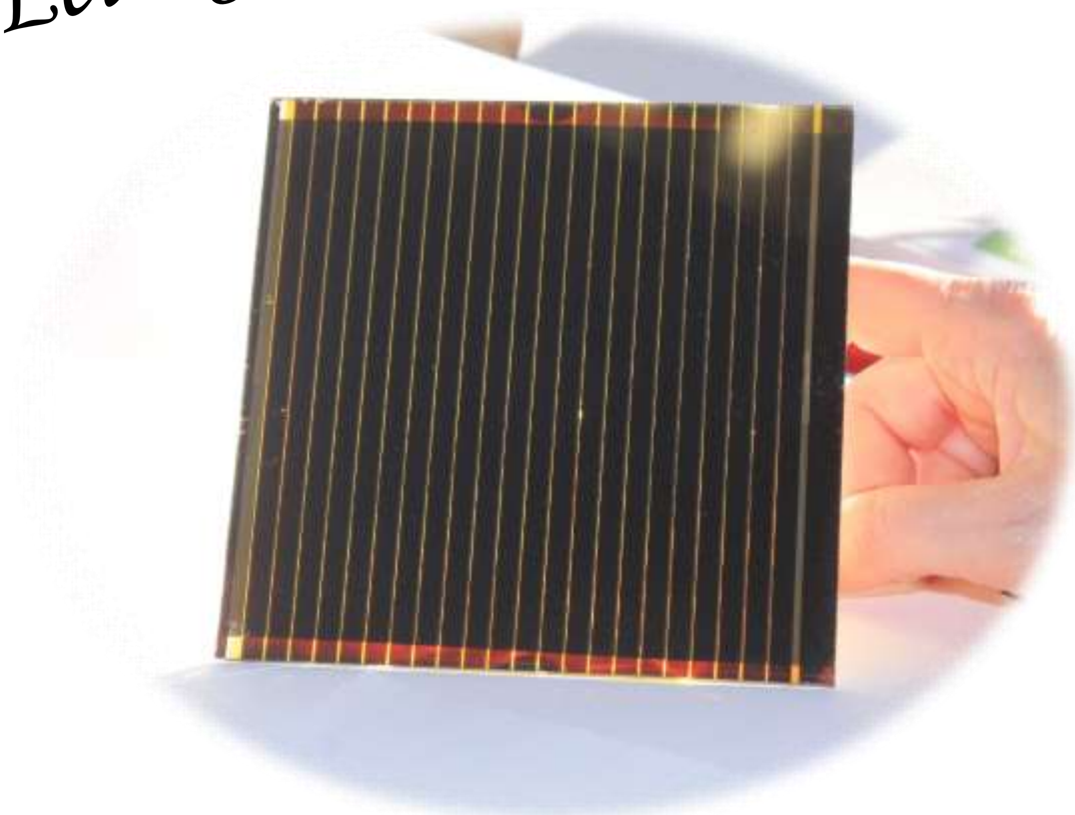
A. Agresti et al. Nature Materials (2019) DOI: 10.1038/s41563-019-0478-1

Graphene Interface Engineering - cells

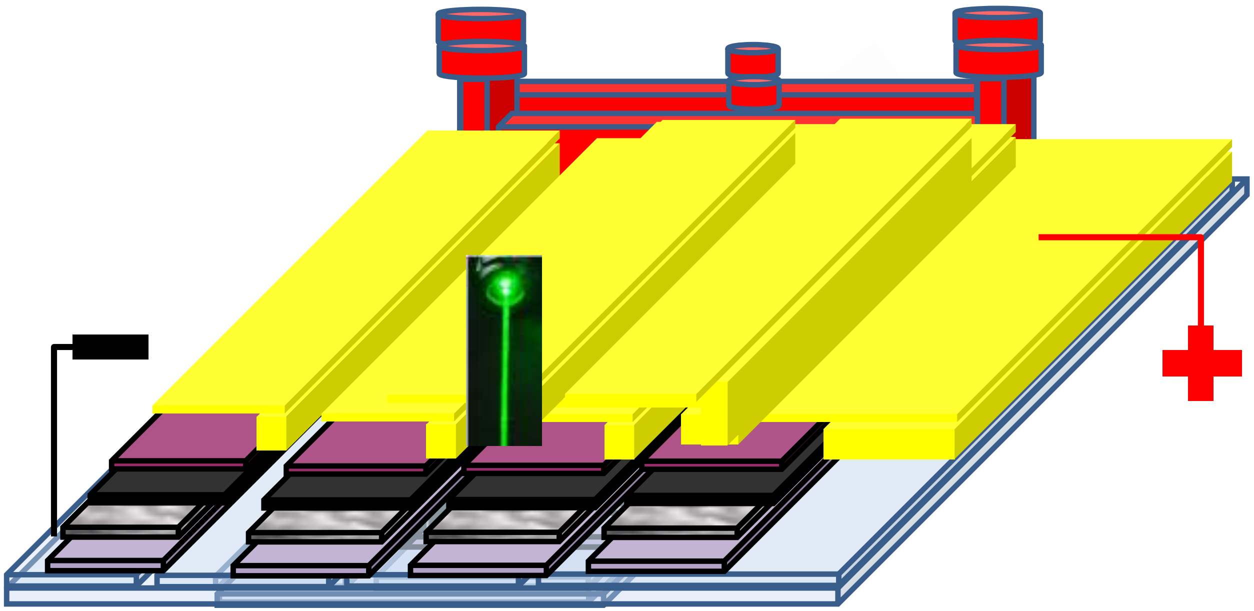


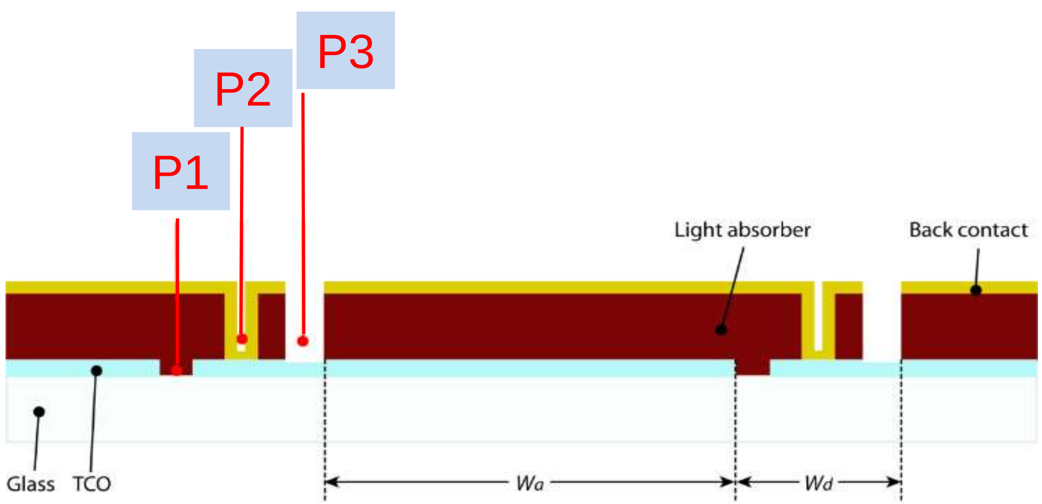
Scaling up to large area modules

Let's get real power from the sun !



Large area module realization





FTO P1 Laser- scribing

G+c-TiO_2- Spray Pirolysis

G+mTiO_2- Blade Coating (screen printing, spin coating)

Perovskite-blade coating (spin coating, slot dye coating)

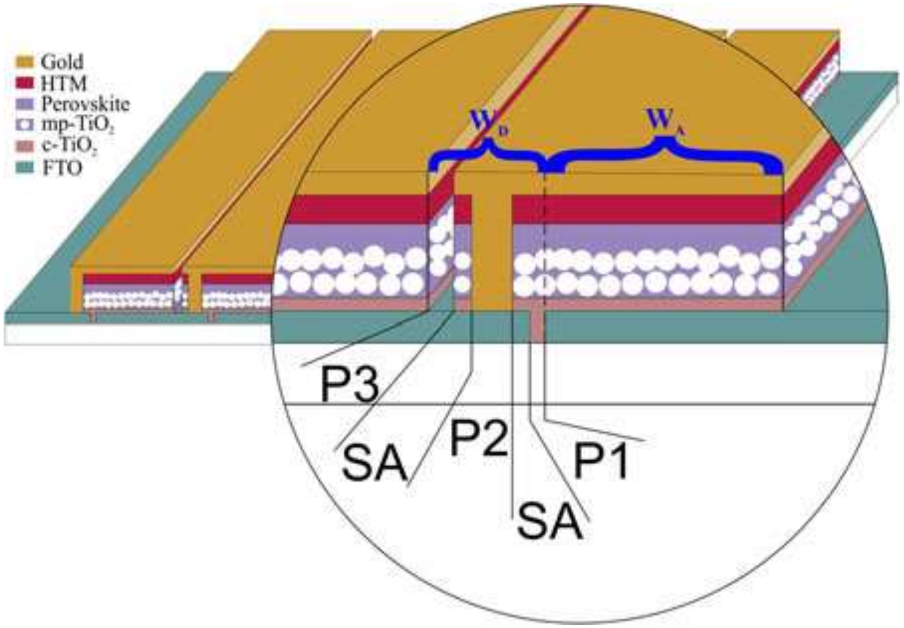
MoS_2+Spiro-MeOTAD- Blade Coating (spin coating)

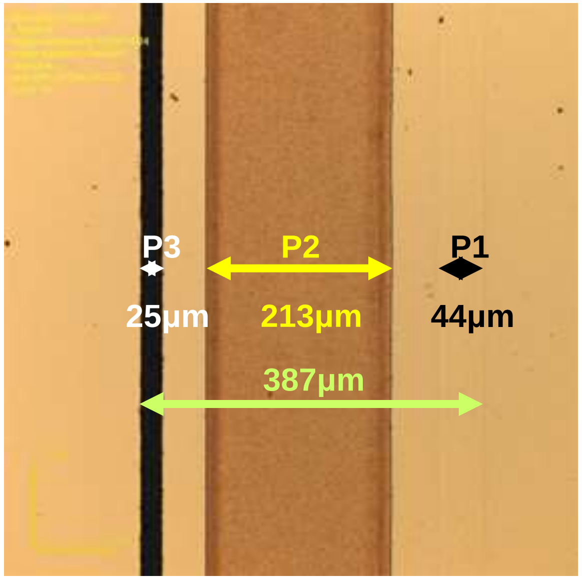
P2 Laser- scribing

Gold- Thermal Evaporation

P3 Laser- scribing

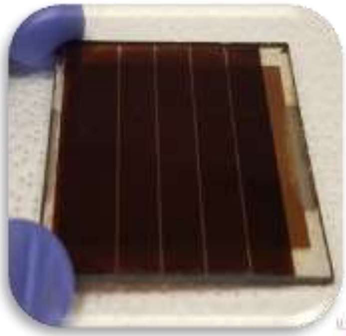
Improved P1 P2 P3 process AR=95%





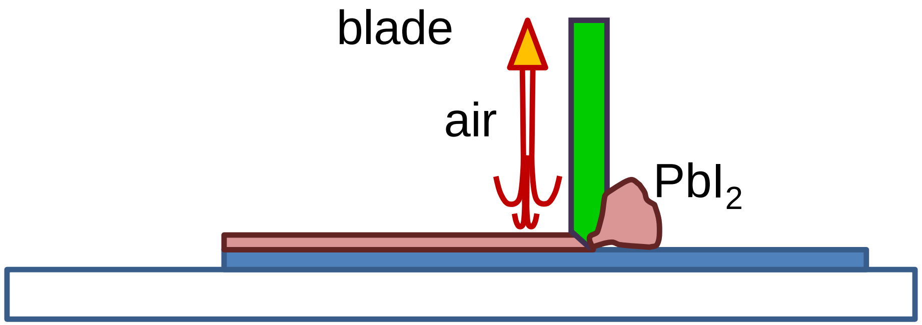
P1: Nd:YVO_4, **λ=1064 nm**, 15 ns pulsed laser on FTO 44 µm wide scribing
P2: Nd:YVO_4, **λ=355 nm**, 10 ps pulsed laser on TiO_2/PSK/HTM 213 µm wide etching
P3: Nd:YVO_4, **λ=532 nm**, 10 ps pulsed, 25 µm wide scribing

Active Area: 14.52 cm^2 Aperture Area: 15.28 cm^2
Aspect Ratio: 95% PCE = 9.5%
Aperture PCE = 9.03%

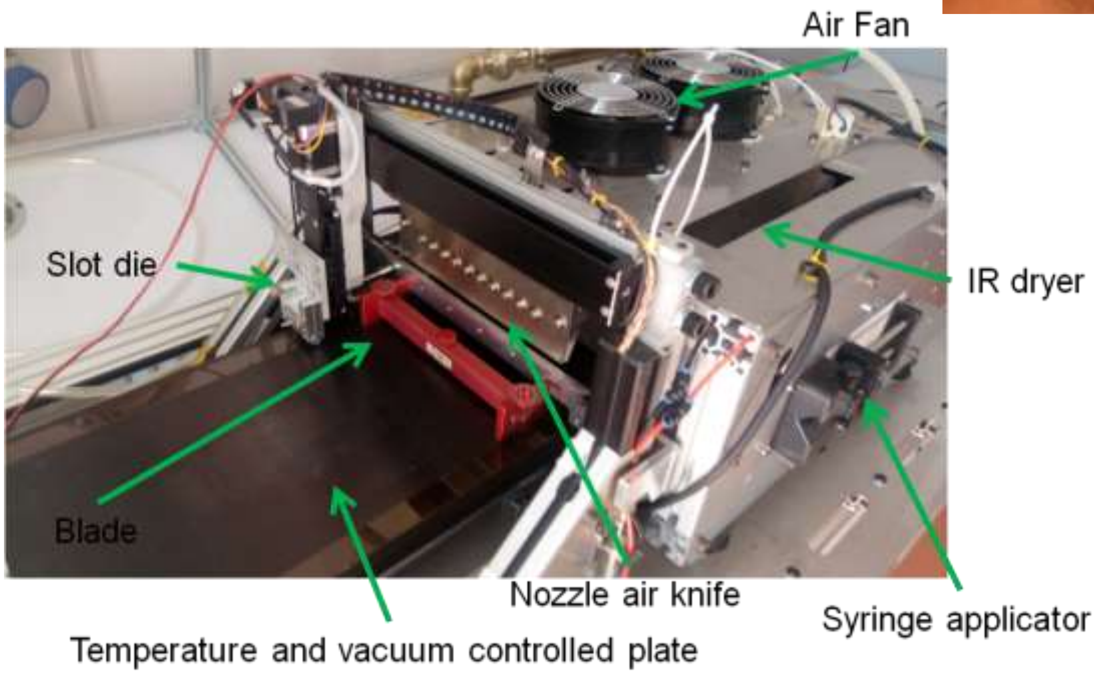


A. L. Palma et al. IEEE J. Photovoltaics 2017 DOI 10.1109/JPHOTOV.2017.2732223

Gas quencing blade coating



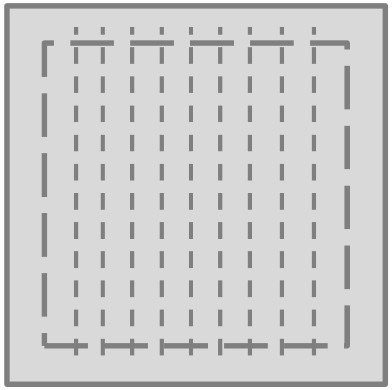
S. Razza, F. Di Giacomo et al. J. Power sources 277, 286 (2015)



cicci research

Compact automated blade/slot-die with Gas quenching, thermal annealing via substrate and/or IR lamp.

Perovskite Solar Modules - CHARON



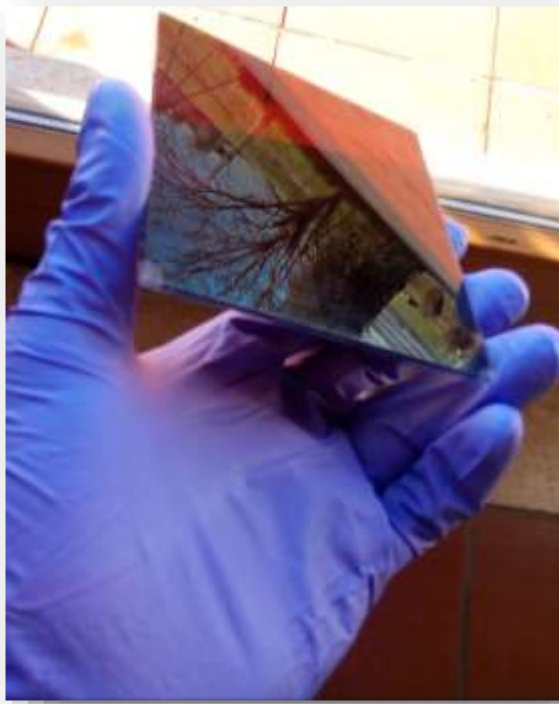
10 cm

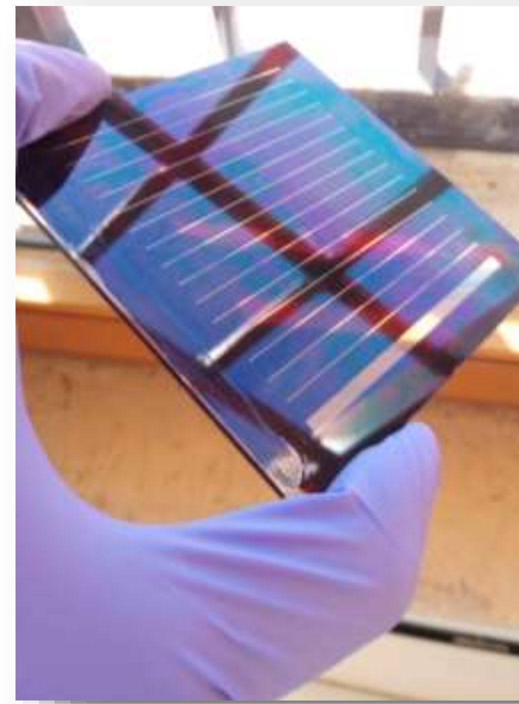
10 cm

Layout
Glass 10x10 cm^2
Module 7x8 cm^2
15 cell 3.1 cm^2 each

Materials
c-TiO_2 BL
diluted 30NRD mp-TiO_2
MAPI PSK
Spiro-OMeTAD
Gold

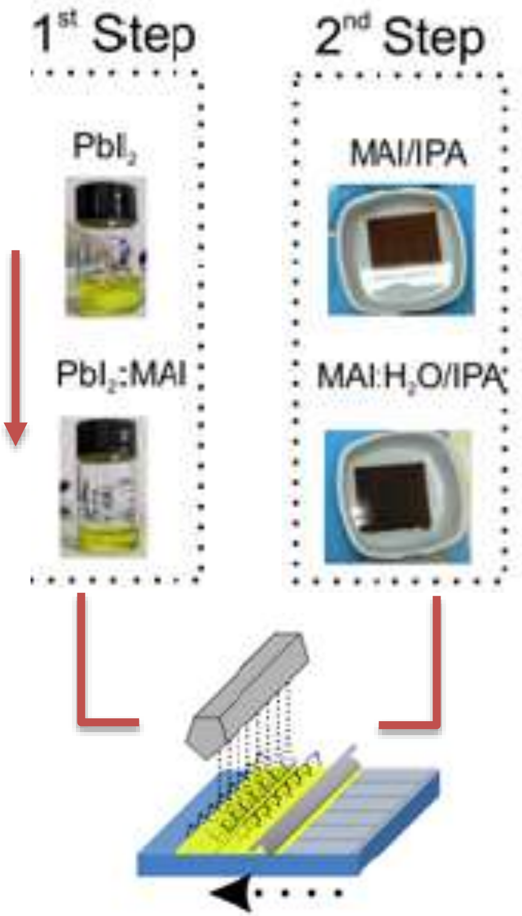
Process
- **P1 laser**
- Substrate cleaning
- Bladed mp-TiO_2
- Bladed PbI_2
- MAI dipping
- Bladed Spiro
- **P2 laser**
- Gold evaporation
- **P3 laser**



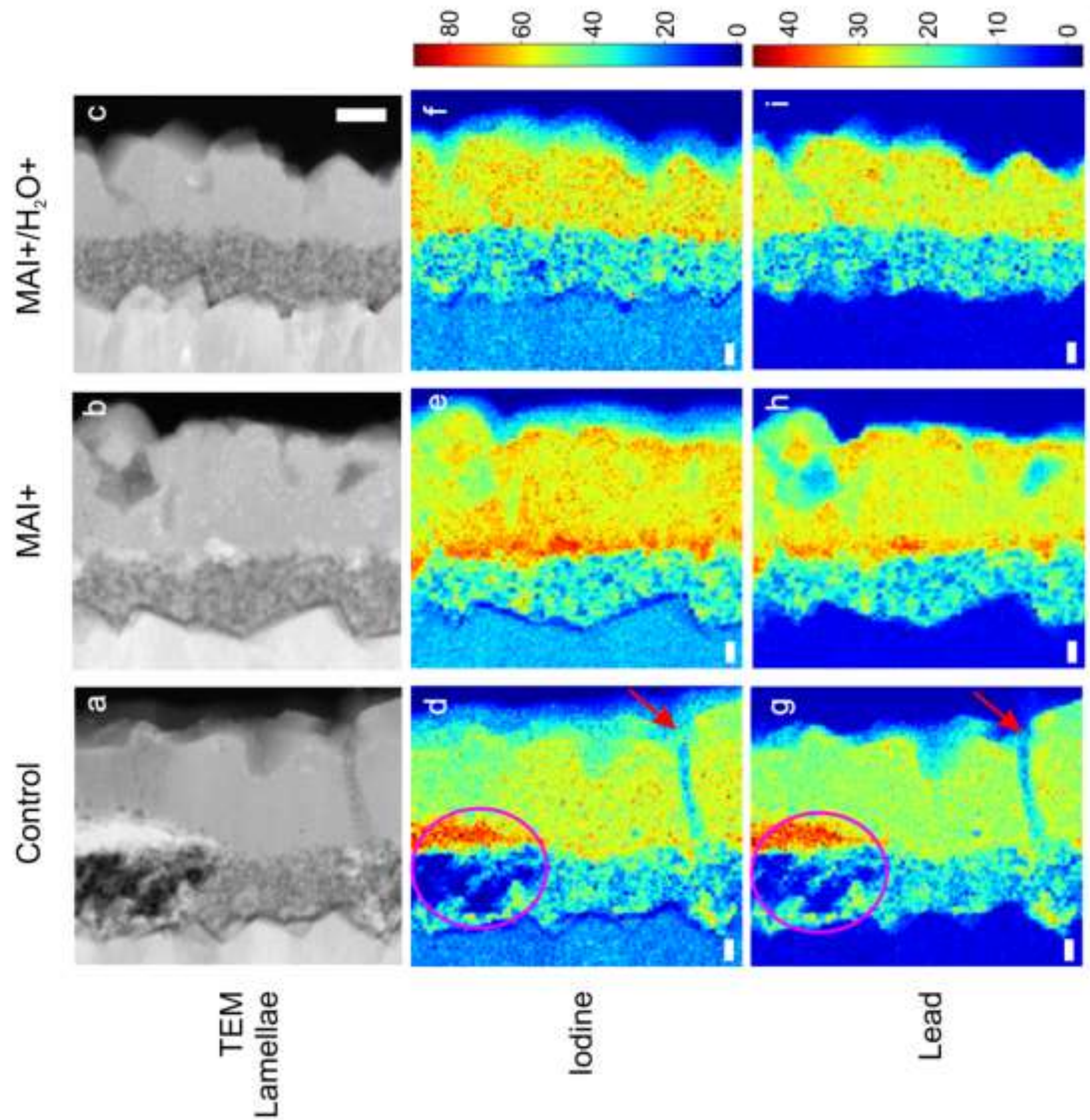


F. Matteocci et al. ACS Applied Materials & Interfaces (2019) 11, 25195

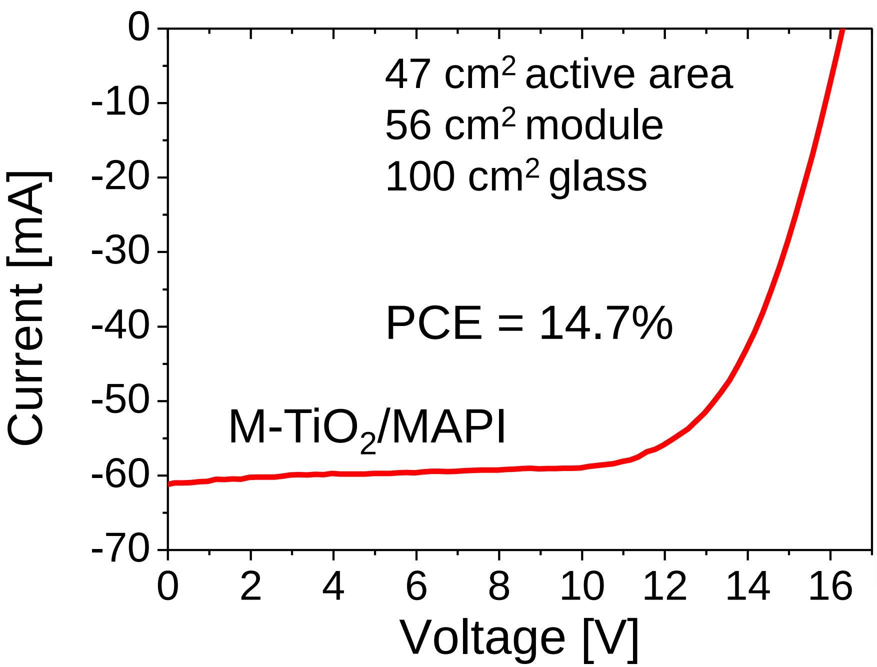
Two-step deposition optimization

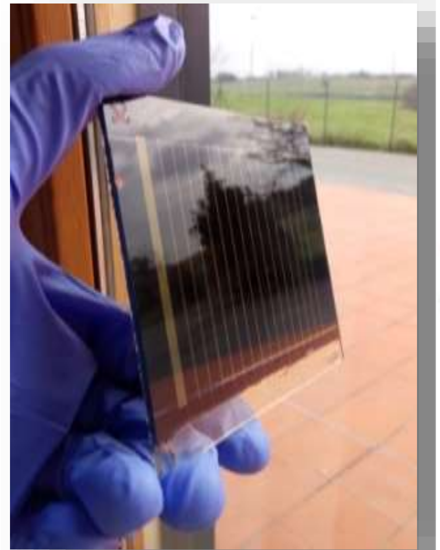


Development of the PbI_2 deposition technique by air-jet assisted blade coating

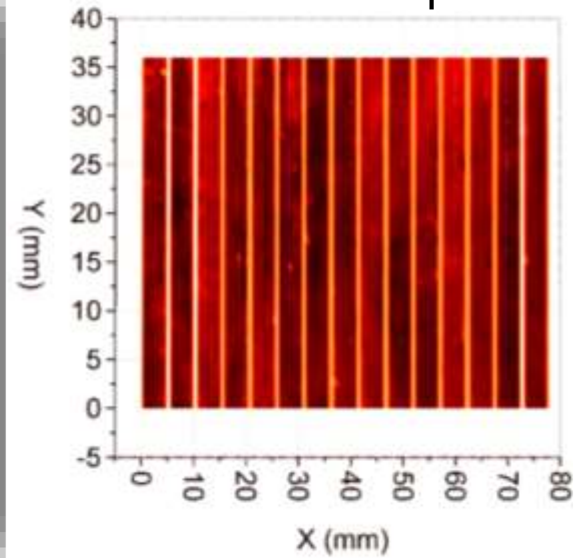


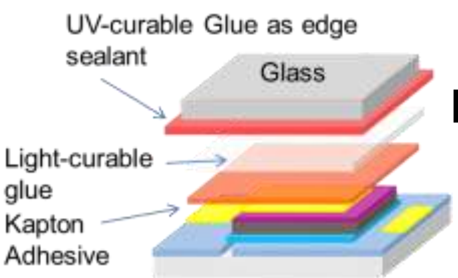
Perovskite Solar Modules - CHARON





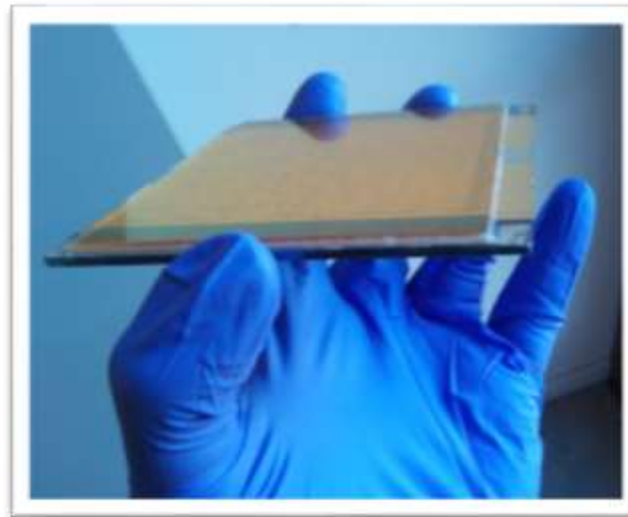
LBIC map





Encapsulation with Glass/Kapton

F. Matteocci Nano Energy 30, 162-172 (2016)



Low temperature with SnO_2 gives 14%

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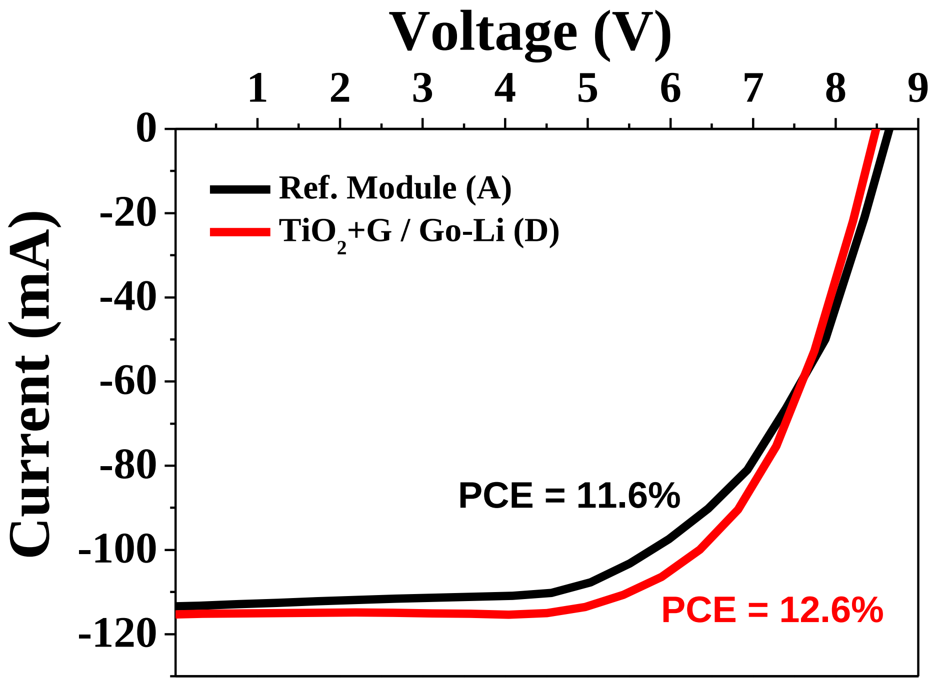
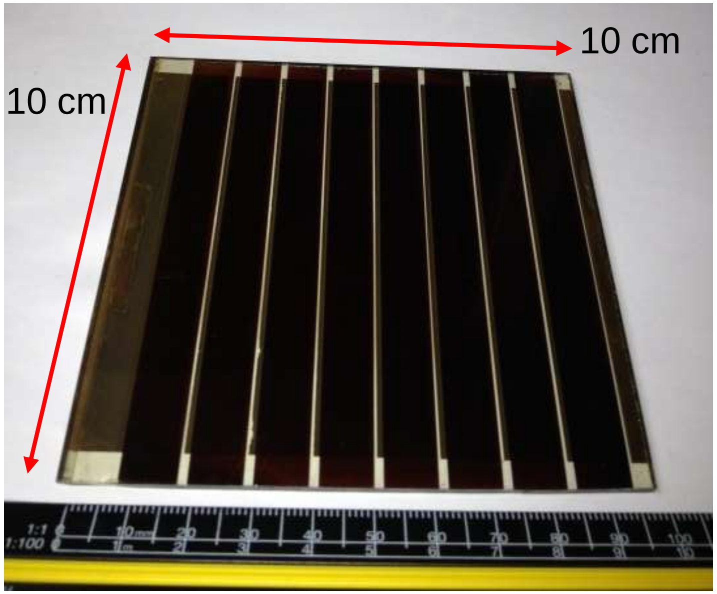
Graphene based module



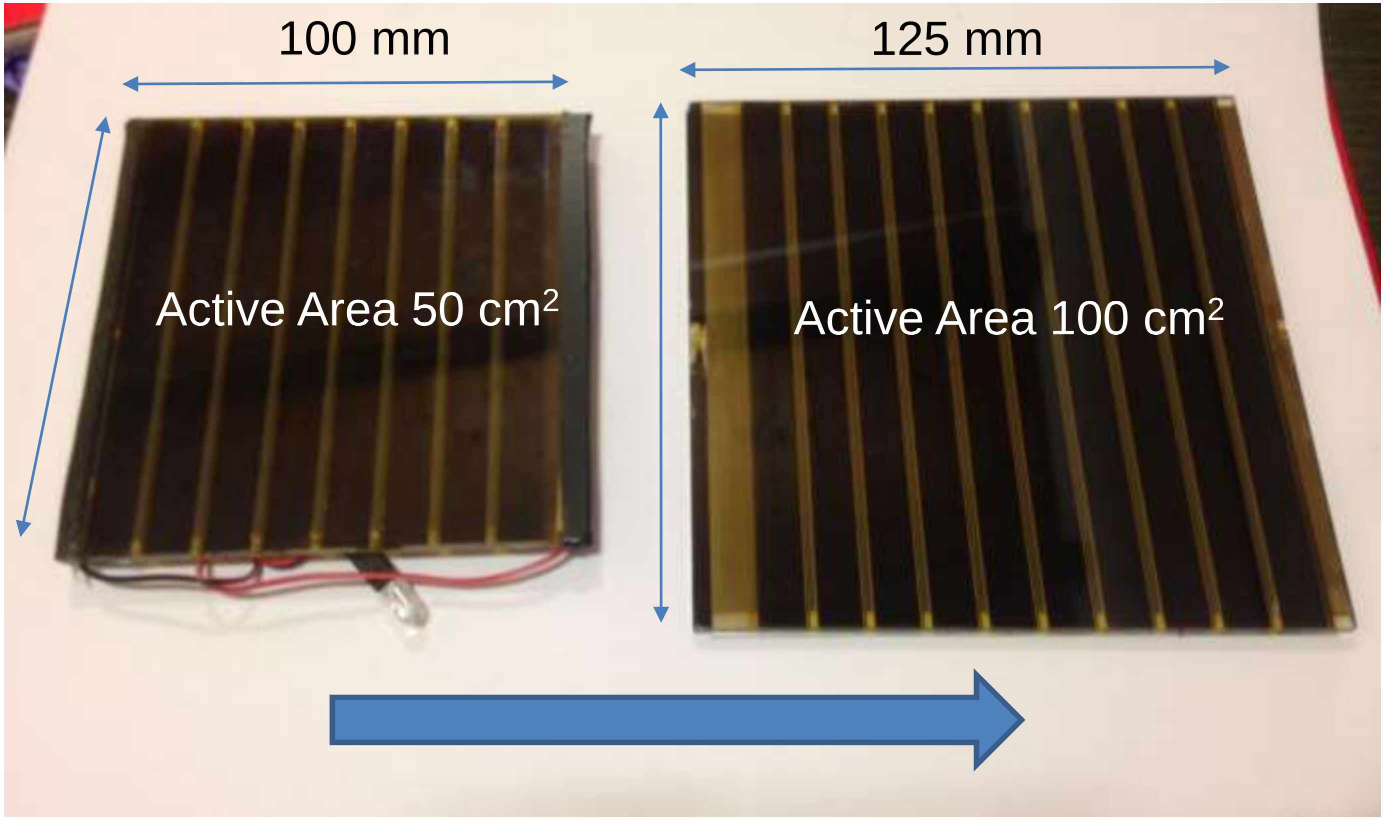
1 SUN illumination condition
50 cm^2 active area



Module type	Electrical parameters				
	V_{OC} (V)	I (mA)	FF (%)	PCE(%)	ΔPCE(%)
Ref	8.72	-112.8	59.4	11.6	-
$mTiO_2$+G	8.23	-118.1	62.4	11.9	+3%
$mTiO_2$/GOLi	8.46	-121.6	61.4	12.5	+8%
$mTiO_2$+G/GOLi	8.6	-114.8	64.6	12.6	+9%

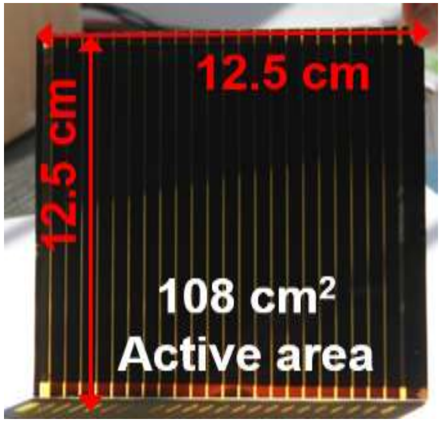
A. Agresti et al. ACS Energy Lett. 2017, 2, 279−287

Scaling up Graphene/Perovskite module

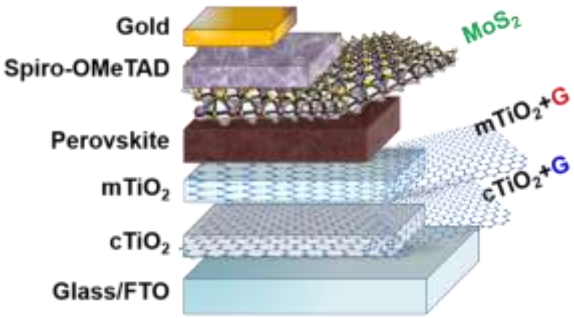


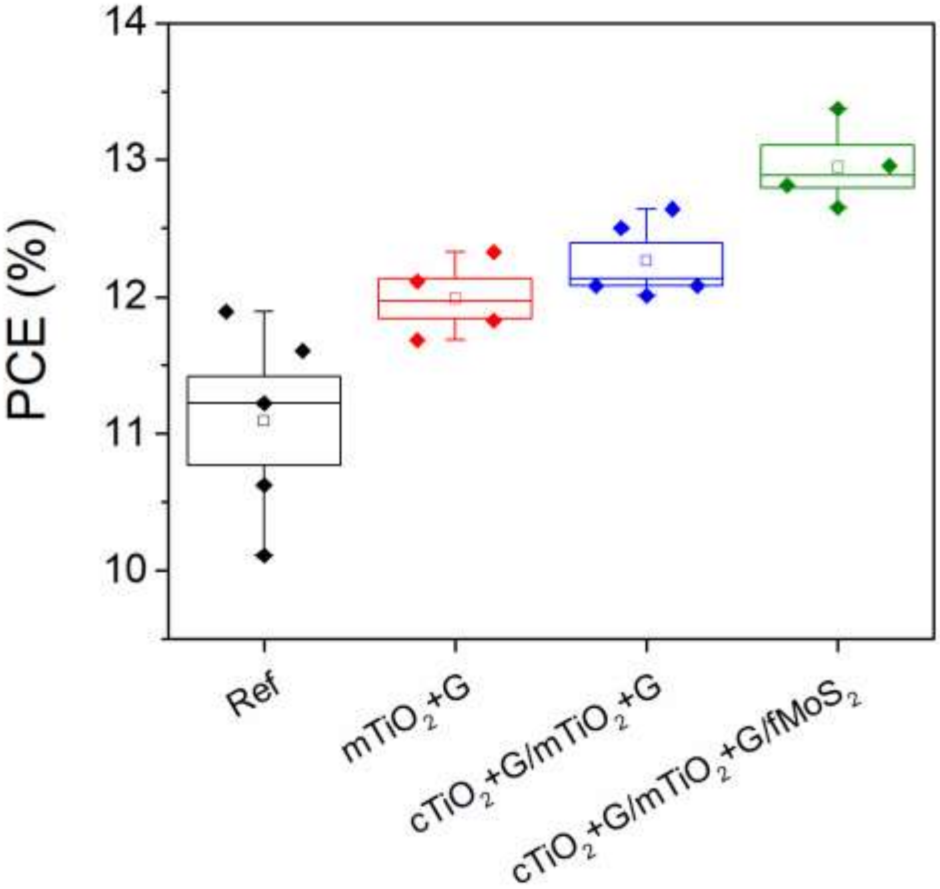
2D/Perovskite modules scaling-up

Max Efficiency=13.4%



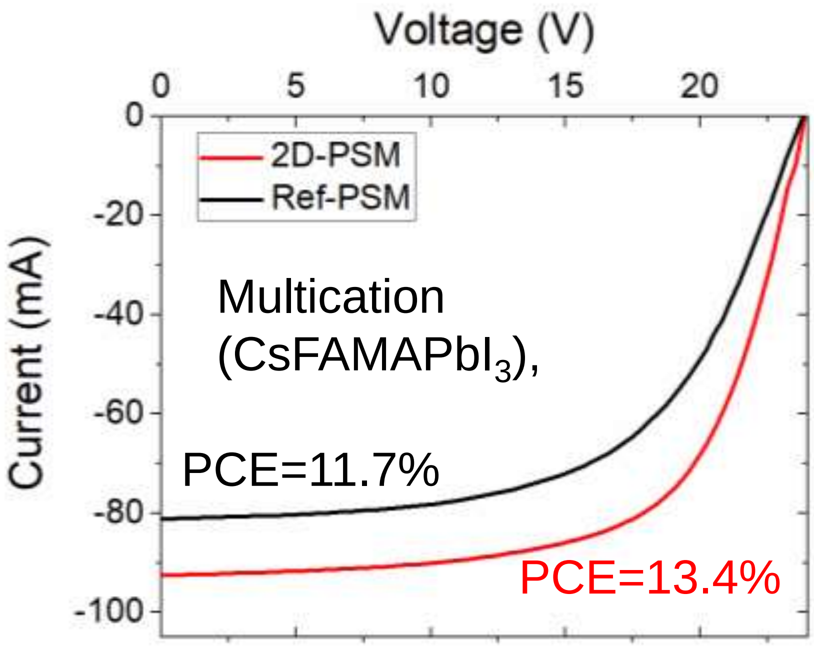
12.6% → 13.4%

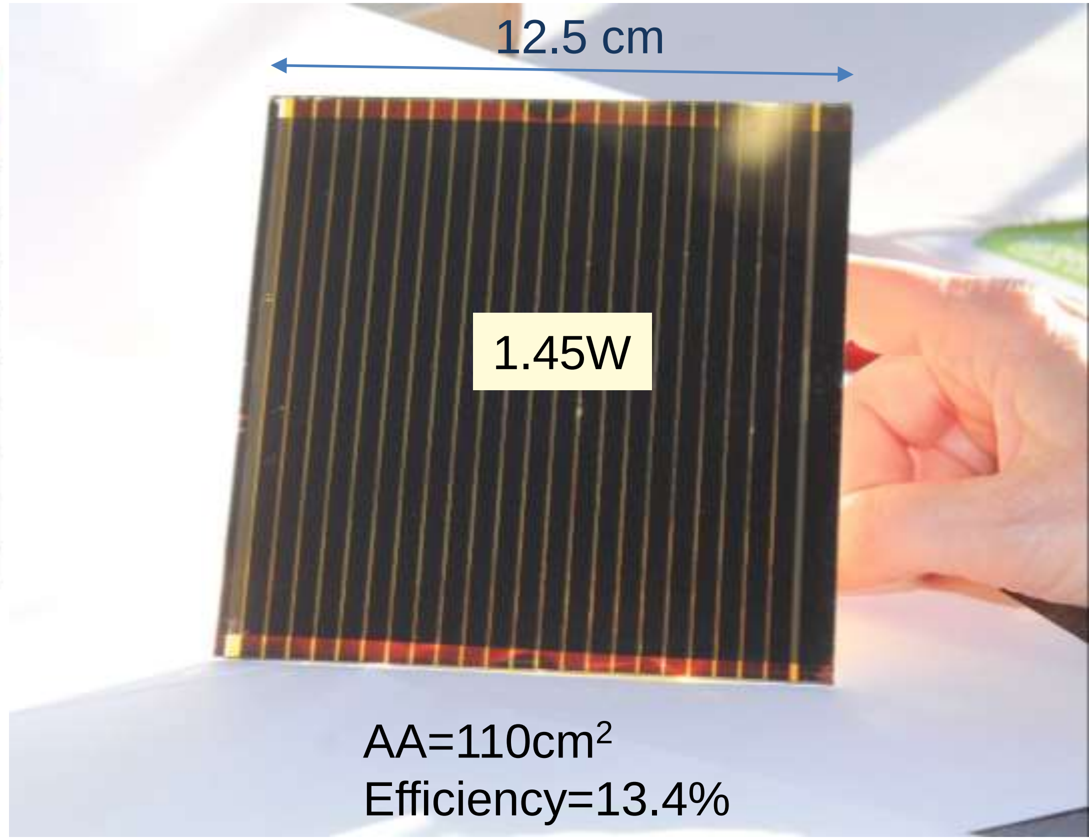


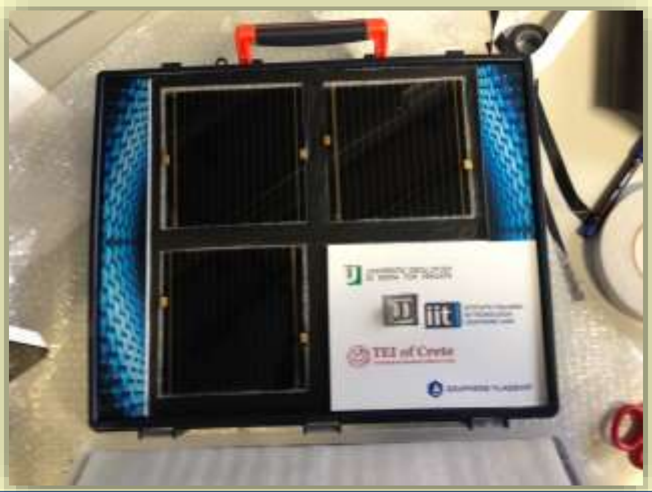


A. Agresti et al. ACS Energy Lett. (2019) 48, 1862

Graphene/Perovskite module (2018)







World Mobile Congress 2018
Mobile charger up to 10 smartphones

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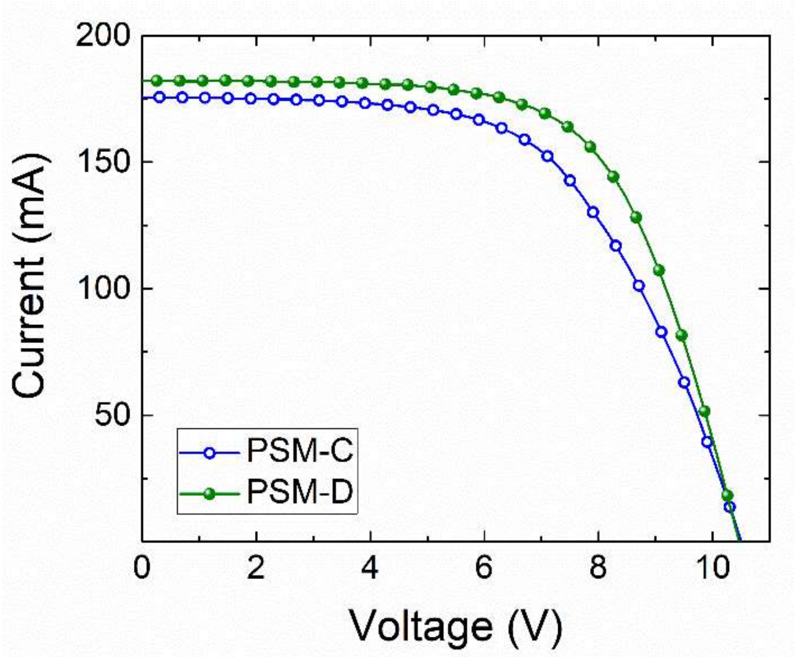
82cm2 module with 15.27% efficiency



I−V characteristics of tested modules (active area 82 cm^2, substrate area 12.5×12.5 cm^2, ten series-connected solar cells.)

	V_{OC} (V)	I_{SC} (mA)	FF (%)	η (%)
With 2D materials	10.46	180.53	65.08	15.27
Without 2D materials	10.46	173.78	60.09	13.56

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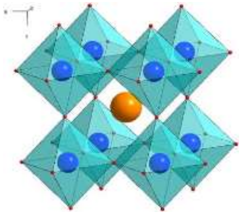
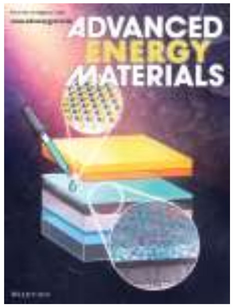
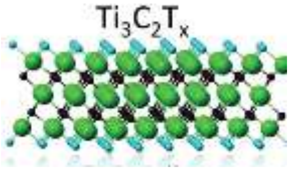
Conclusions



Graphene and related material are very effective for interface engineering in Perovskite Solar Cells.

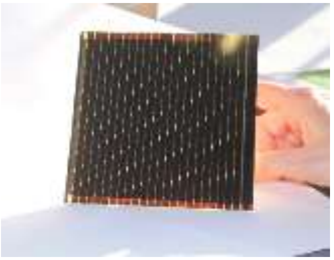


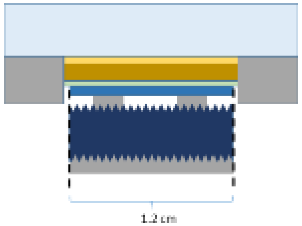
MoS_2 and **Graphene doped m-TiO_2** can be used to boost the efficiency of PSC exceeding 20 %.



MXenes a very promising class of 2D material for Work function and interface engineering in Perovskite solar cells.

The **graphene-based modules** (108 cm^2 active area) showed improved **PCE values up to 13.4%** and enlarged long-term stability.
PCE > 15% on 80 cm2





2D material rimproved the efficiency of mechanically stacked perovskite/silicon 2T tandem up fo 26.3& (25.9% stabilized)

Acknowledgments:

Funded by the European Union

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