Metal Halide Perovskites: a New Family of Semiconductors for Photovoltaics and Optoelectronics

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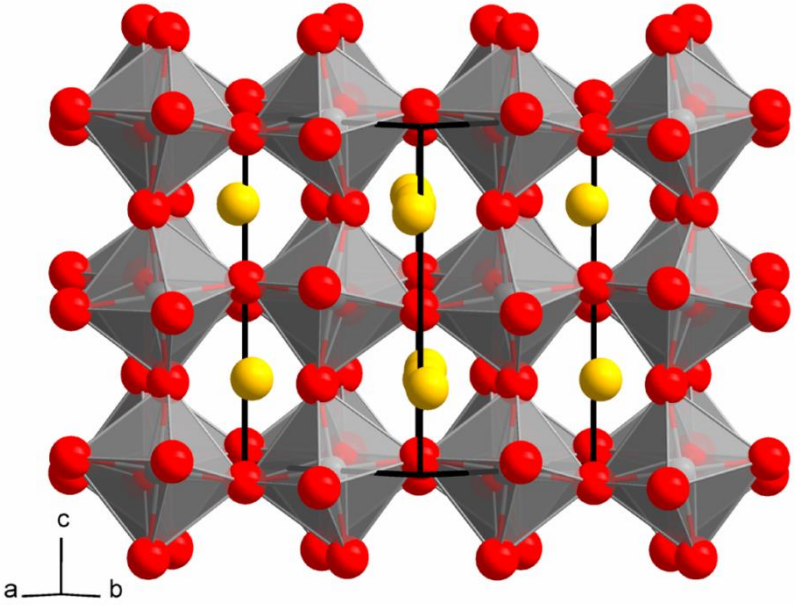
Photovoltaics and
Optoelectronic Devices Group

Perovskites

Perovskite is a **calcium titanium oxide**, with the chemical formula **$CaTiO_3$**. The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist **Count Lev Alekseevich Perovski** (1792–1856)."

All materials with the same crystal structure as $CaTiO_3$, namely **ABX_3**, are termed perovskites.



1892: 1st paper on lead halide perovskites

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Über die Cäsium- und Kalium-Bleihalogenide.

Von

H. L. Wells.[1]

Als Fortsetzung der in diesem Laboratorium[2] begonnenen Arbeit über Doppelhalogenide ist von den Herren G. F. Campbell, P. T. Walden und A. P. Wheeler eine Untersuchung über die Cäsium-Bleisalze unternommen worden. Diese Herren haben die Untersuchung mit vielem Eifer und Geschick durchgeführt, und es macht mir Freude, ihnen meinen Dank auszusprechen. Sie haben die Existenz folgender Salze konstatiert:

Cs_4PbCl_6	Cs_4PbBr_6	—
$CsPbCl_3$	$CsPbBr_3$[3]	$CsPbJ_3$
$CsPb_2Cl_5$	$CsPb_2Br_5$	—

Sheffield Scientific School, New Haven, Conn., Oktober 1892.

Structure deduced 1959:

Kongelige Danske Videnskabernes Selskab, Matematisk-Fysike Meddelelser (1959) 32, p1-p17

Author: **Moller, C.K**.

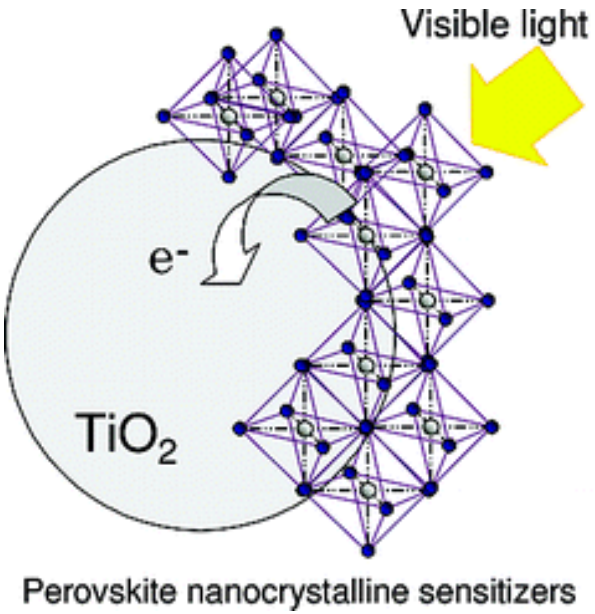
Title: The structure of cesium plumbo iodide Cs Pb I_3

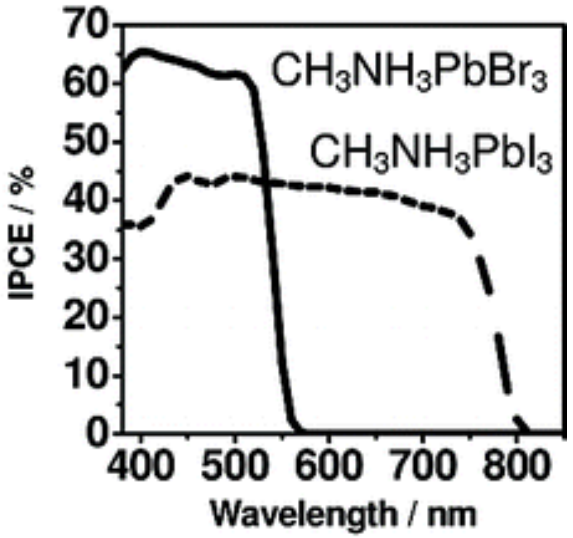
First Solar Cells

Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

Akihiro Kojima,[†] Kenjiro Teshima,[‡] Yasuo Shirai,[§] and Tsutomu Miyasaka*[,†,‡,∥]

J. AM. CHEM. SOC. 2009, *131*, 6050–6051





Perovskite solar cells

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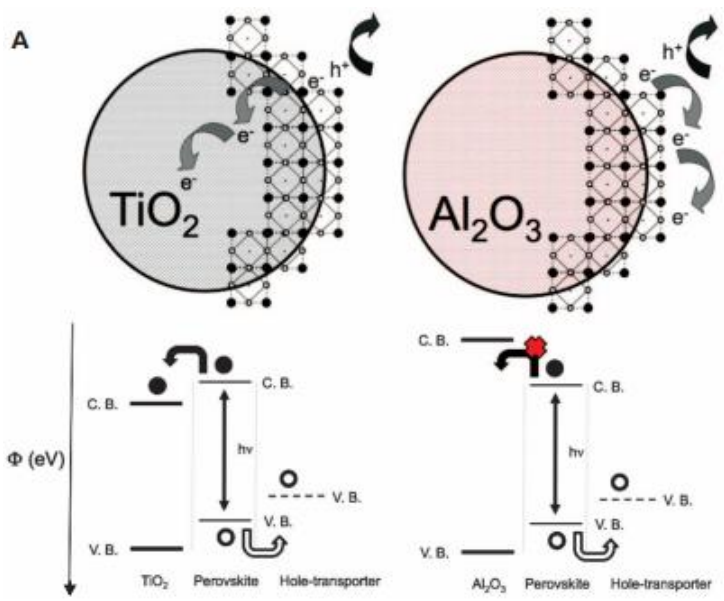
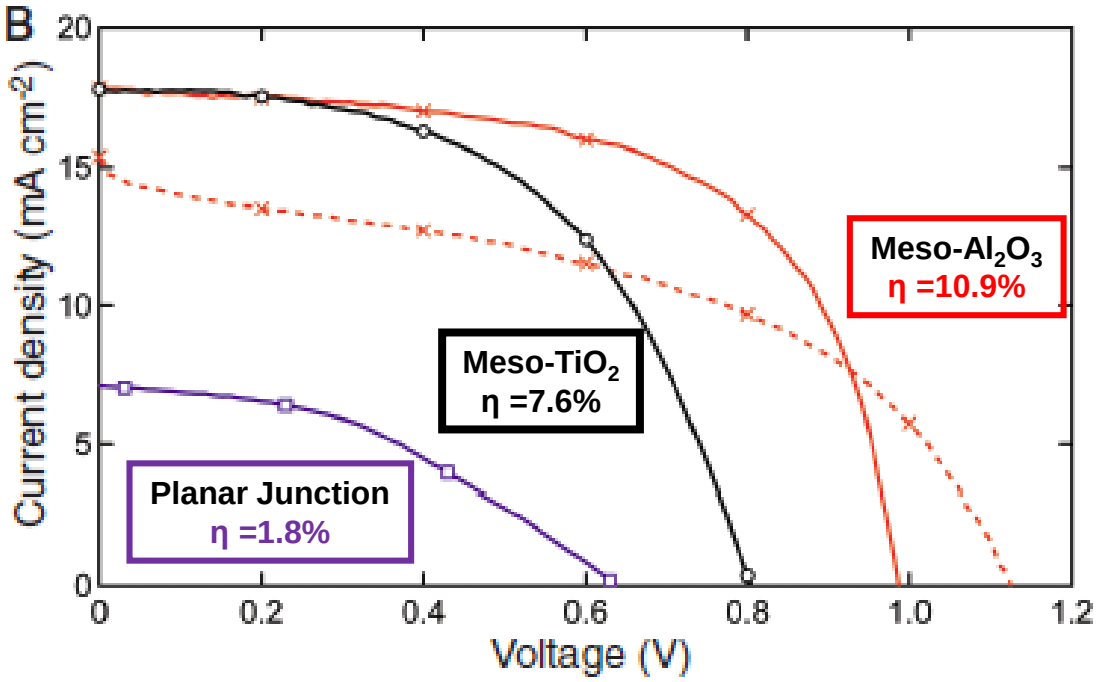
Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites

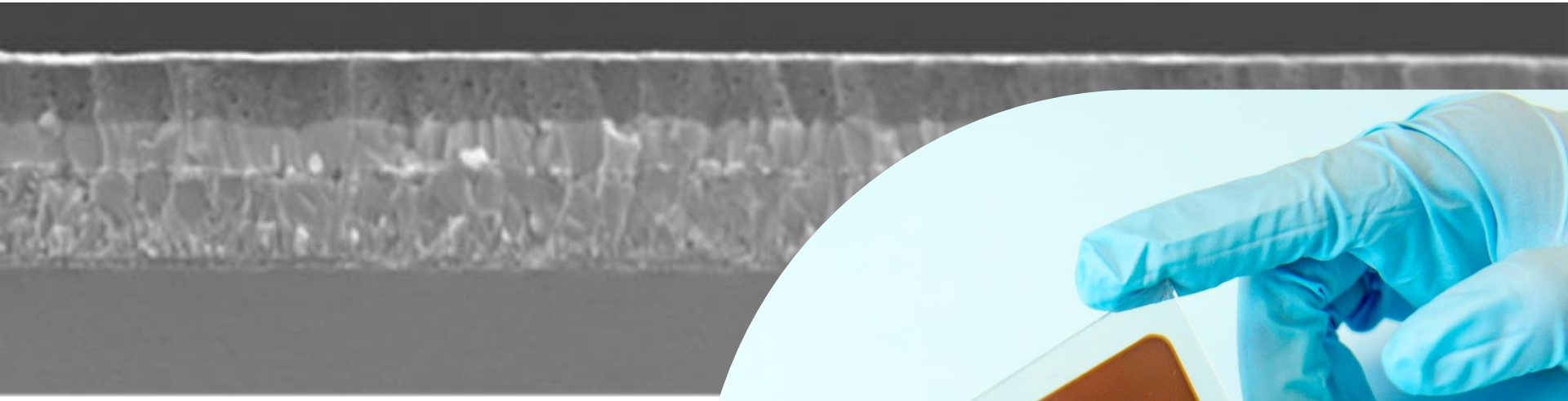
Michael M. Lee,[1] Joël Teuscher,[1] Tsutomu Miyasaka,[2] Takurou N. Murakami,[2,3] Henry J. Snaith[1]*

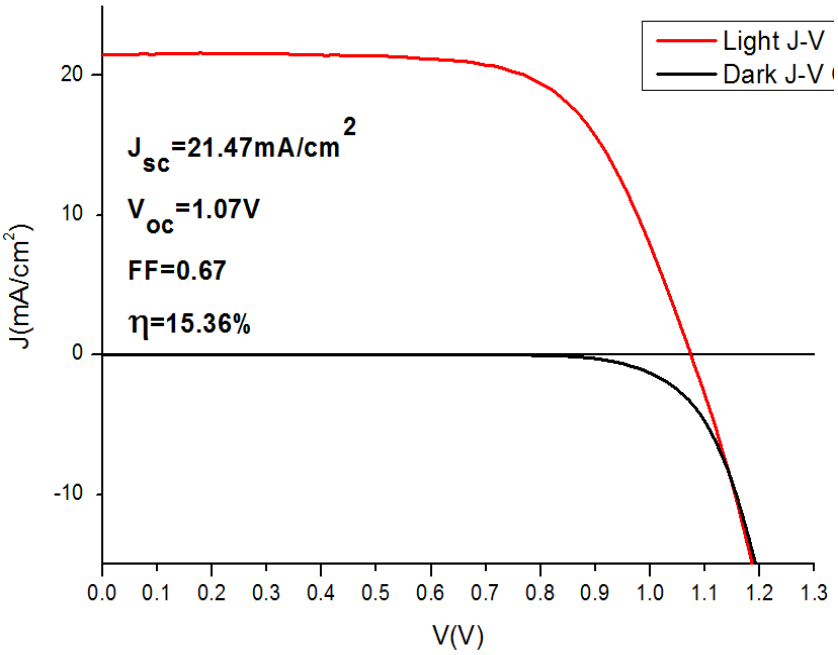
SCIENCE VOL 338 2 NOVEMBER 2012 643



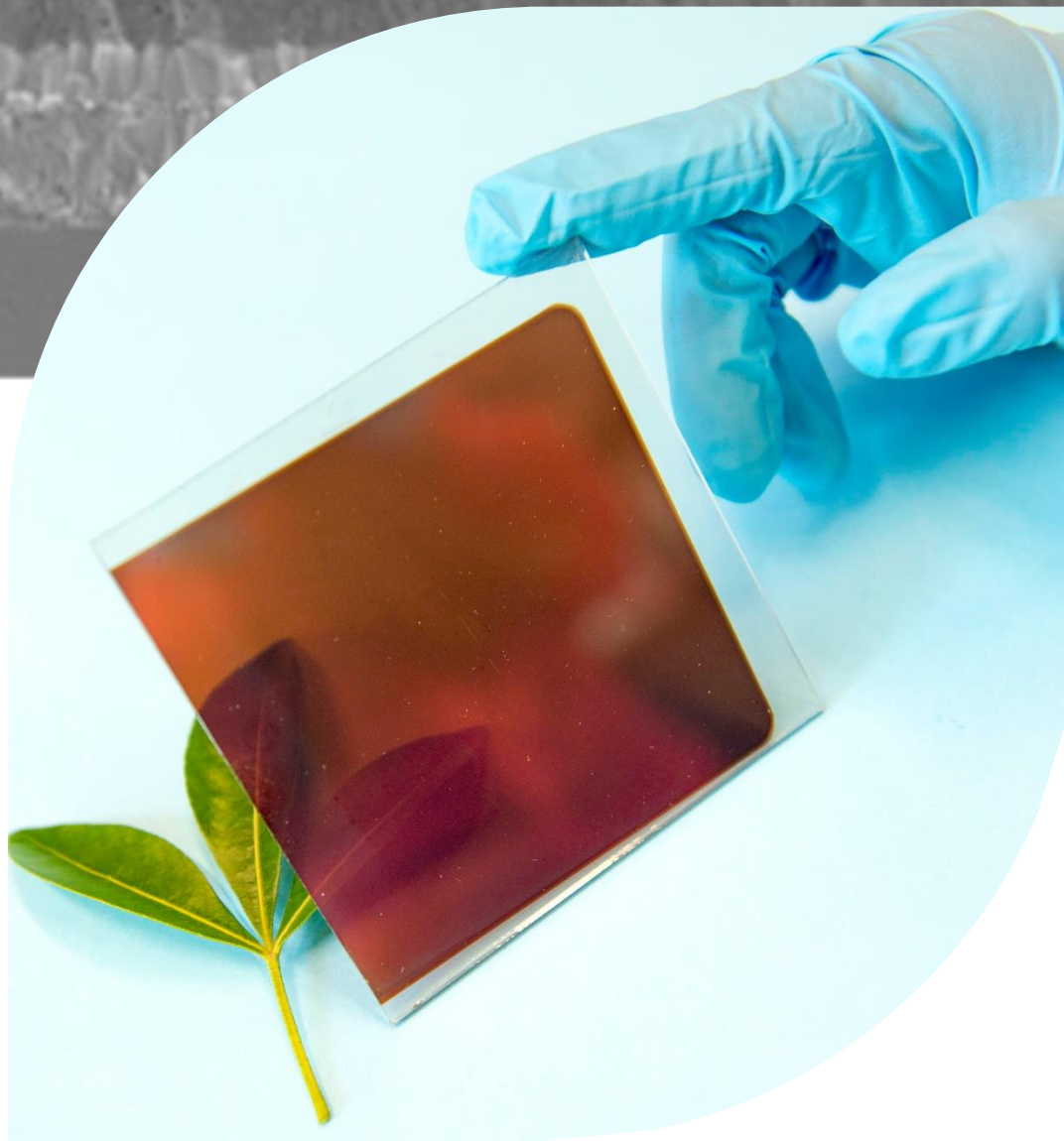


Efficient Planar Heterojunction Solar Cells

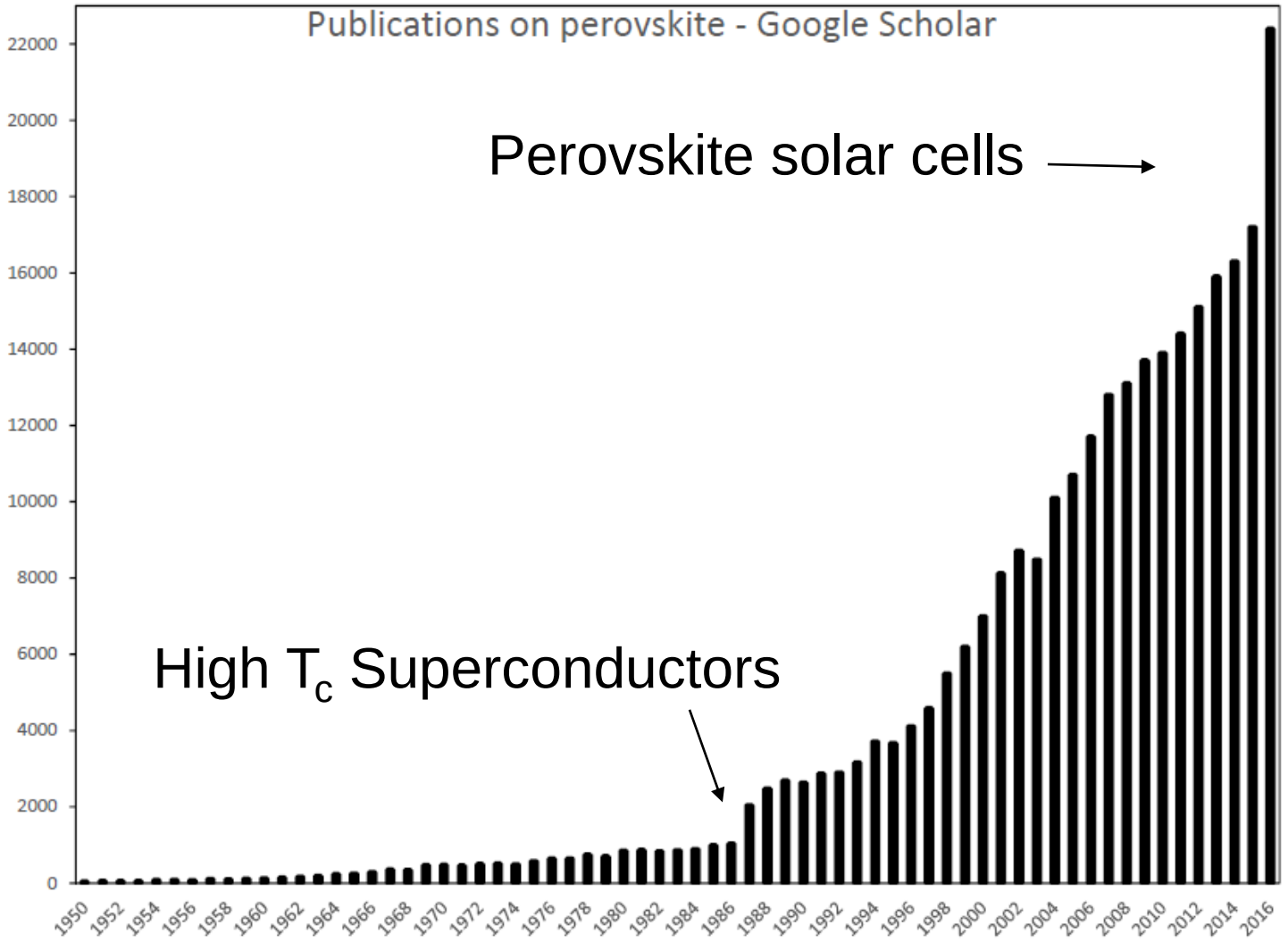




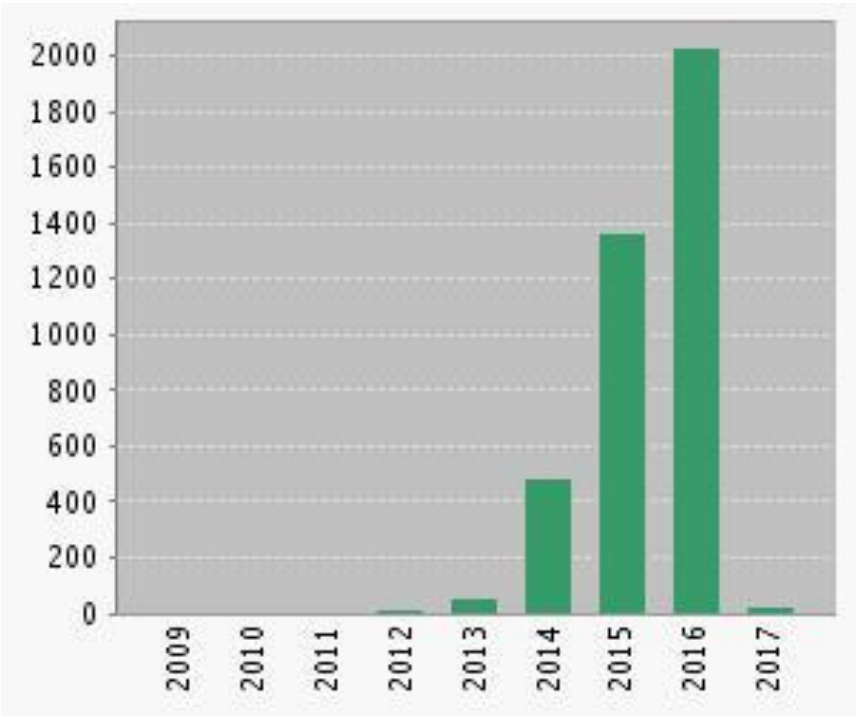
M. Liu et al. Nature 2013

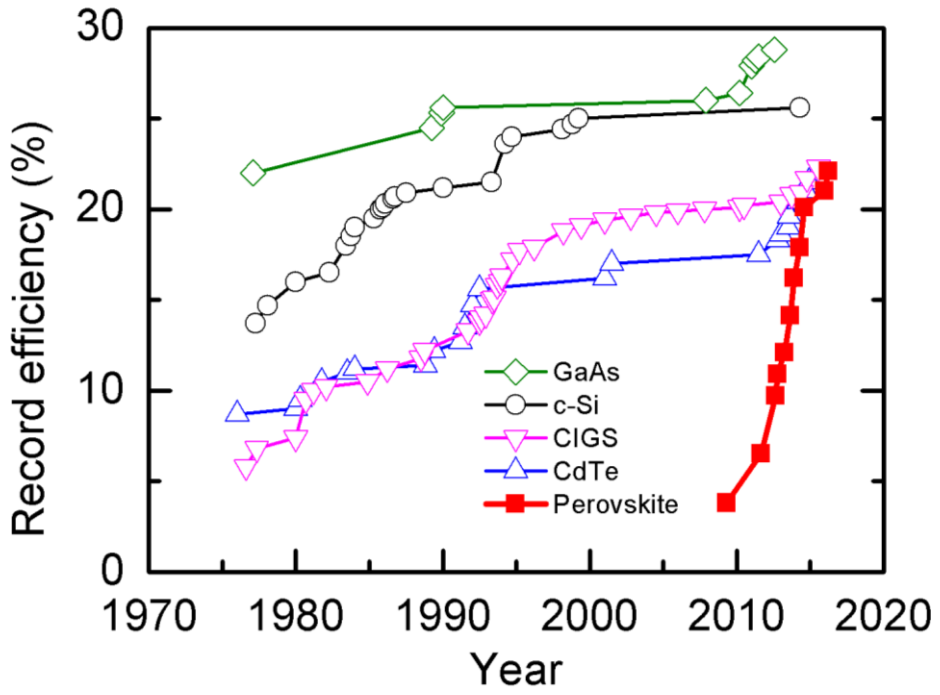


Publications on perovskites



Publications Vs Efficiency



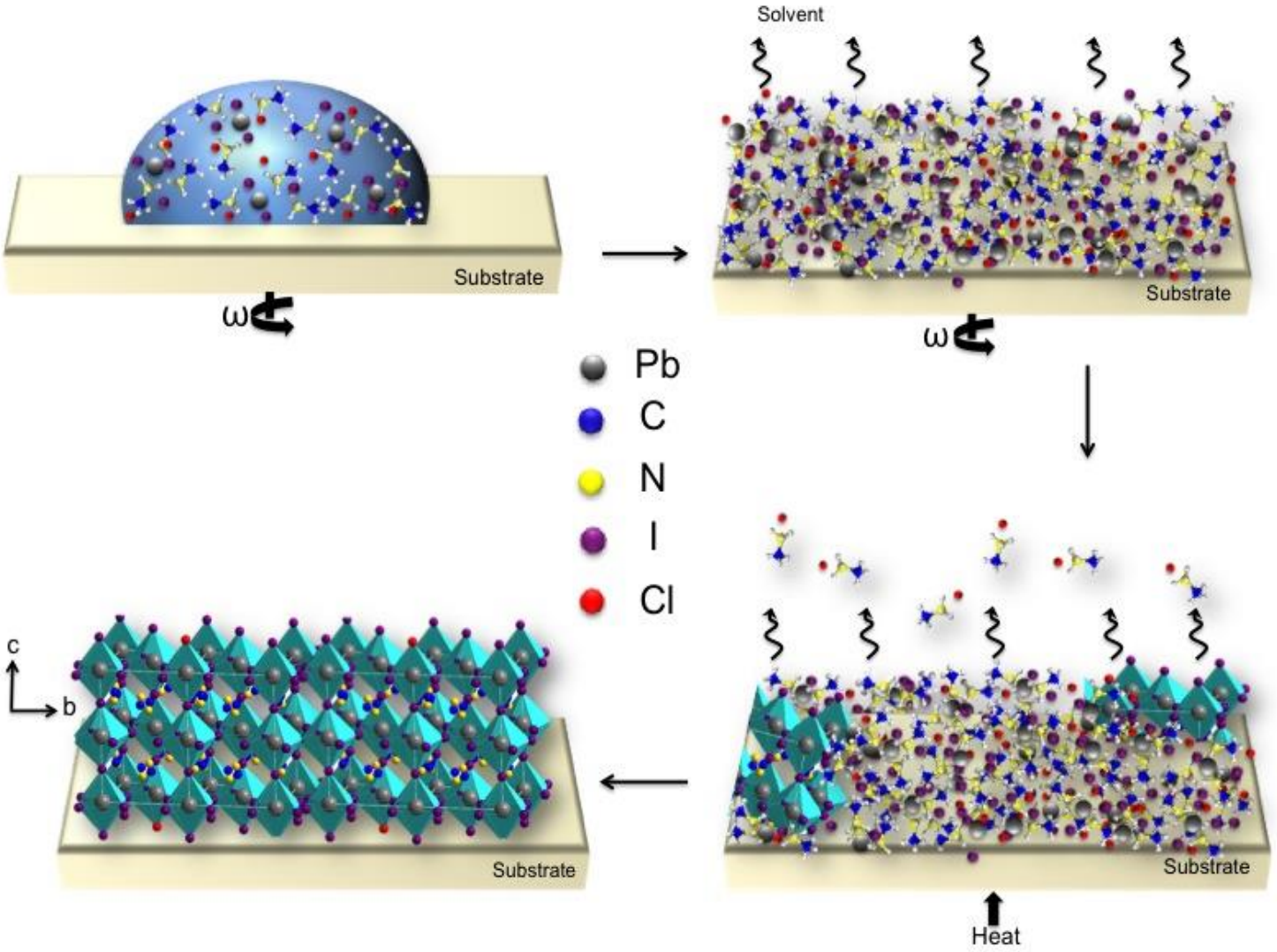


Perovskite Solar Cells

Crystallisation of Perovskite Thin Films

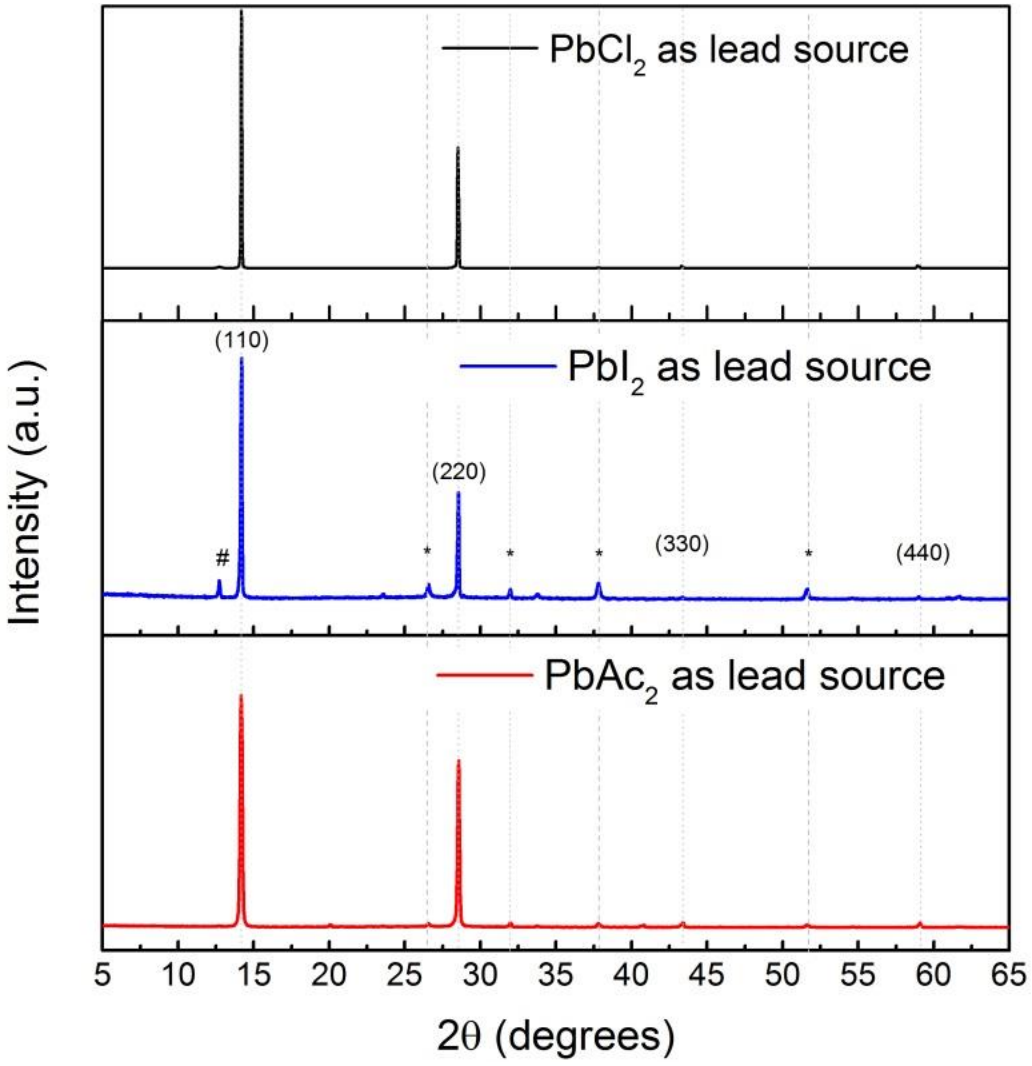
Crystallisation of perovskite thin films

$$PbX_2 + 3\ CH_3NH_3I \longrightarrow CH_3NH_3PbI_3 + 2\ CH_3NH_3X \quad (X = Cl, I, Ac)$$



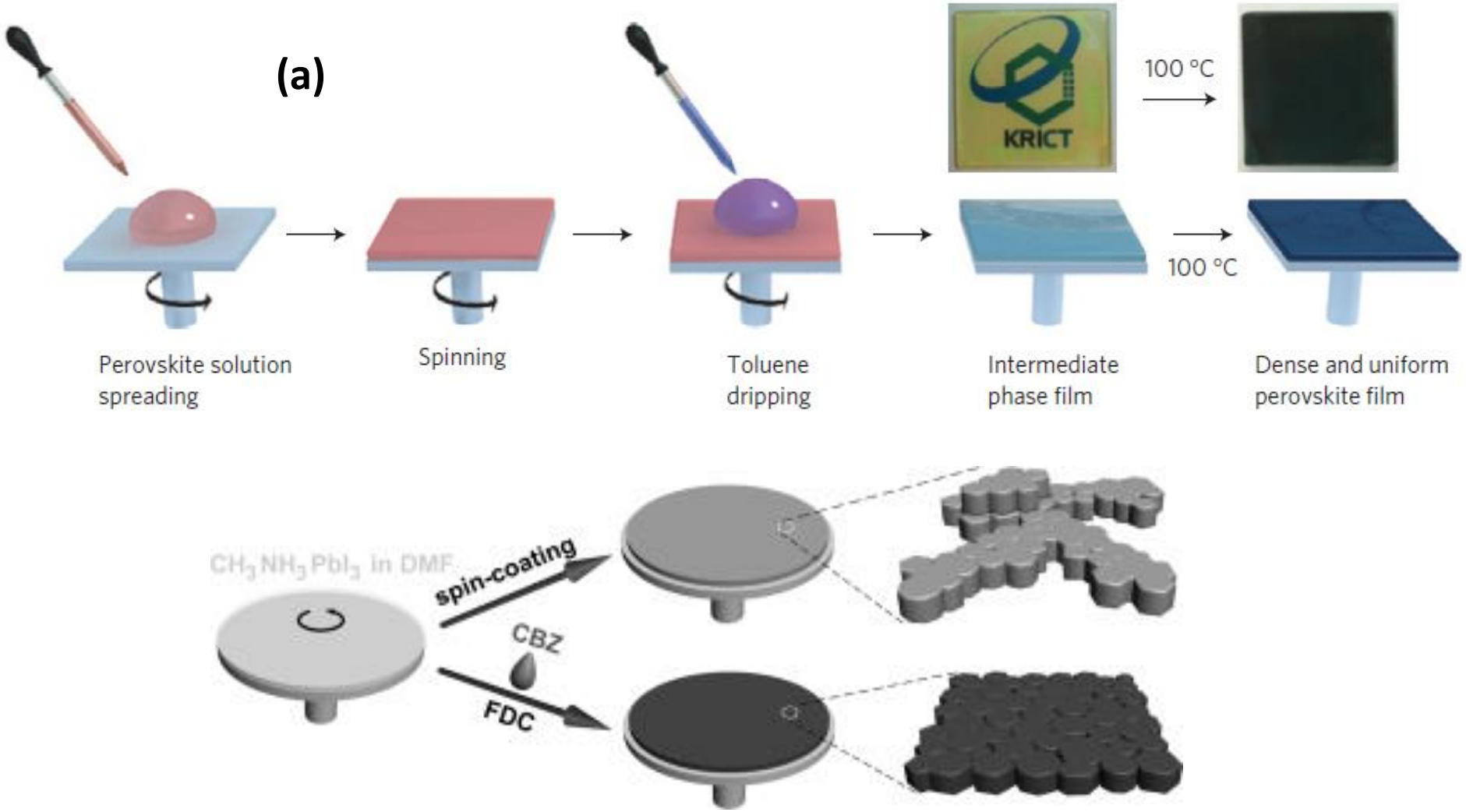
W. Zhang et al. 2014 Nature Communications

XRD



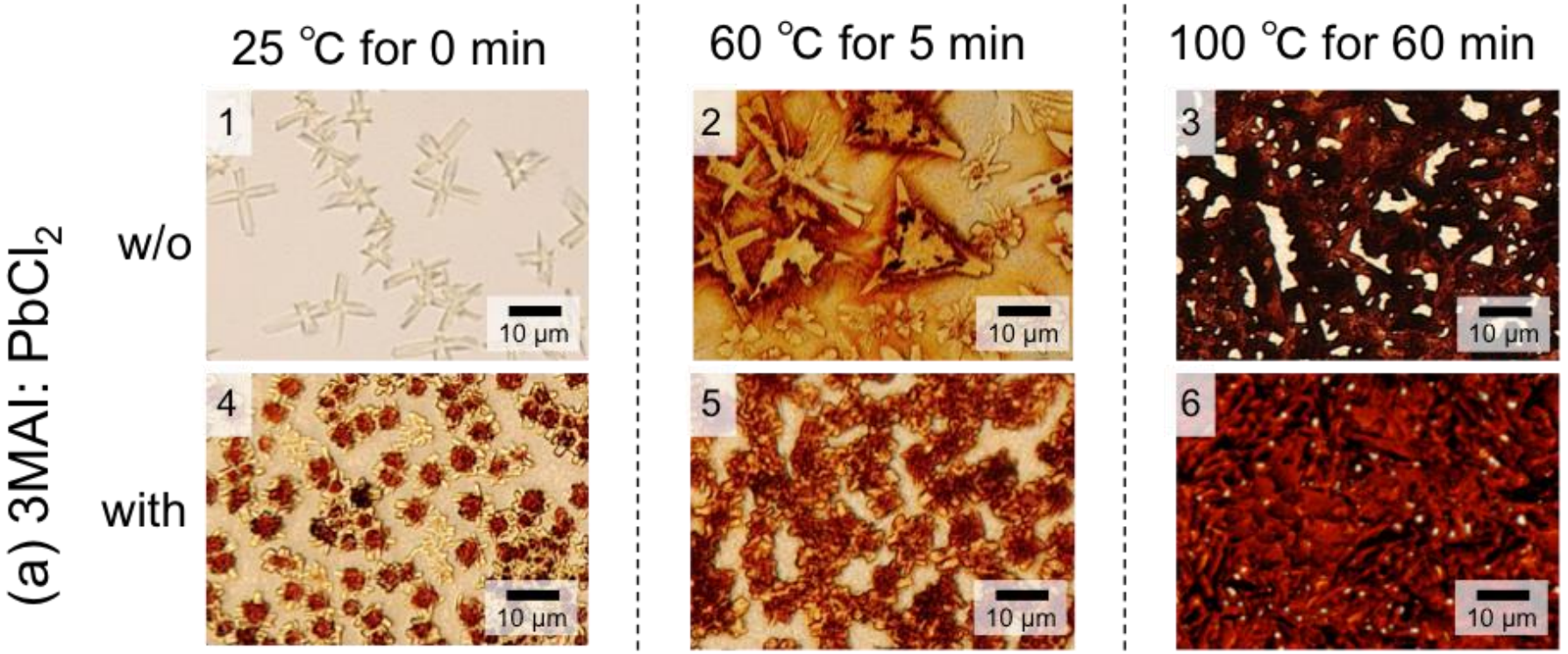
The more volatile the MAX component, the faster crystallisation occurs

“Anti-solvent” quenching crystallisation



Routes developed by Seok et al. and Spiccia et al.

Anti-solvent + Excess organic



Excess organic + excess PbI_2

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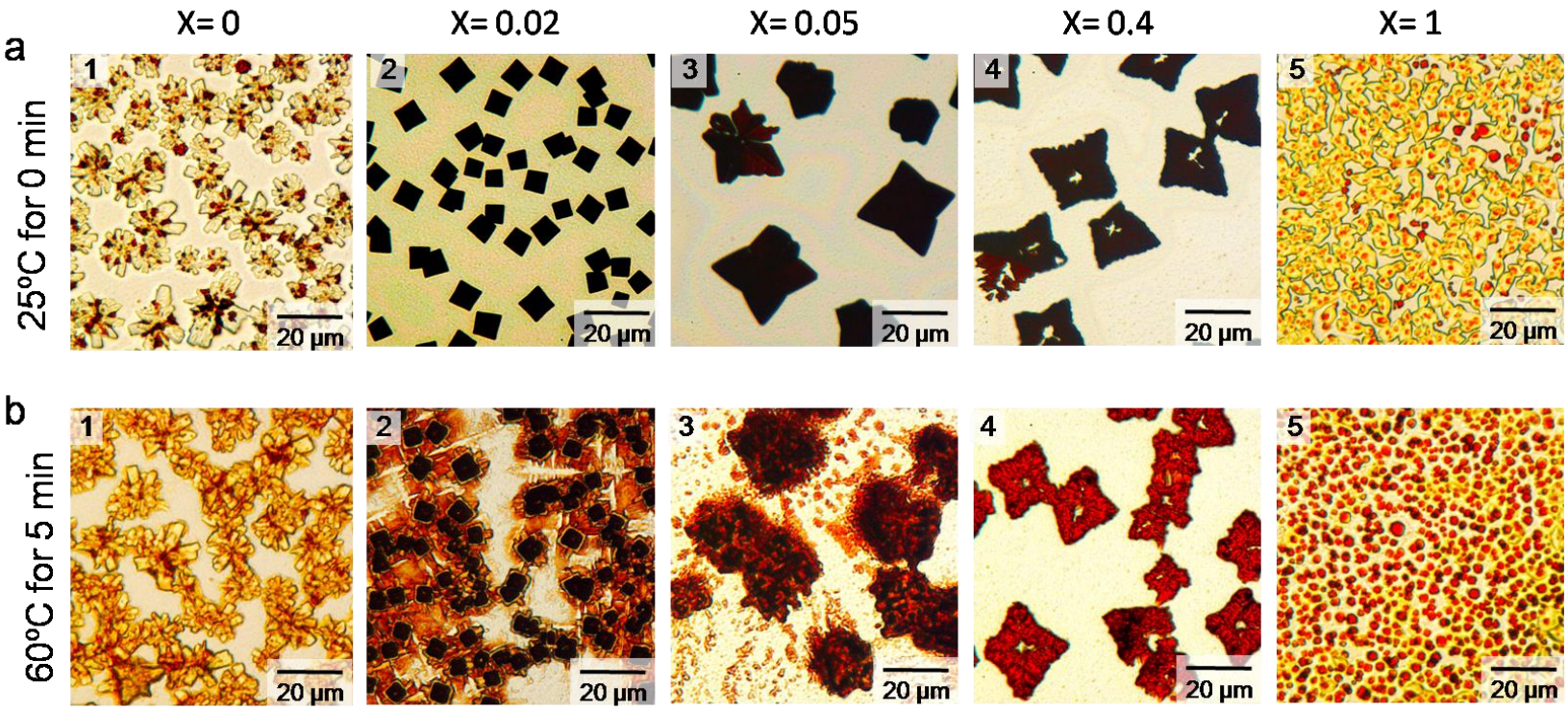
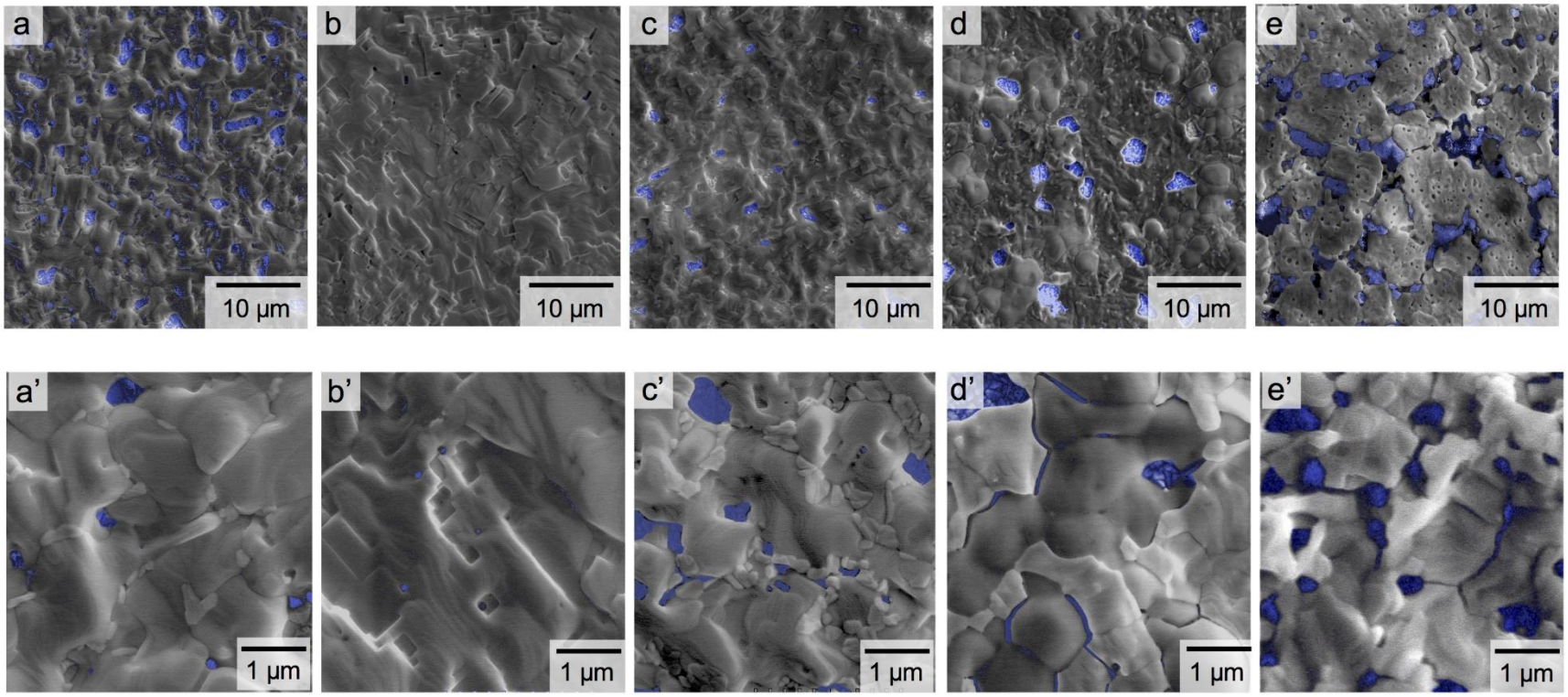
$3MAI:(PbCl_{(2-2x)}PbI_{(2x)})$



$3MAI:PbCl_2$ $2\%\ PbI_2$ $5\%\ PbI_2$ $40\%\ PbI_2$ $100\%\ PbI_2$

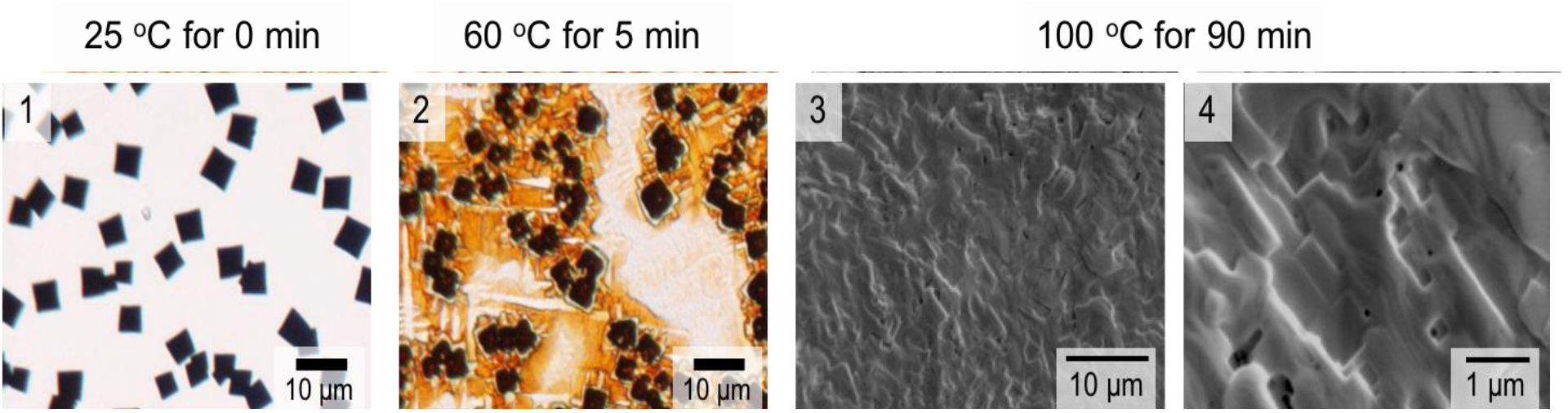
N. Saki et al. Small 2017 (in-press)

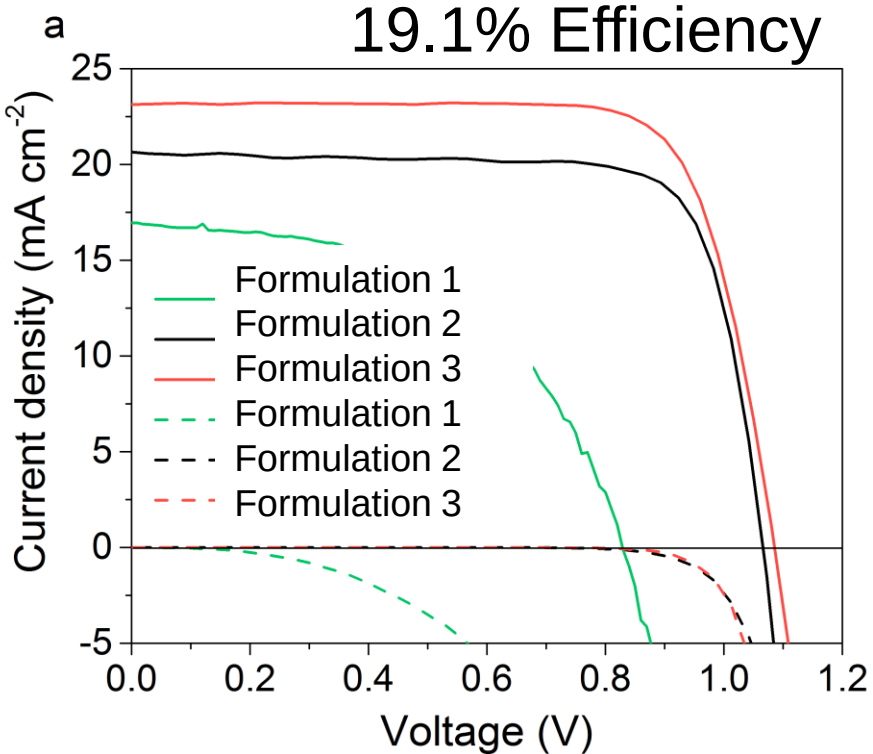
Excess organic + excess PbI_2

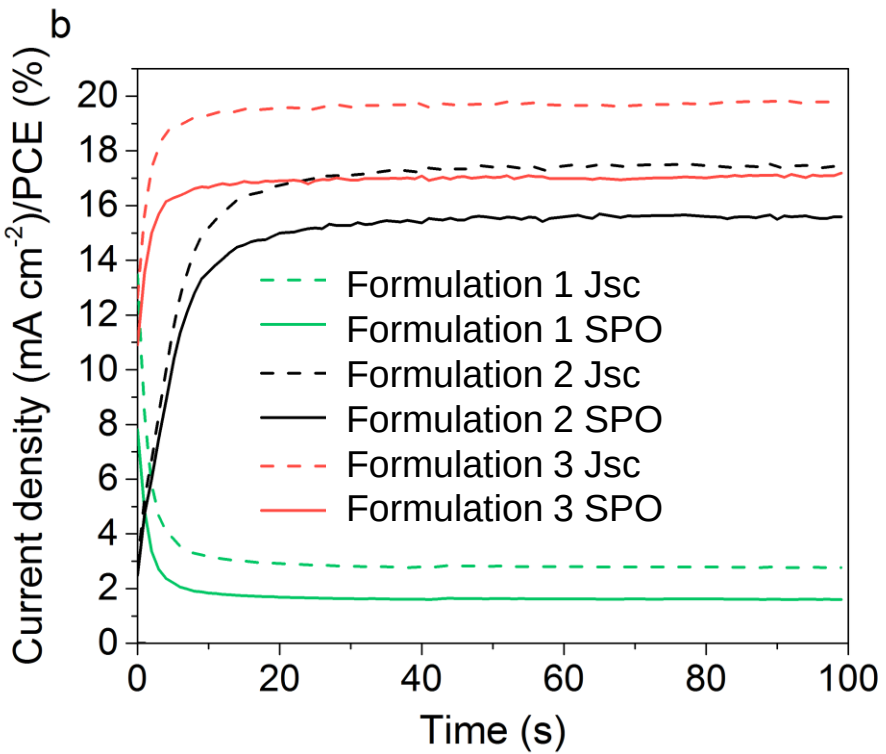


3MAI:$PbCl_2$ 2% PbI_2 5% PbI_2 30% PbI_2 100% PbI_2

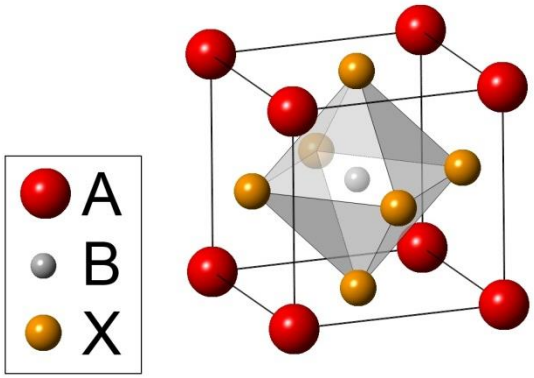
Control over “nucleation” and growth

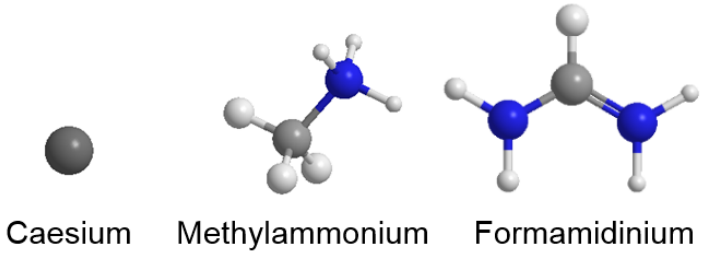




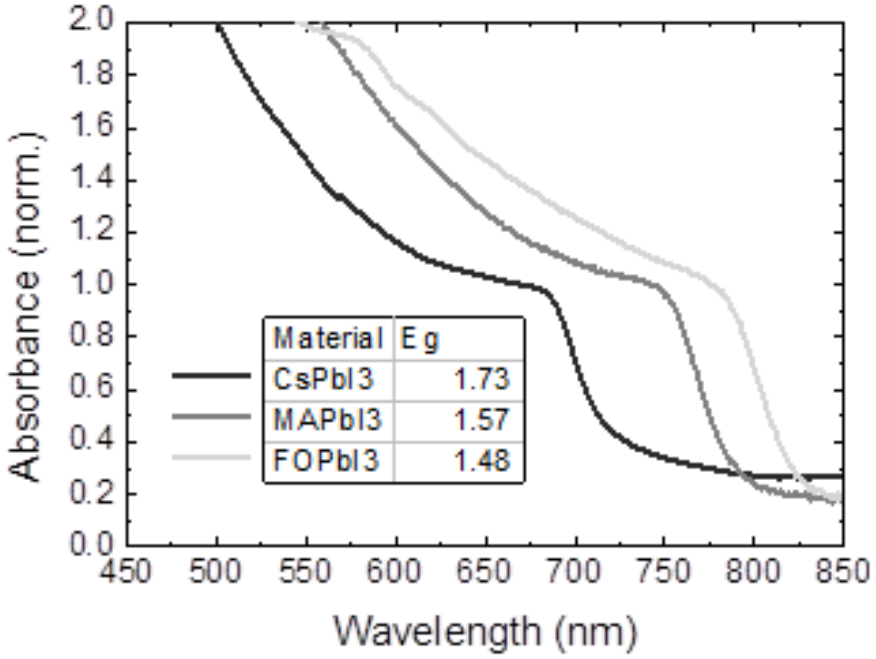


What are the cation options?





Goldshmidt Tolerance factor $(R_A + R_X) = t\sqrt{2}(R_B + R_X)$



G. Eperon et al. 2014

Adding a small amount of Cs to $FAPb(I_{1-x}Br_x)_3$

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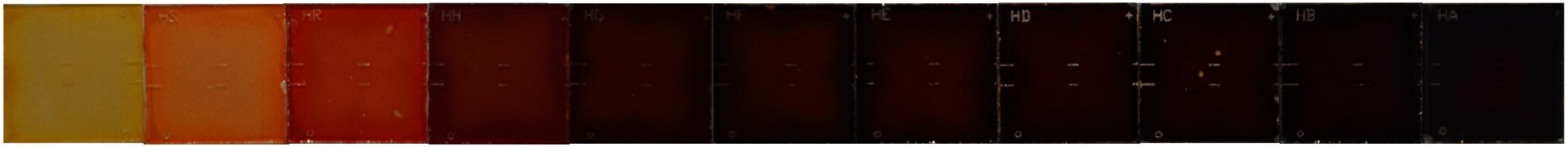
A $FAPb(I_{(1-x)}Br_x)_3$

X = 1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 X = 0

B $FA_{0.83}Cs_{0.17}Pb(I_{(1-x)}Br_x)_3$

X = 1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 X = 0



Ability to crystallise throughout the entire I-Br compositional range

Influence of Colloids In solution

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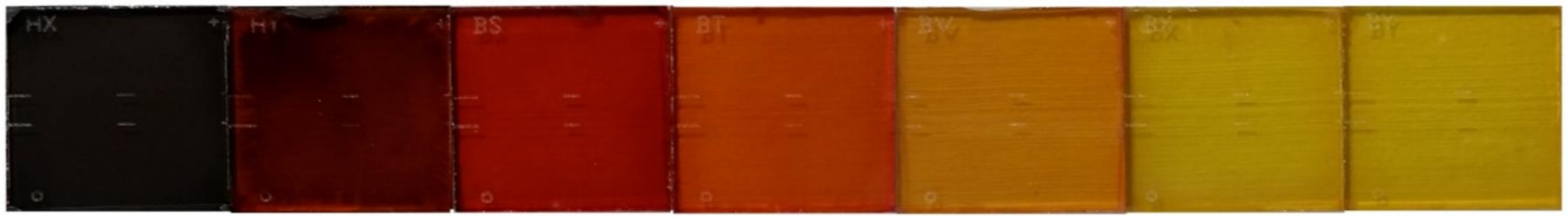
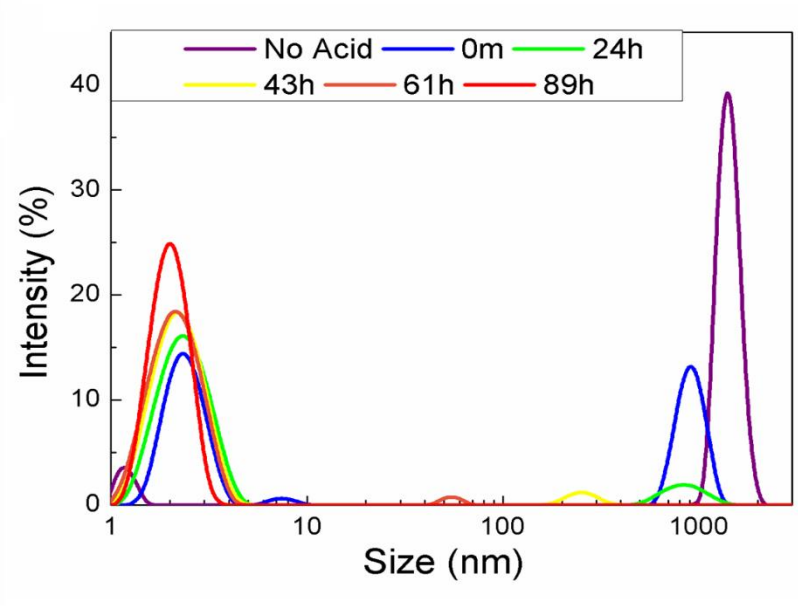
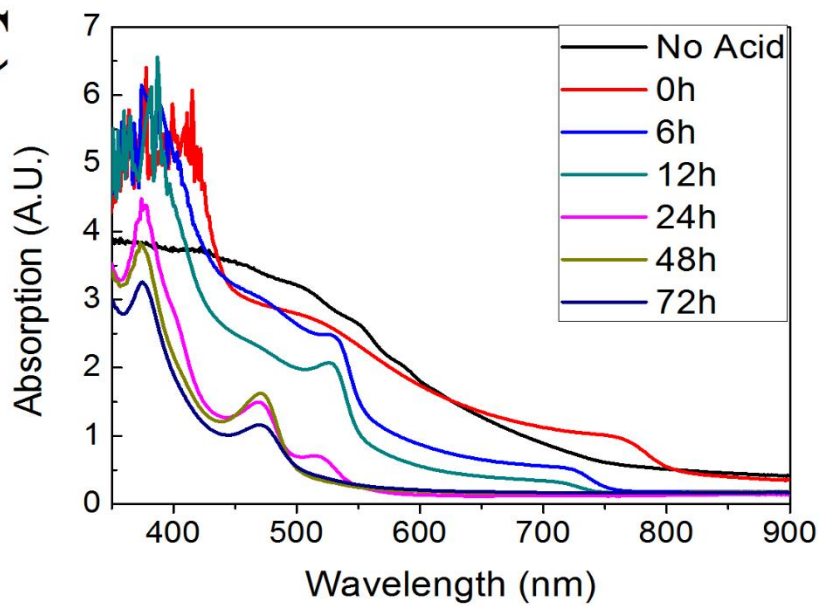
A



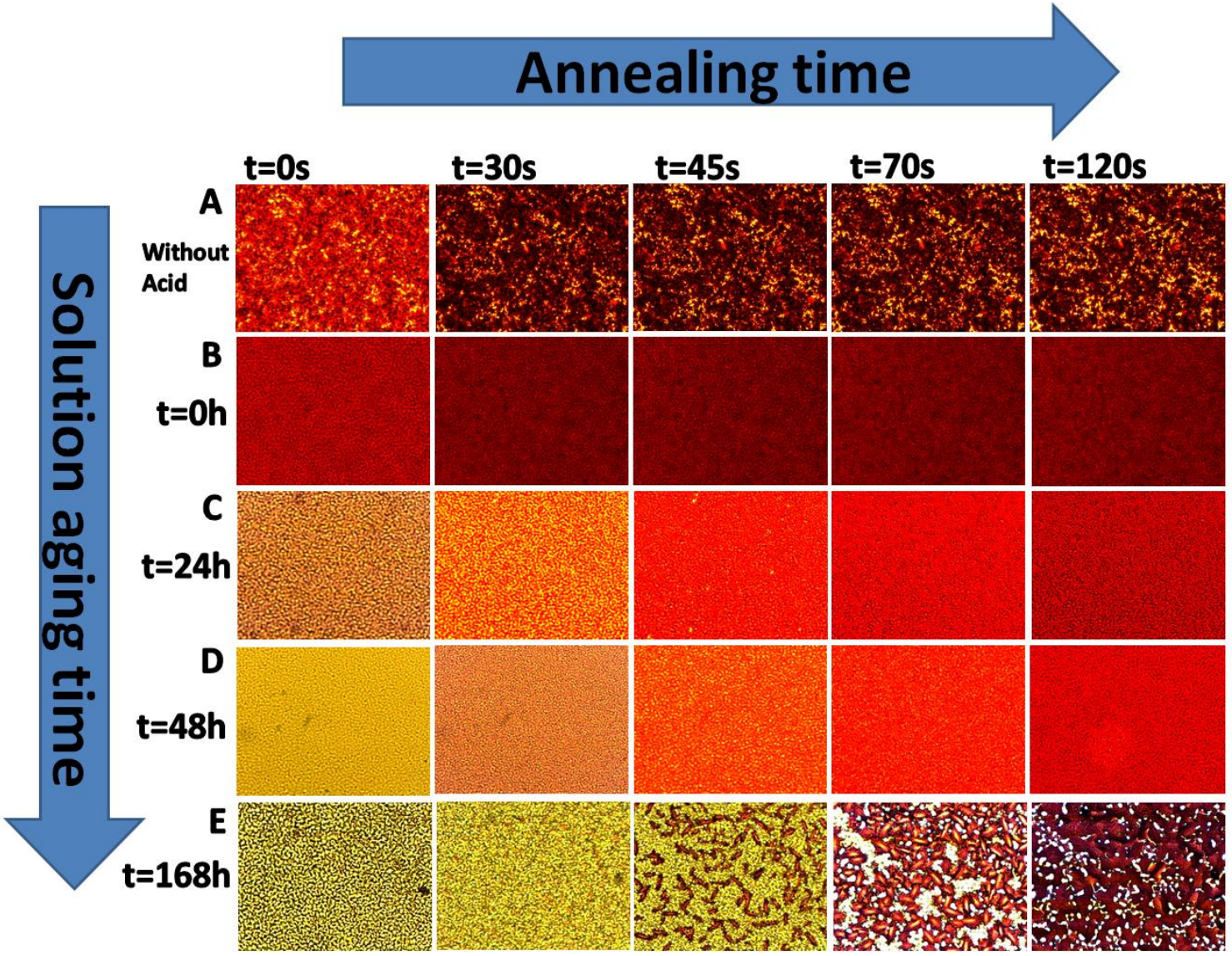
B



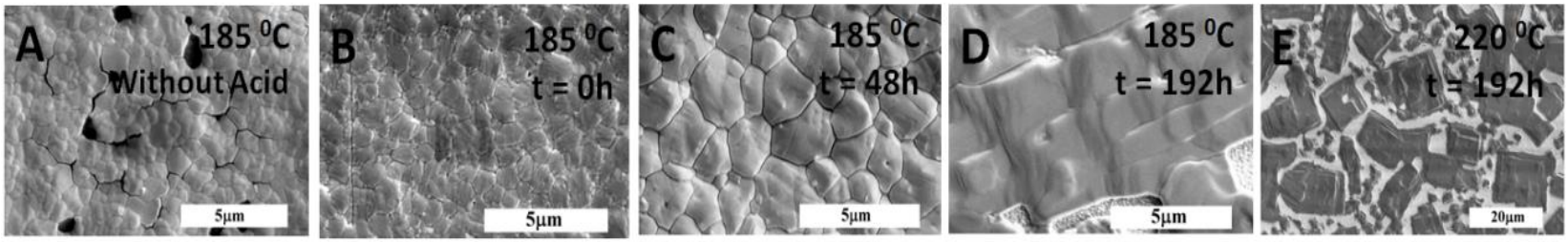
C

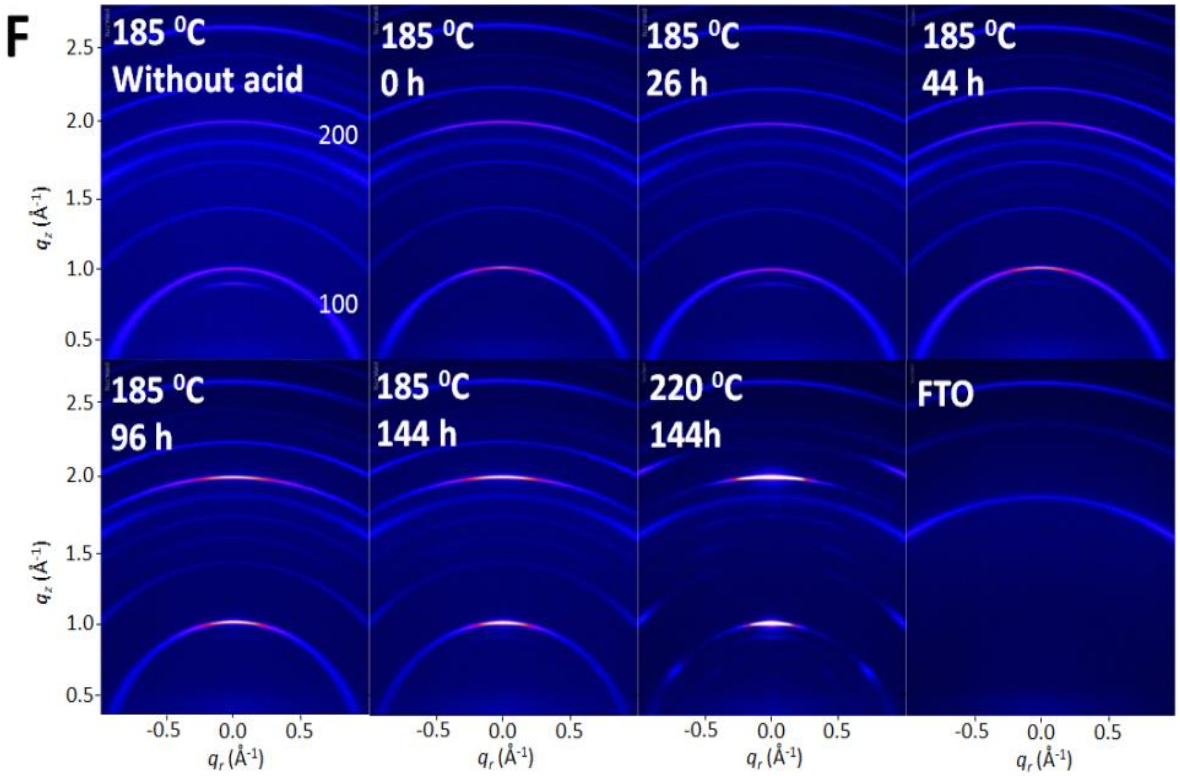


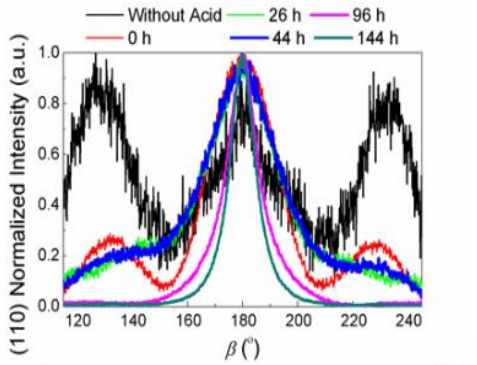
Influence of Addition of Acid (HI and HBr)

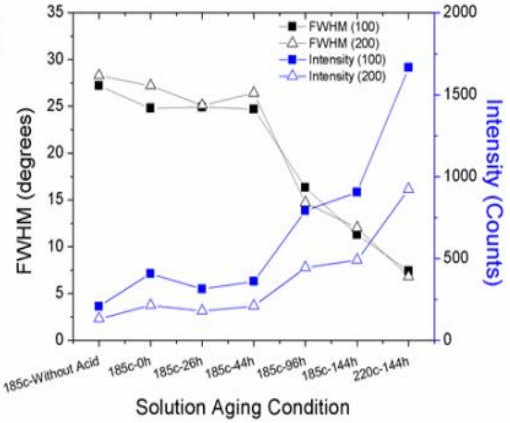


Increased crystallinity and crystal orientation

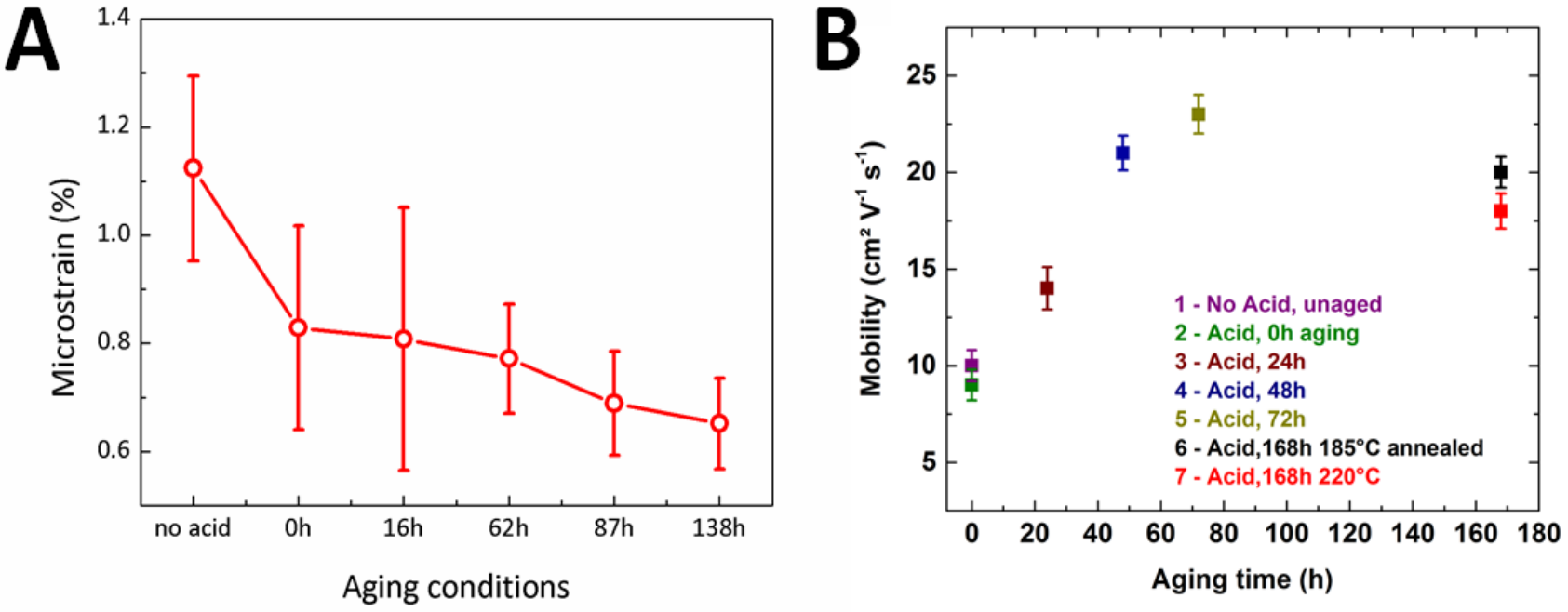




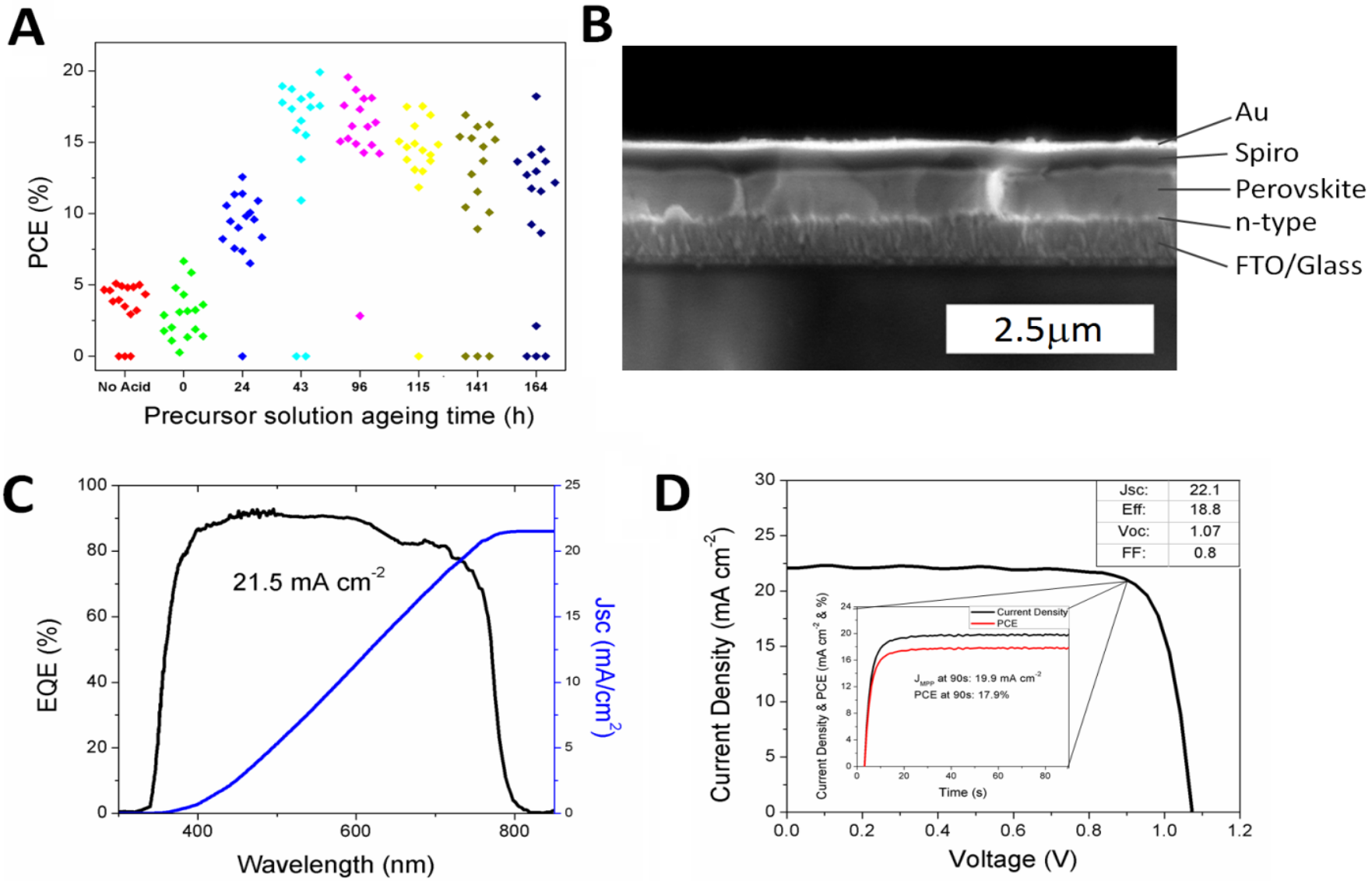




Microstrain and Charge Carrier Mobility



Crystallinity Matters



D. McMeekin et al. 2017 Submitted

A new route for single crystal Growth

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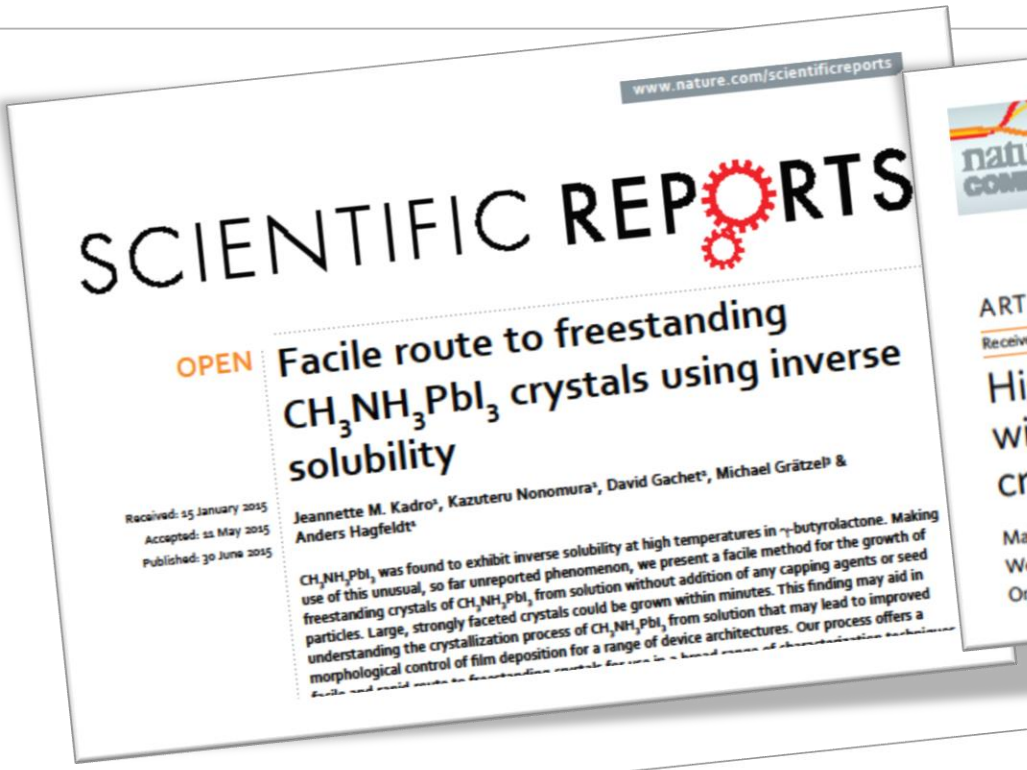

www.nature.com/scientificreports

SCIENTIFIC REPORTS

OPEN

Facile route to freestanding $CH_3NH_3PbI_3$ crystals using inverse solubility

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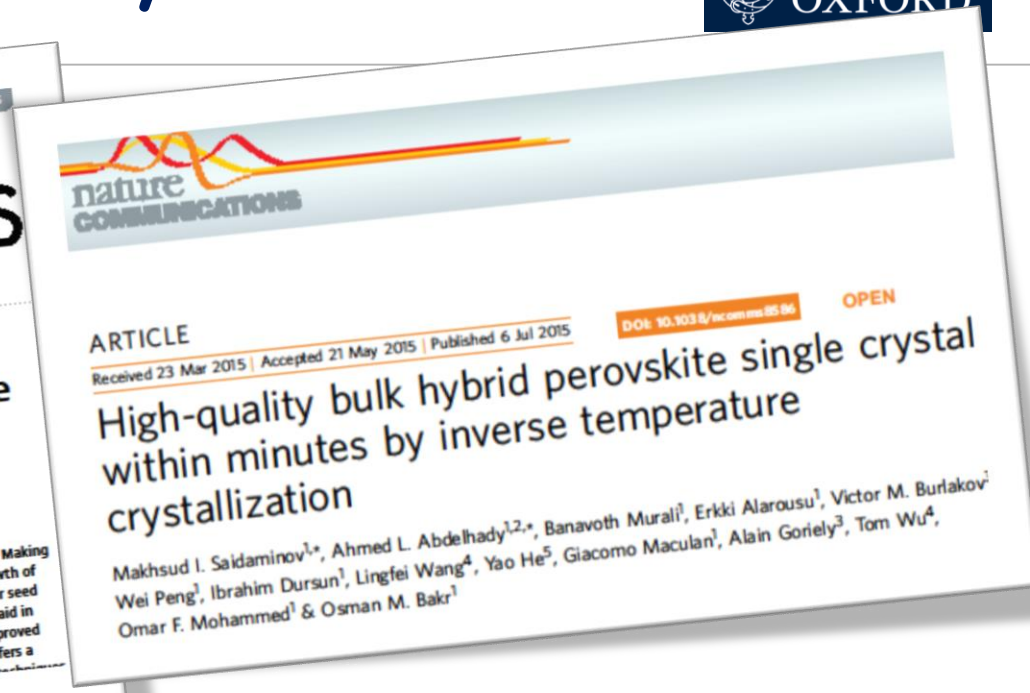
Published: 30 June 2015

Jeannette M. Kadro[a], Kazuteru Nonomura[a], David Gachet[a], Michael Grätzel[b] & Anders Hagfeldt[a]

$CH_3NH_3PbI_3$ was found to exhibit inverse solubility at high temperatures in γ-butyrolactone. Making use of this unusual, so far unreported phenomenon, we present a facile method for the growth of freestanding crystals of $CH_3NH_3PbI_3$ from solution without addition of any capping agents or seed particles. Large, strongly faceted crystals could be grown within minutes. This finding may aid in understanding the crystallization process of $CH_3NH_3PbI_3$ from solution that may lead to improved morphological control of film deposition for a range of device architectures. Our process offers a



nature COMMUNICATIONS

ARTICLE

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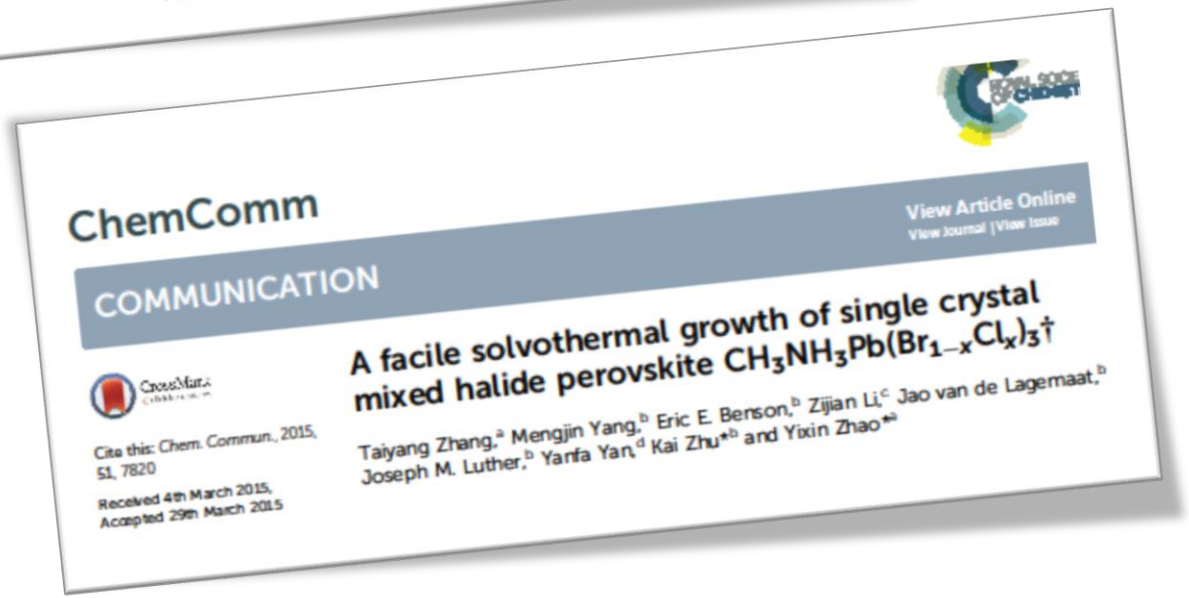
DOI: 10.1038/ncomms8586

OPEN

High-quality bulk hybrid perovskite single crystal within minutes by inverse temperature crystallization

Makhsud I. Saidaminov[1,*], Ahmed L. Abdelhady[1,2,*], Banavoth Murali[1], Erkki Alarousu[1], Victor M. Burlakov[1], Wei Peng[1], Ibrahim Dursun[1], Lingfei Wang[4], Yao He[5], Giacomo Maculan[1], Alain Goriely[3], Tom Wu[4], Omar F. Mohammed[1] & Osman M. Bakr[1]



ChemComm

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COMMUNICATION

A facile solvothermal growth of single crystal mixed halide perovskite $CH_3NH_3Pb(Br_{1-x}Cl_x)_3$†

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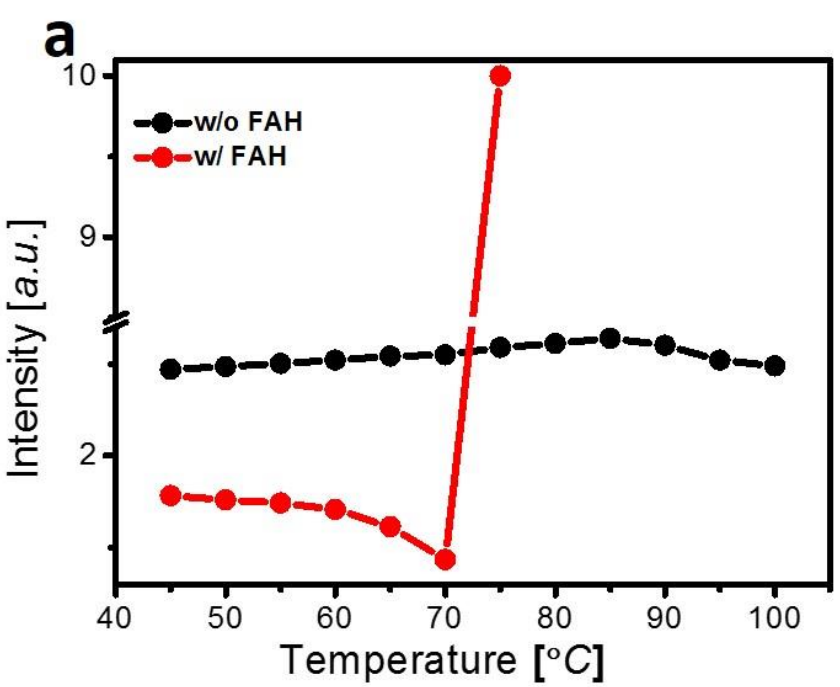
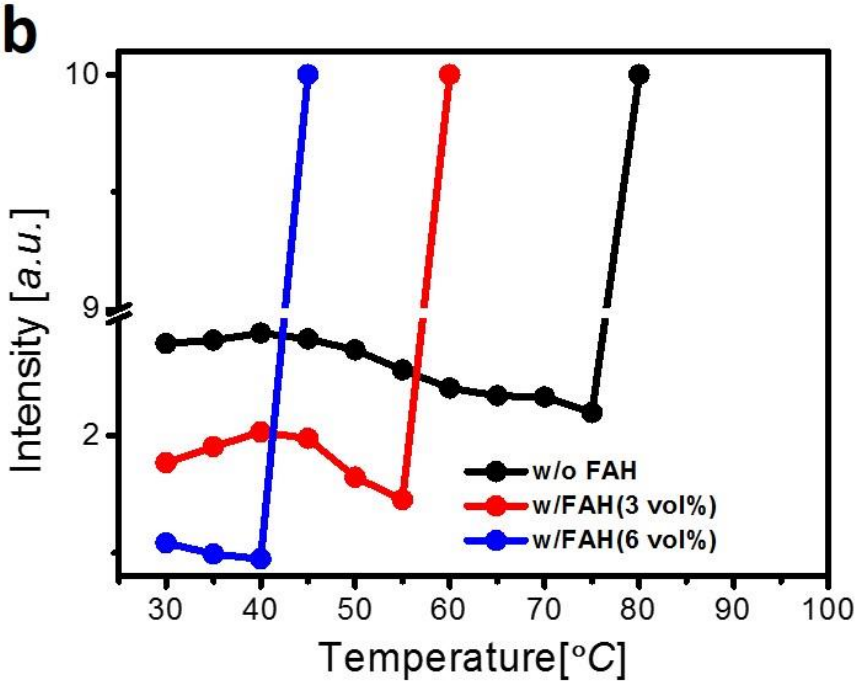
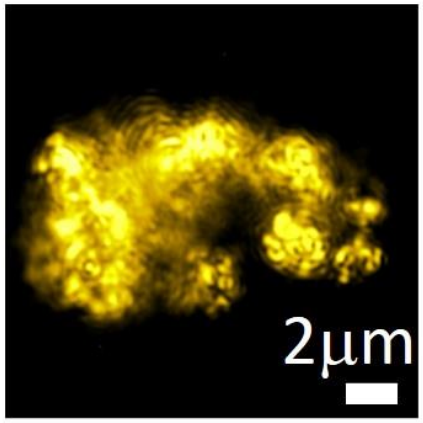
Accepted 29th March 2015

Taiyang Zhang,[a] Mengjin Yang,[b] Eric E. Benson,[b] Zijian Li,[c] Jao van de Lagemaat,[b] Joseph M. Luther,[b] Yanfa Yan,[d] Kai Zhu*[b] and Yixin Zhao*[a]

Breaking up of colloids







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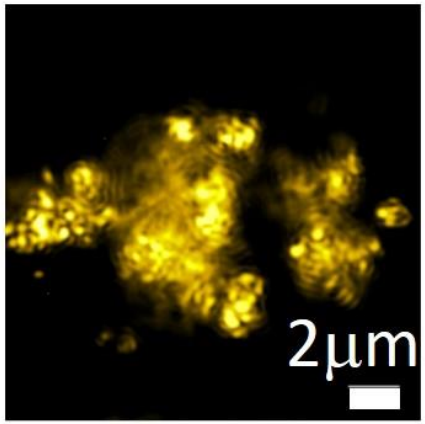

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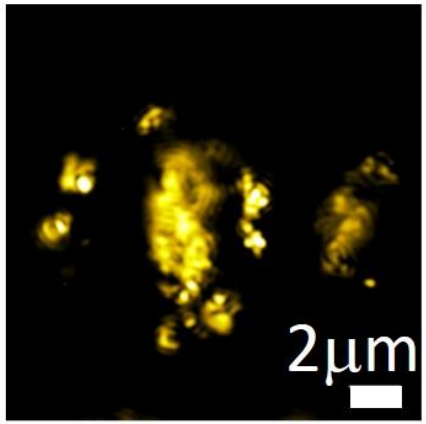

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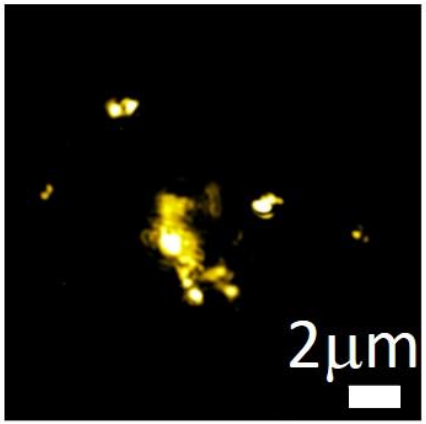
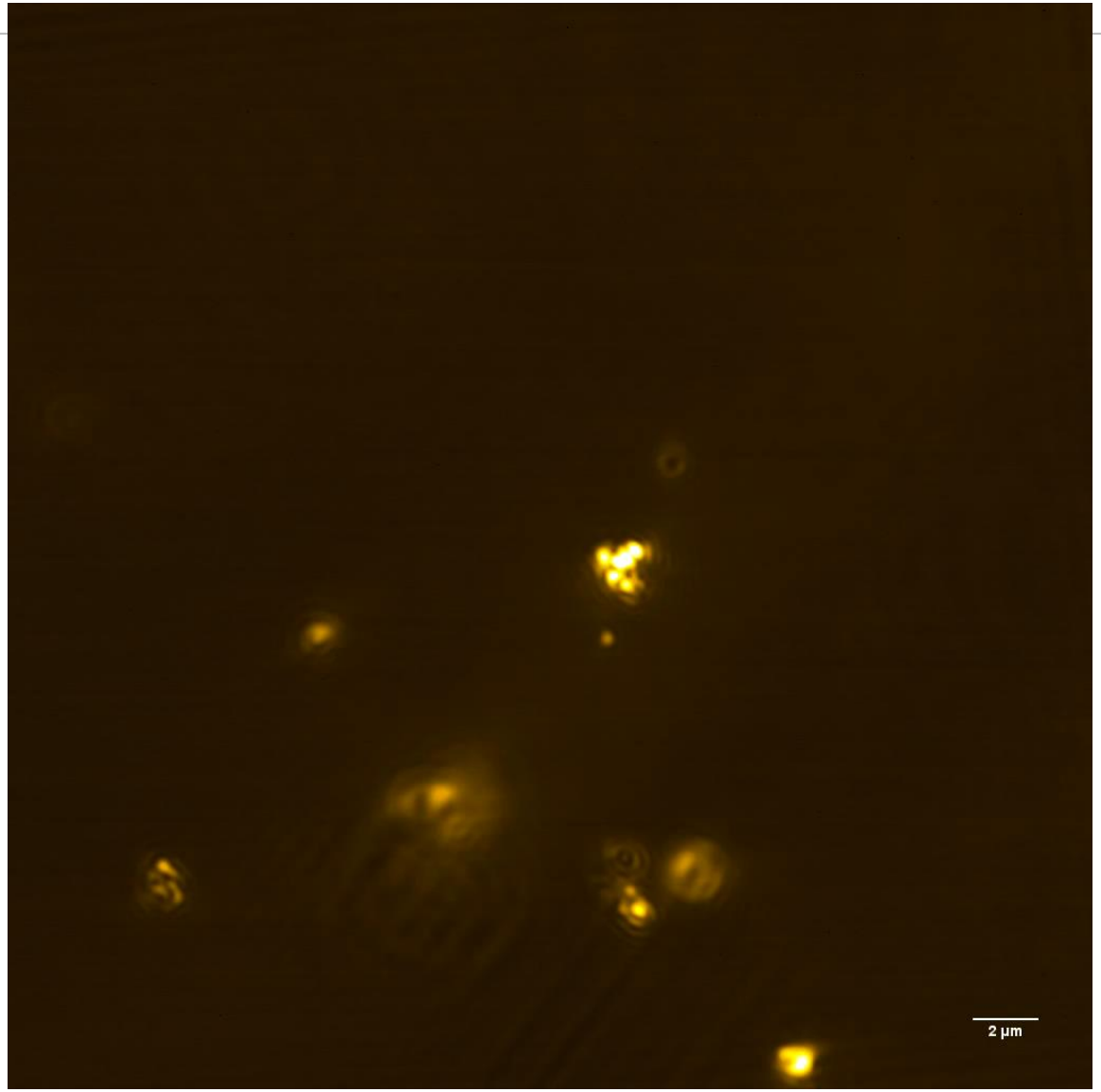


f

Breaking up of colloids



Nature Communications, 2016 (Accepted)

What we think about the mechanism

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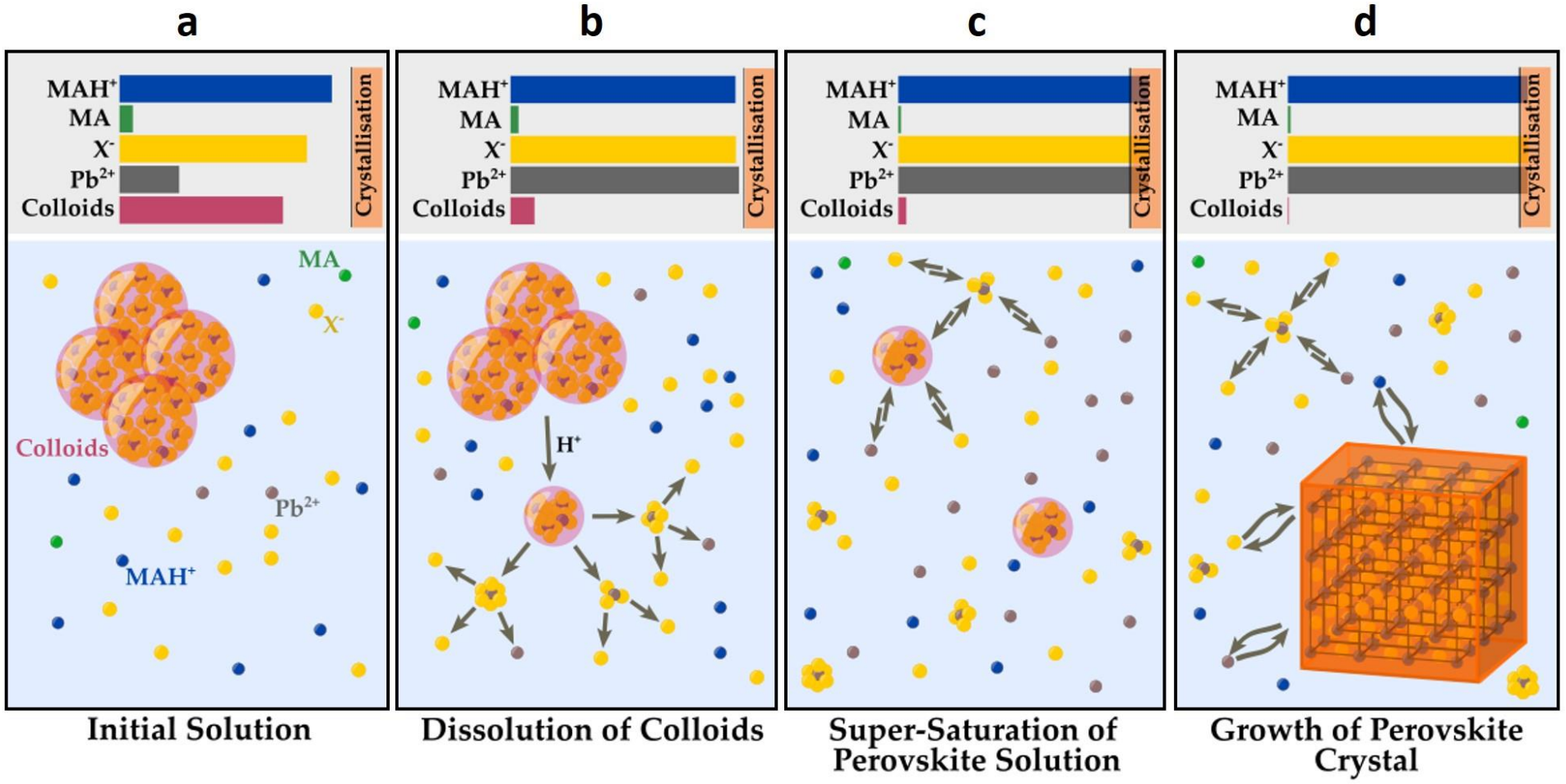
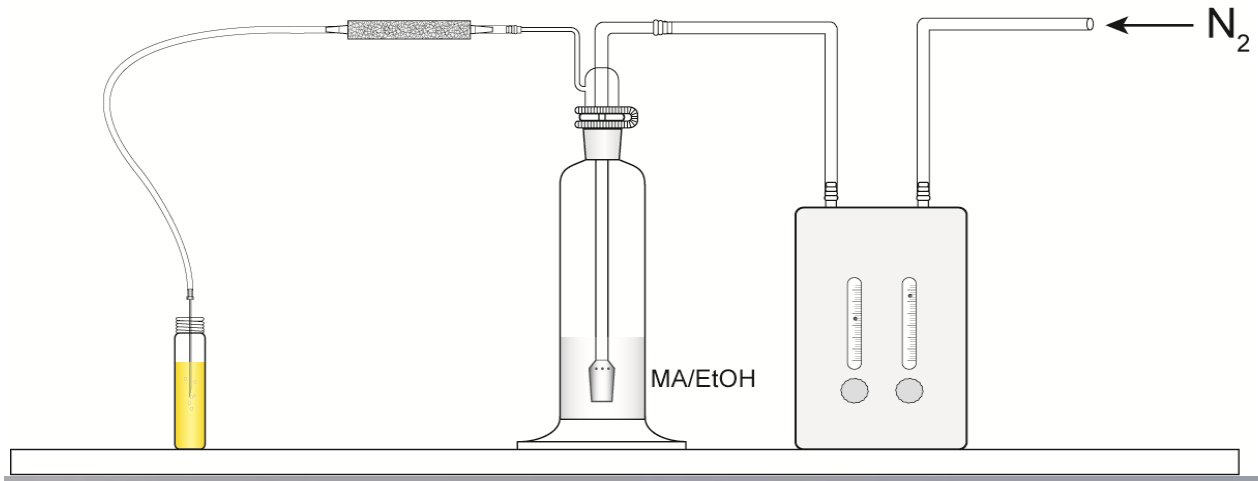
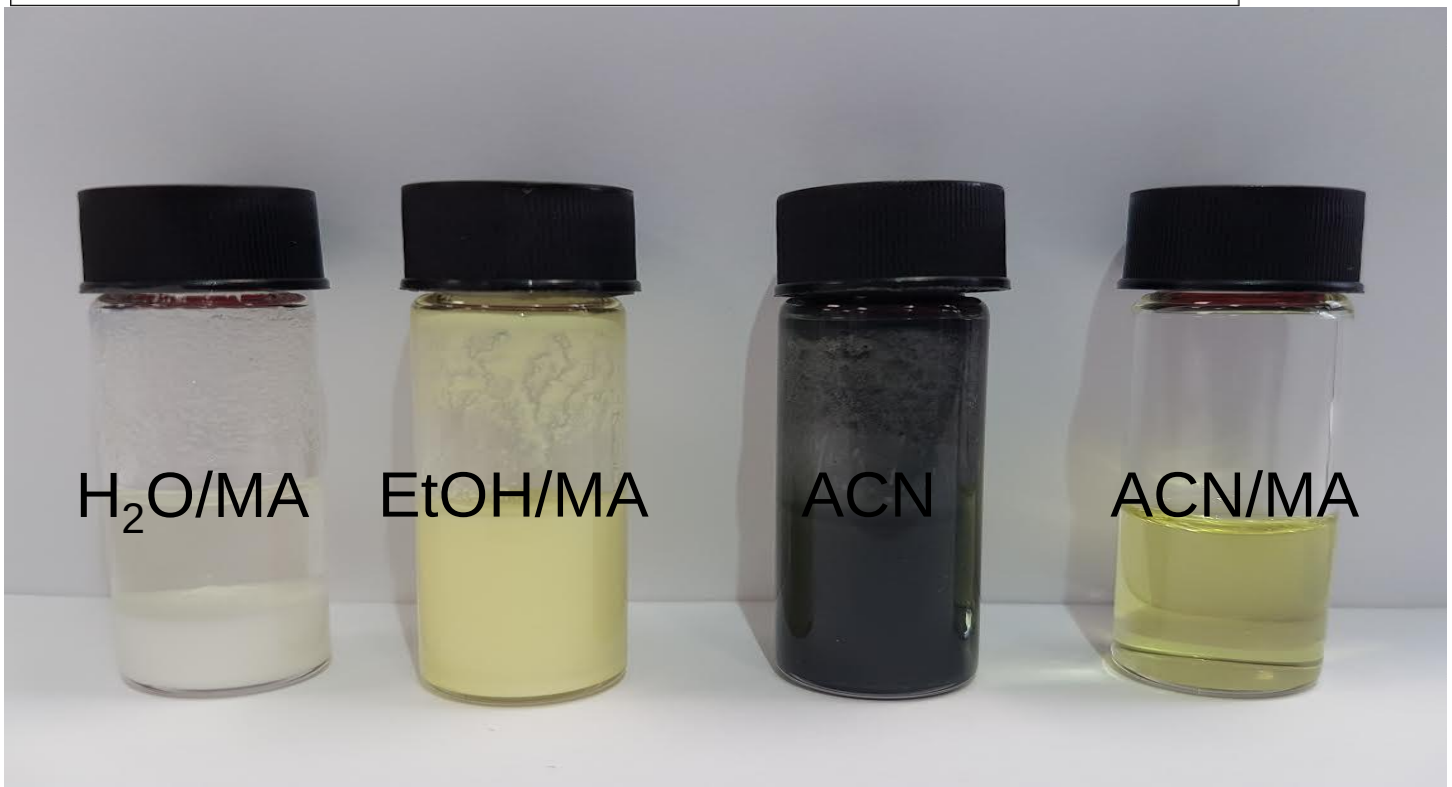
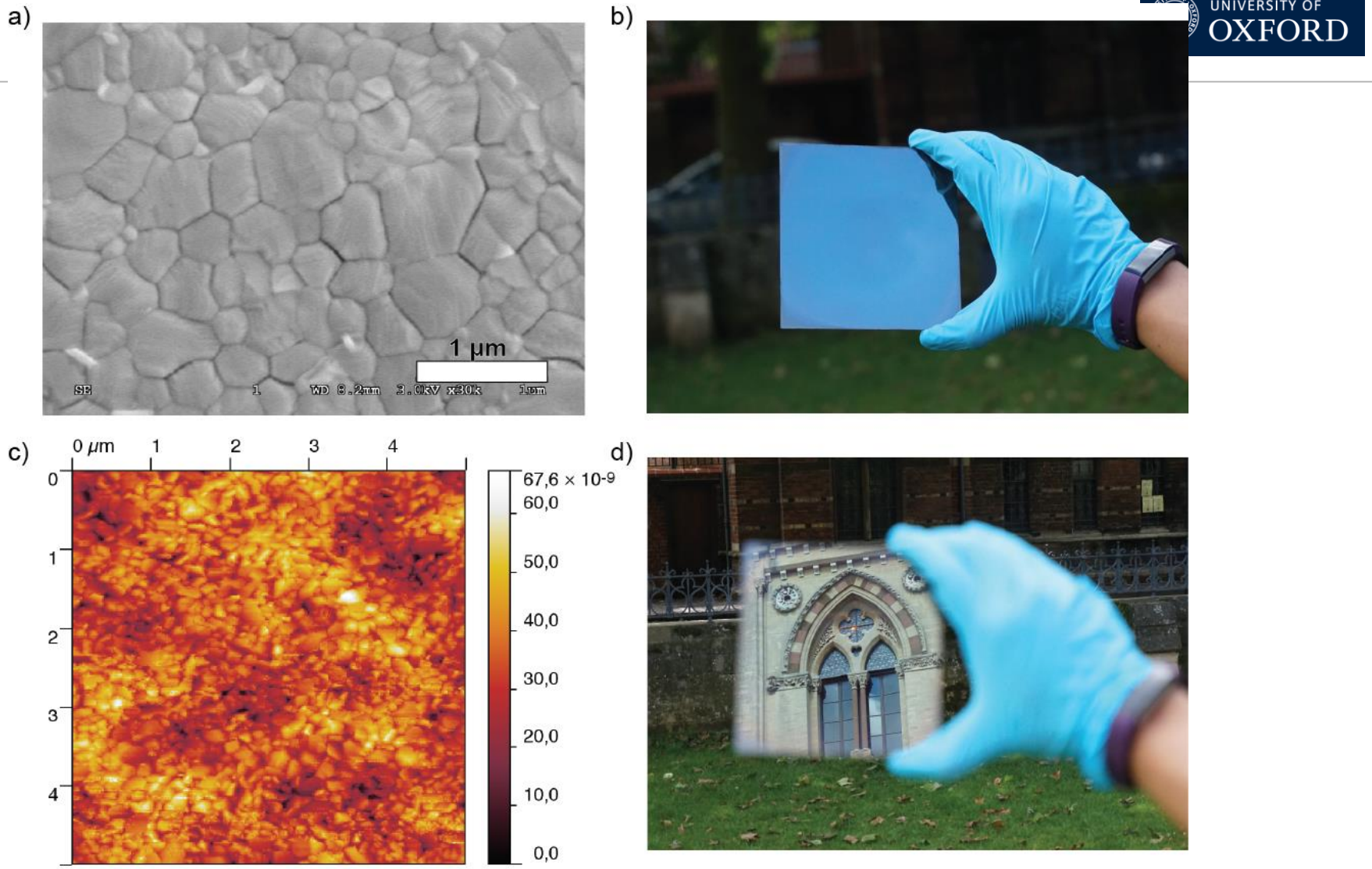


Solvent Mixtures



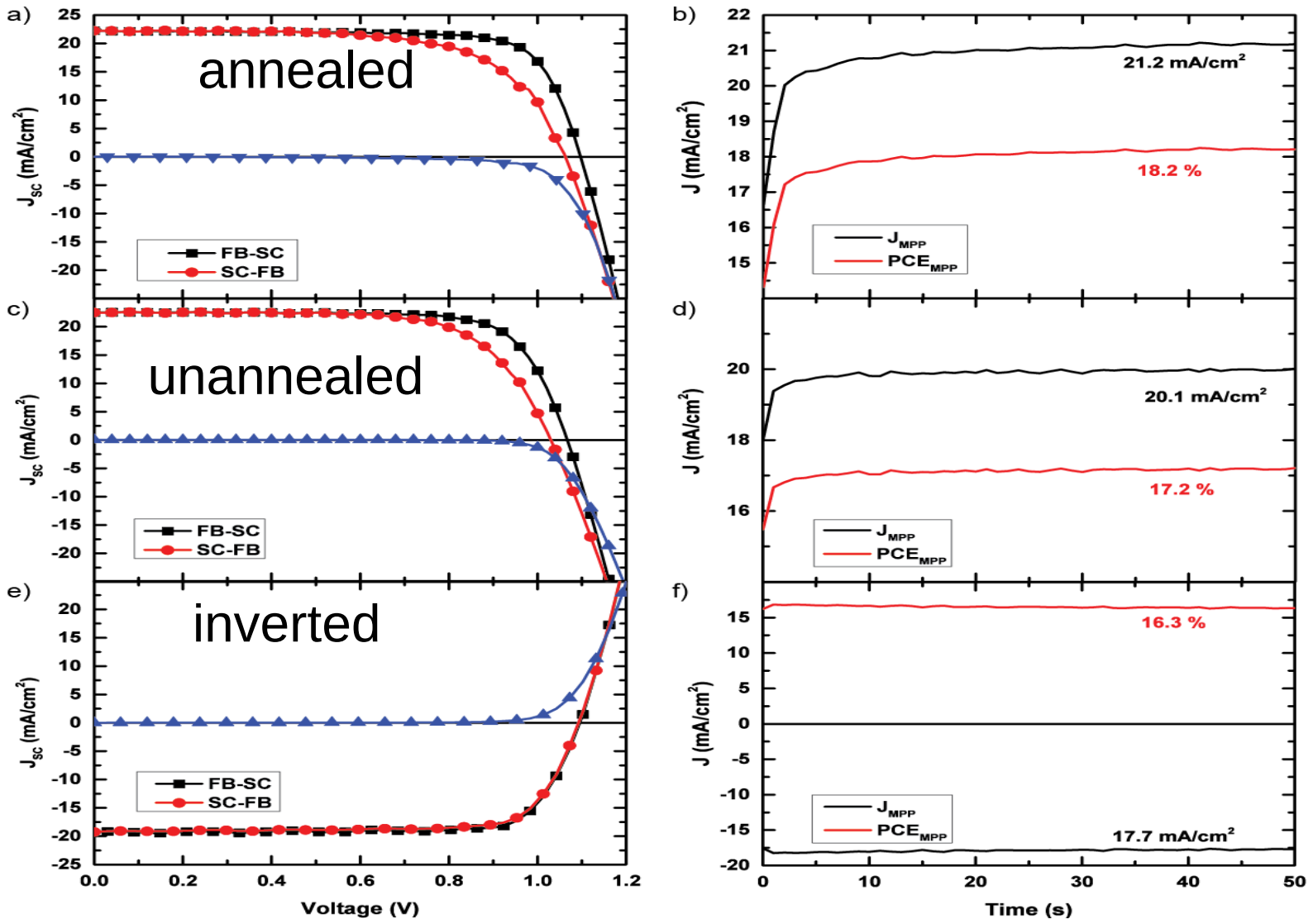
- Solvent needs to be polar and aprotic.





N. Noel et al. EES 2016 In-press

Devices from ACN/MA solvent mix



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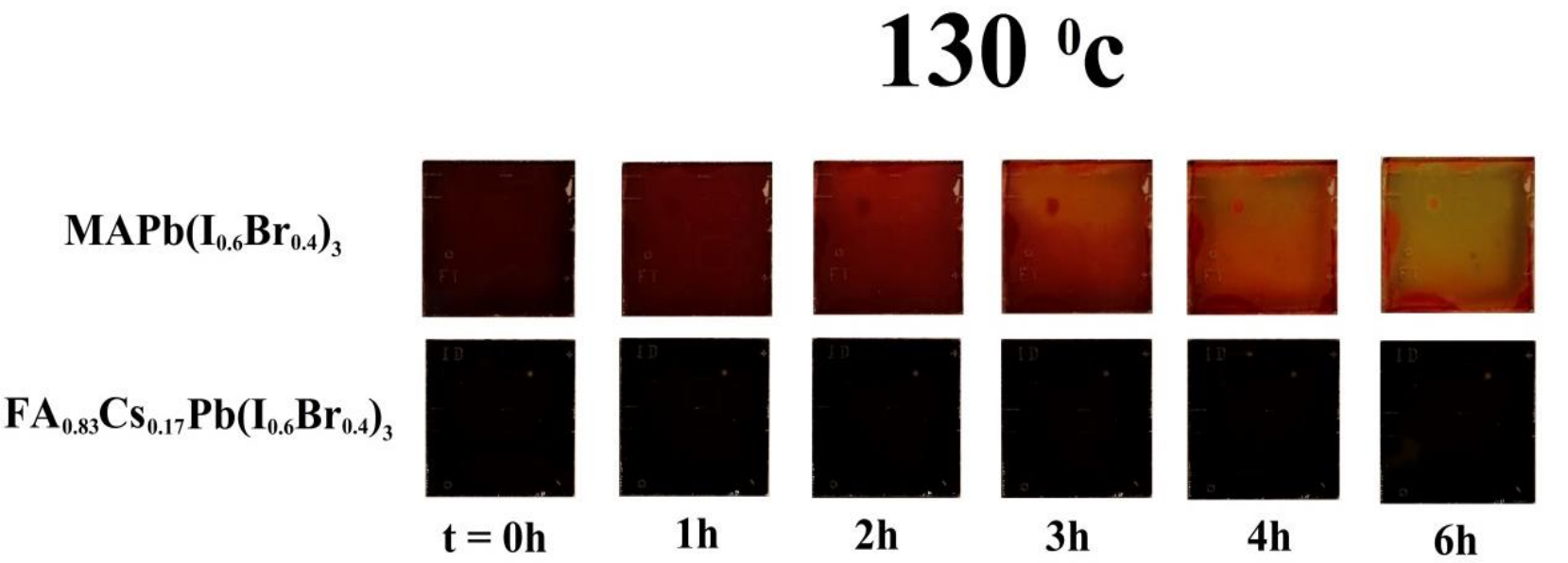
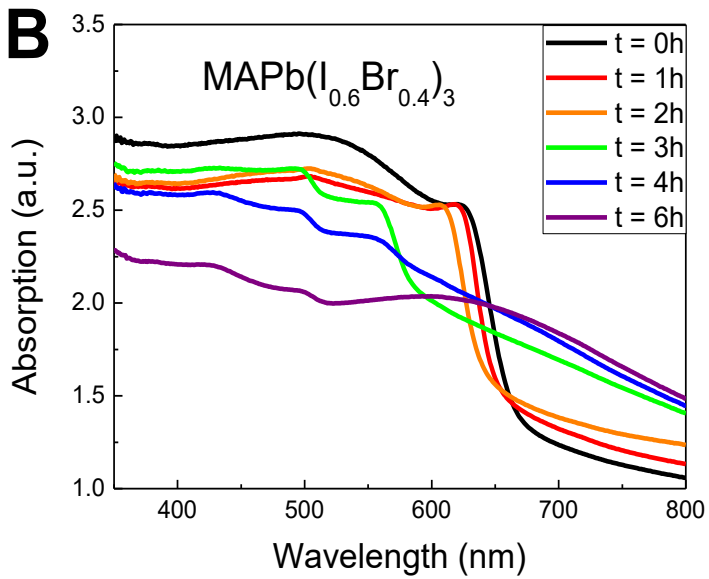
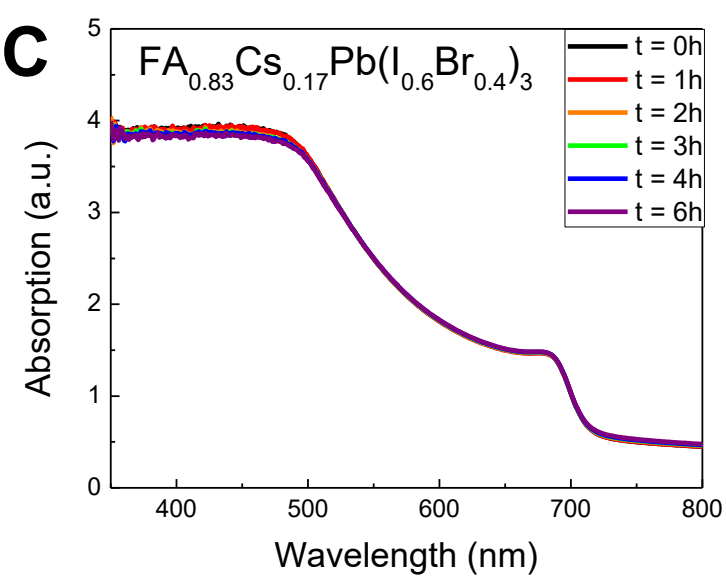
Enhanced Stability Perovskite Solar Cells

Thermal stability good

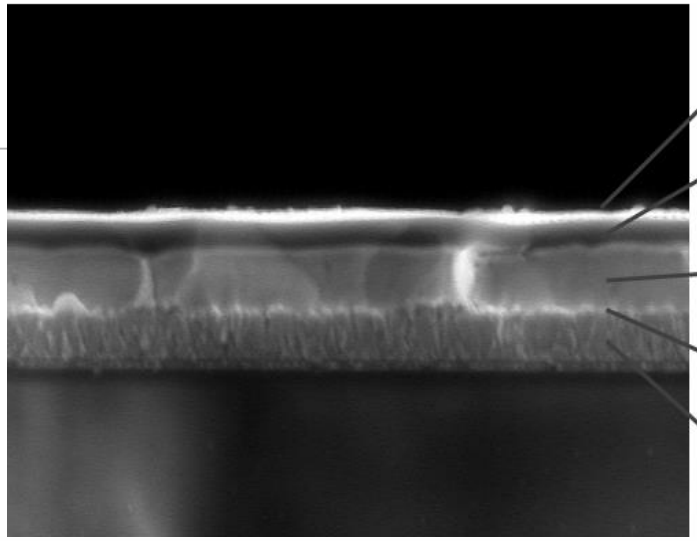






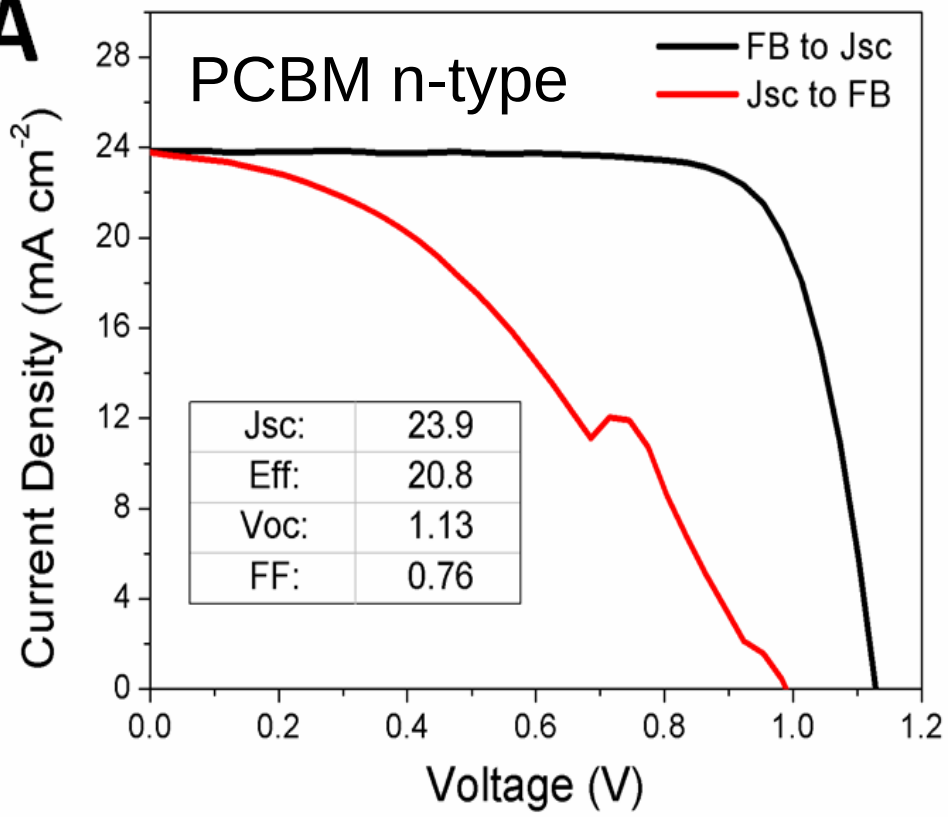
D. McMeekin et al. Science 2016

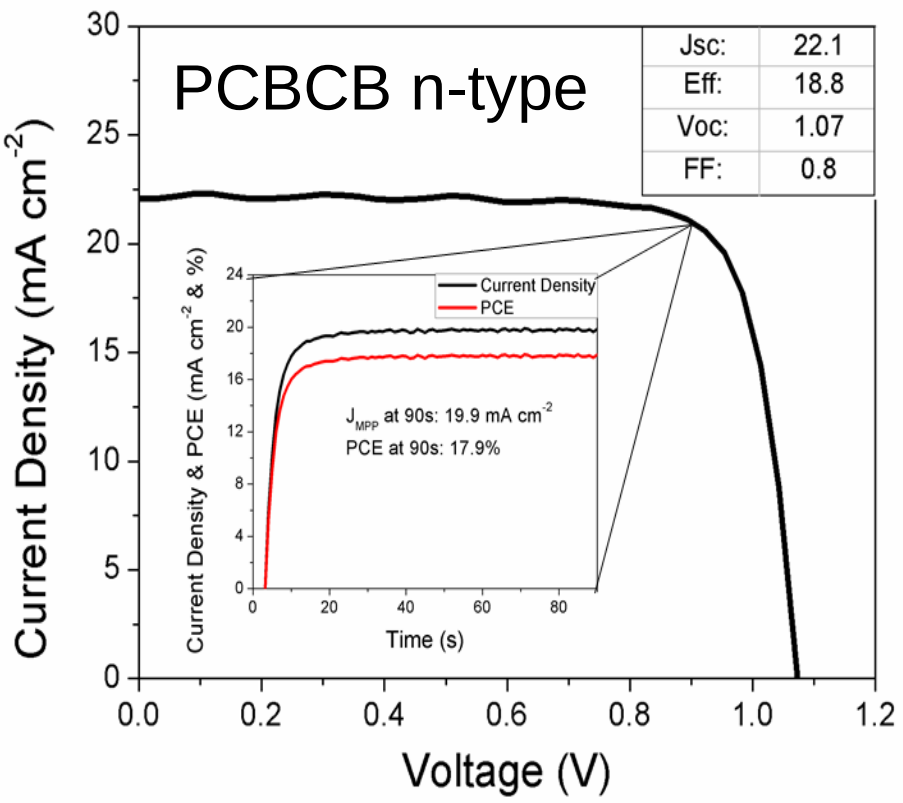
Champion Devices



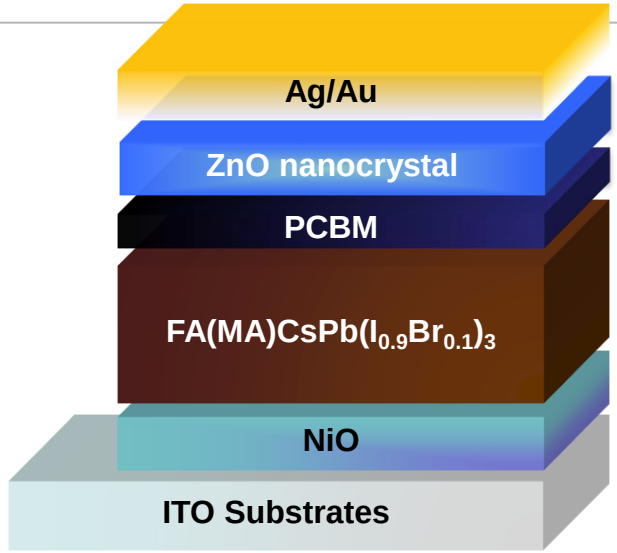
1.6eV gap

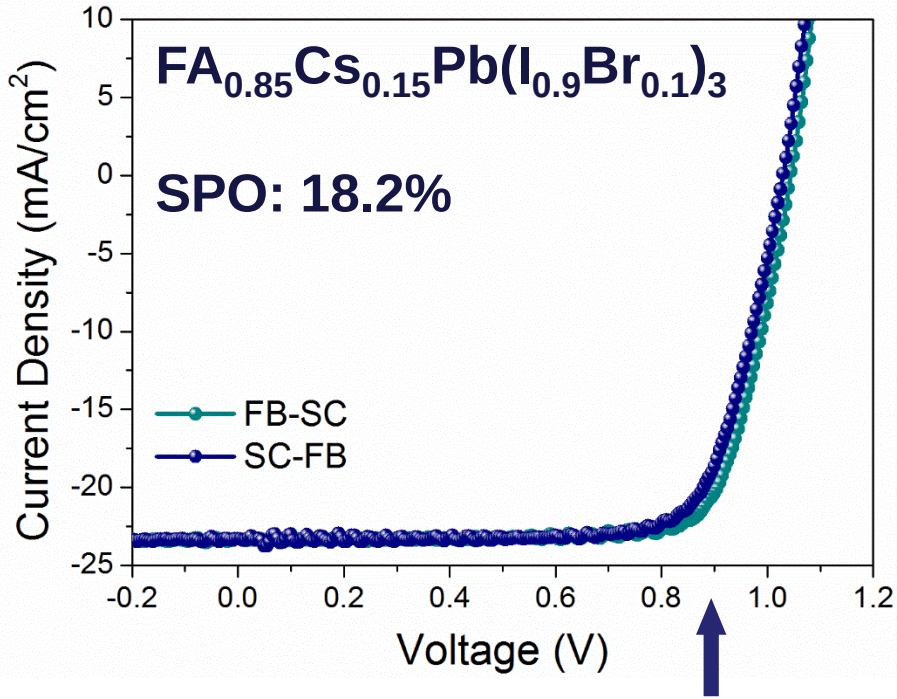
A



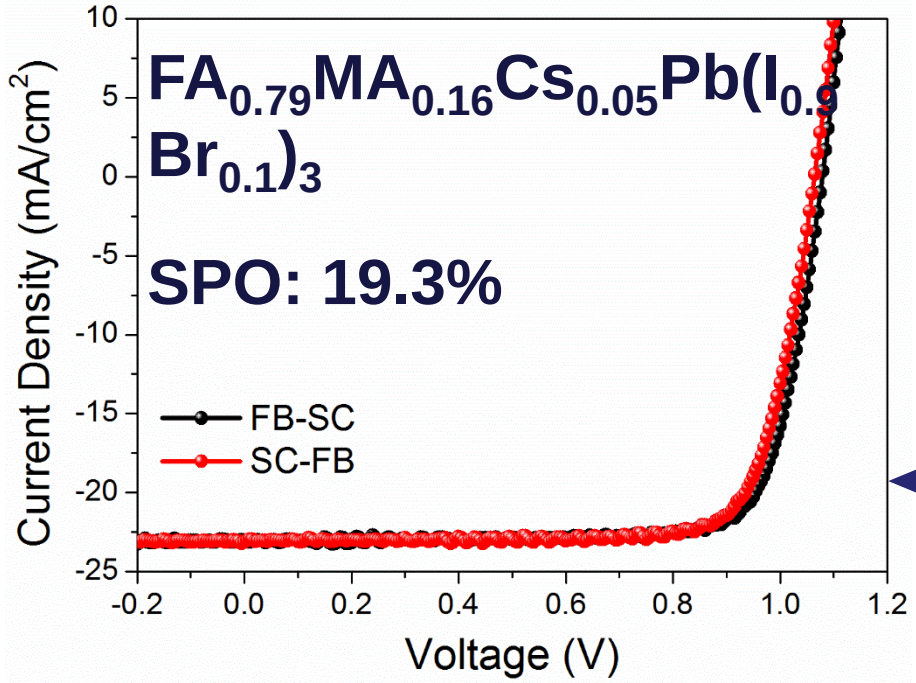


Inverted Cell Architecture





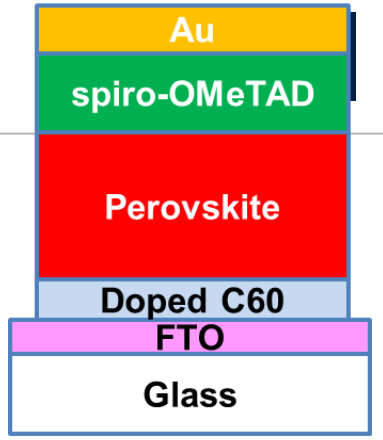
	J_{SC} (mA cm^{-2})	V_{OC}(V)	FF	PCE (%)
FB-SC	23.27	1.04	0.78	18.9
SC-FB	23.30	1.03	0.76	18.1

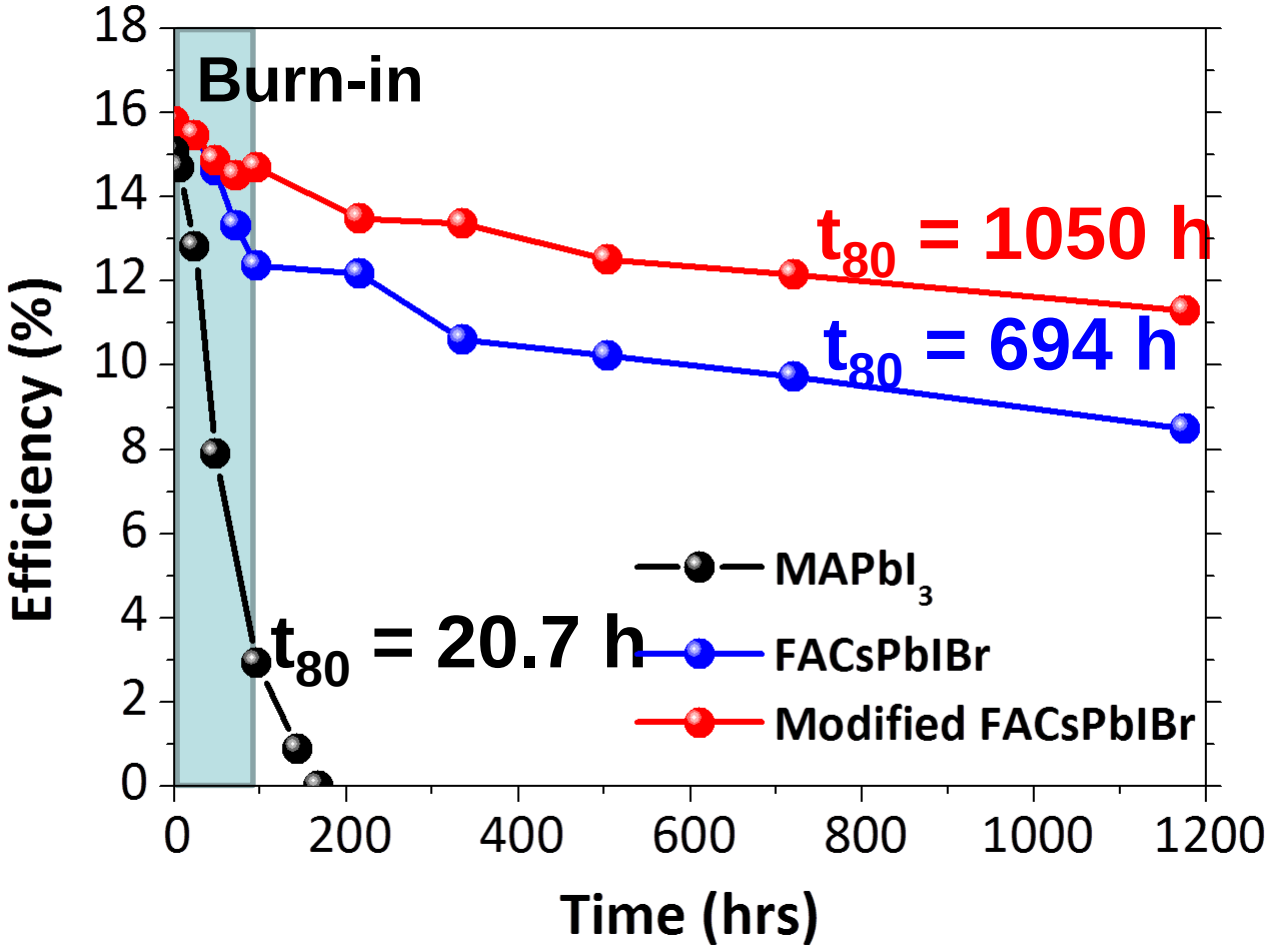


	J_{SC} (mA cm^{-2})	V_{OC}(V)	FF	PCE (%)
FB-SC	23.05	1.08	0.79	19.7
SC-FB	23.15	1.07	0.78	19.2

S. Bai et al. (In preparation) 2017

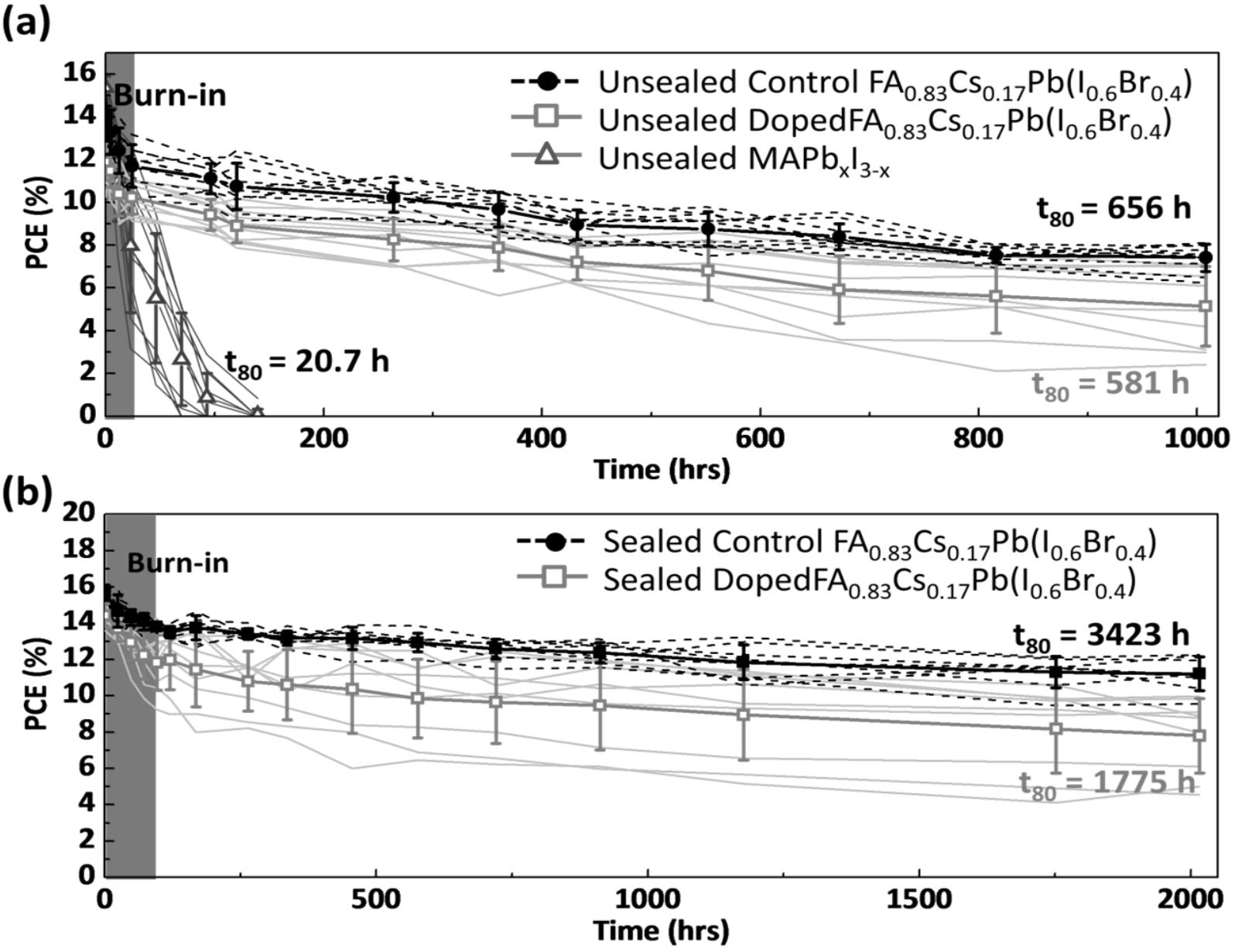
Non-encapsulated solar cells





The devices are aged under full spectrum simulated AM1.5, 76 mWcm^{-2} average irradiance at V_{OC} in air without a UV filter, 53℃. The Suntest XLS+ aging box irradiates pulsed light.

Sealed vs unsealed



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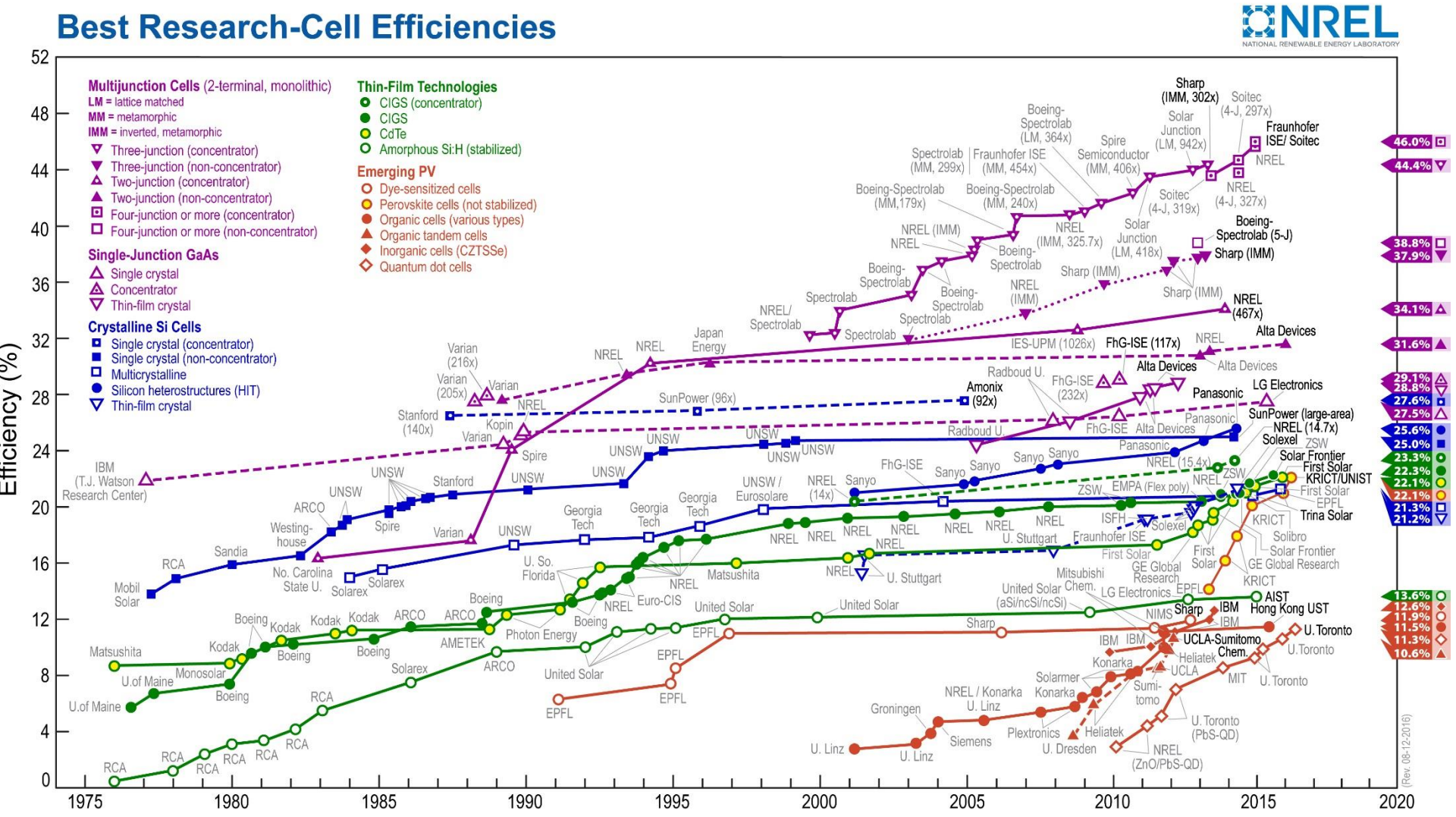
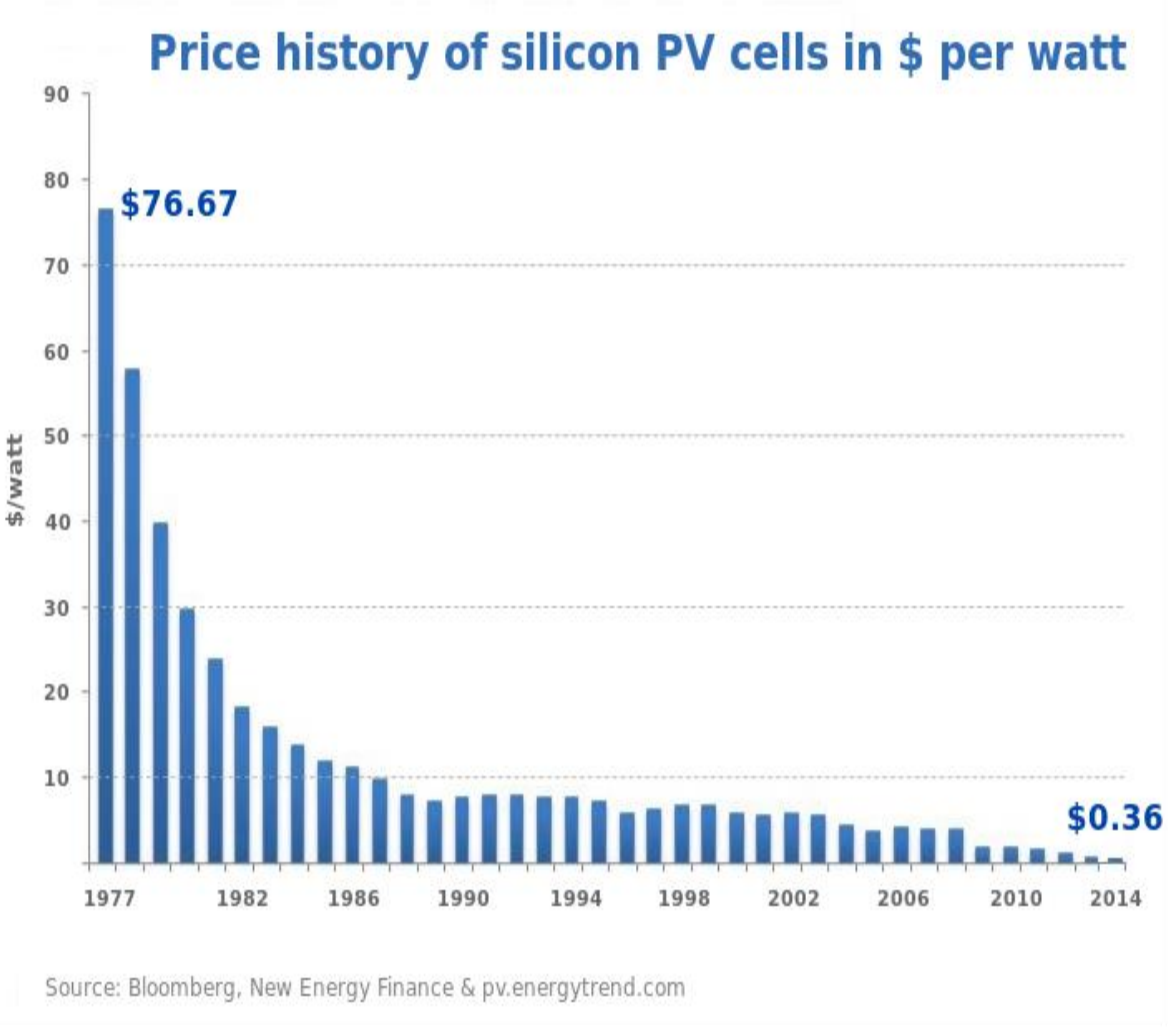
Best Research-Cell Efficiencies



But…


Price history of silicon PV cells in $ per watt
$/watt
90
80
70
60
50
40
30
20
10
$76.67
$0.36
1977
1982
1986
1990
1994
1998
2002
2006
2010
2014
Source: Bloomberg, New Energy Finance & pv.energytrend.com

And cheaper…

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Sweihan PV IPP – Bids Opening Summary

- Opening of Proposals occurred on 19th September 2016 at the offices of ADWEA in Abu Dhabi.
- Six Bidders submitted Proposals, the consortium formed of **Marubeni & Jinko Solar submitted the most competitive Proposal with a weighted LEC of 8.888 Fils/kWh.**
- The information in this summary is taken directly from the Bidders' submissions and is subject to the Advisors' further review and verification over the next few weeks of the due diligence process which may result in changes.

Managing Member	Consortium Member(s)		IRR (%)	LEC (in fils/kWh)	NPV of Weighted Net Electrical Energy (in MWh)	Weighted LEC (in fils/kWh)	Ranking based on Weighted LEC
Marubeni	Jinko Solar		7.00%	10.796 (USD 2.940c)	24,422,894	8.888 (USD 2.420c)	1
Masdar	EDF	PAL	7.00%	11.311 (USD 3.080c)	24,361,555	9.304 (USD 2.533c)	2
Tenaga	Phelan Energy		7.15%	11.512 (USD 3.135c)	18,097,309	9.543 (USD 2.598c)	3
RWE	B-Electric		7.00%	13.038 (USD 3.550c)	19,539,720	10.720 (USD 2.919c)	4
JGC	First Solar	Sojitz	8.46%	13.840 (USD 3.769c)	22,235,300	11.339 (USD 3.088c)	5
Kepco	Q Cells	GSE	7.00%	15.980 (USD 4.351c)	10,446,040	13.349 (USD 3.635c)	6

Based on the Evaluated Weighted LEC formula provided in section 6.4 of the RfP (which takes into account (a) each Bidder's Weighted LEC and (b) the average of all Bidder's NPV Net Electrical Energy), the Marubeni/Jinko Solar consortium still ranks first and the Masdar/EDF/PAL consortium still ranks second.

FICHTNER Consulting Engineers Limited

ALDERBROOK FINANCE

Akin Gump STRAUSS HAUER & FELD LLP

Best Way to Raise Efficiency

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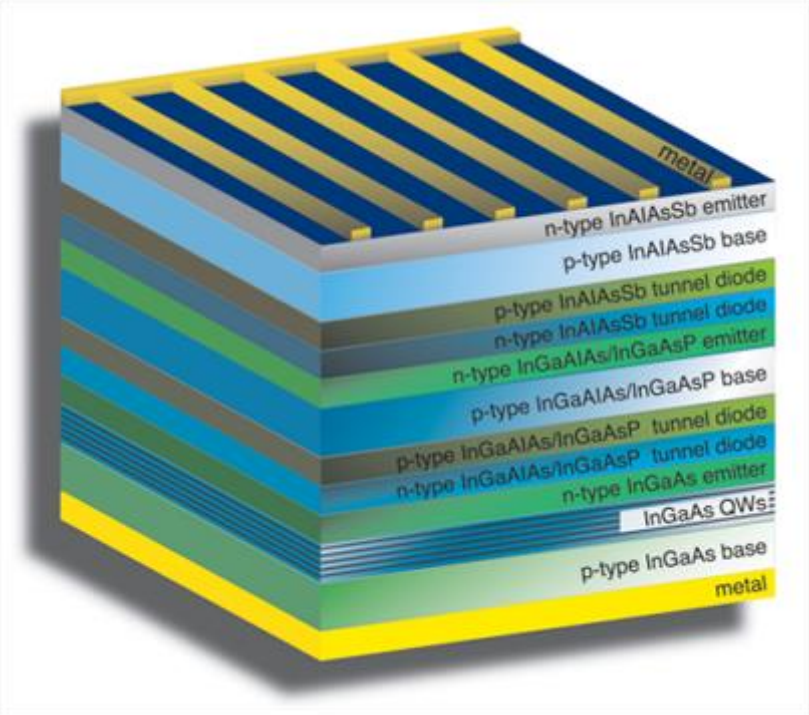
Epitaxially Grown Single Crystal III-V Tandem

46% efficient

>$40,000/m²



Perovskite on Conventional Silicon Tandem

Up to 33% efficient

<$100/m²

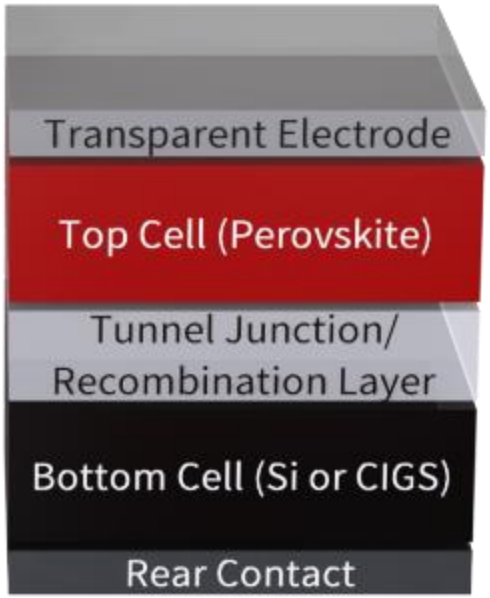
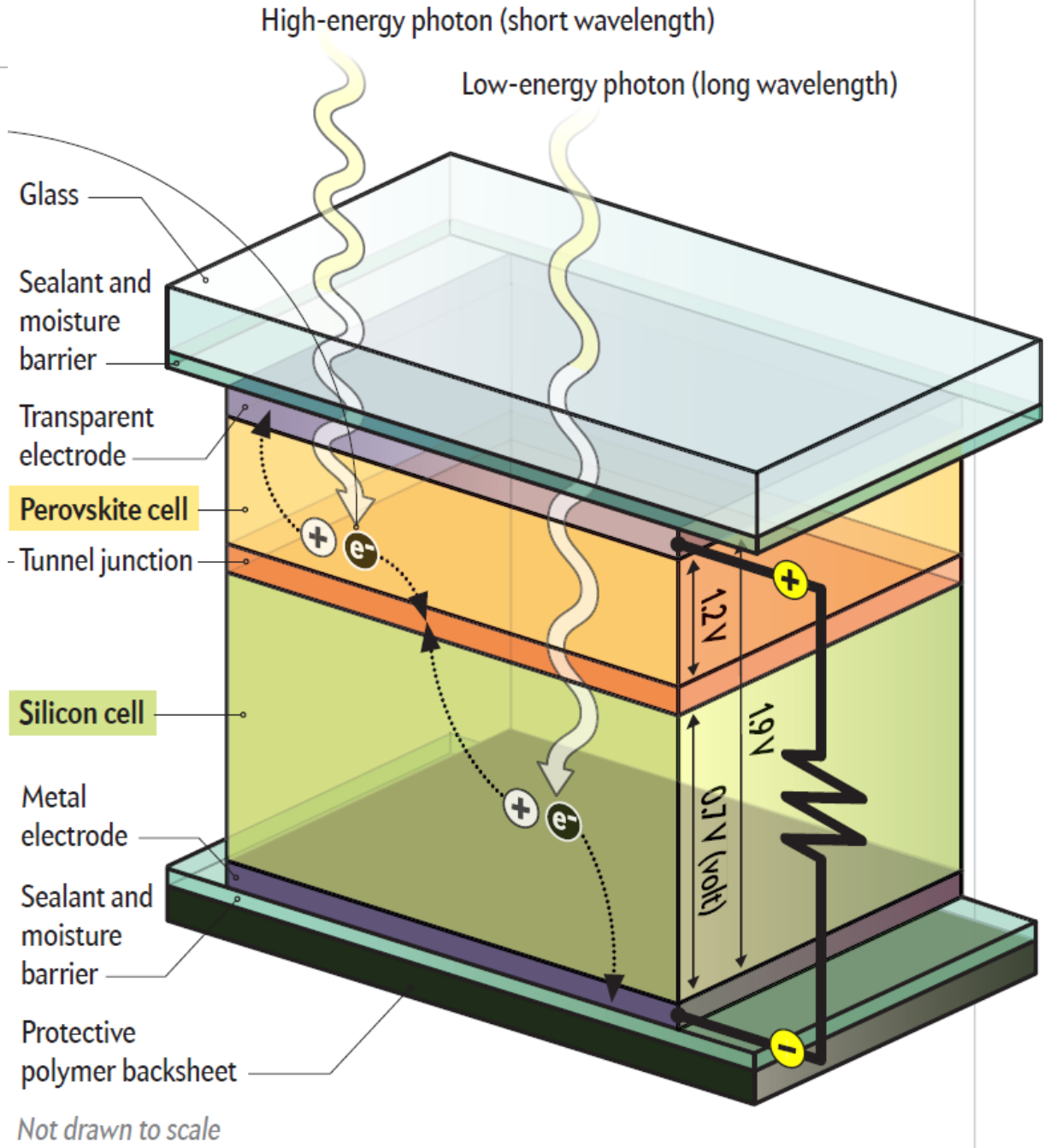


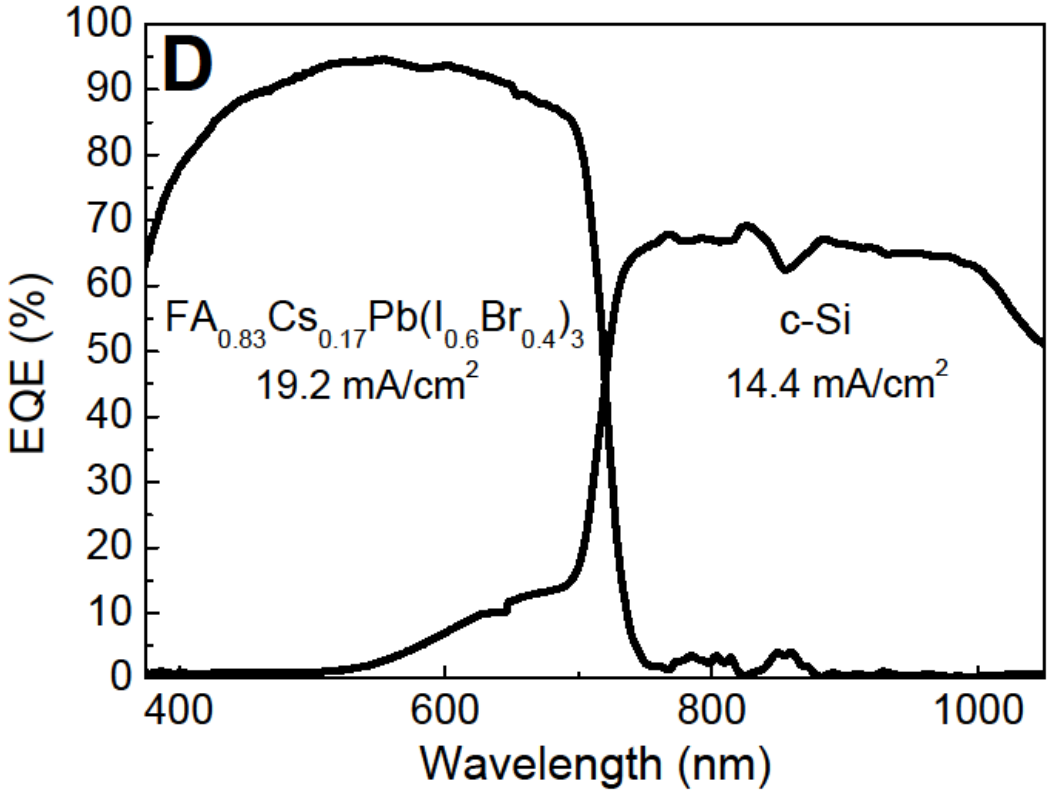
Image: US Naval Research Lab

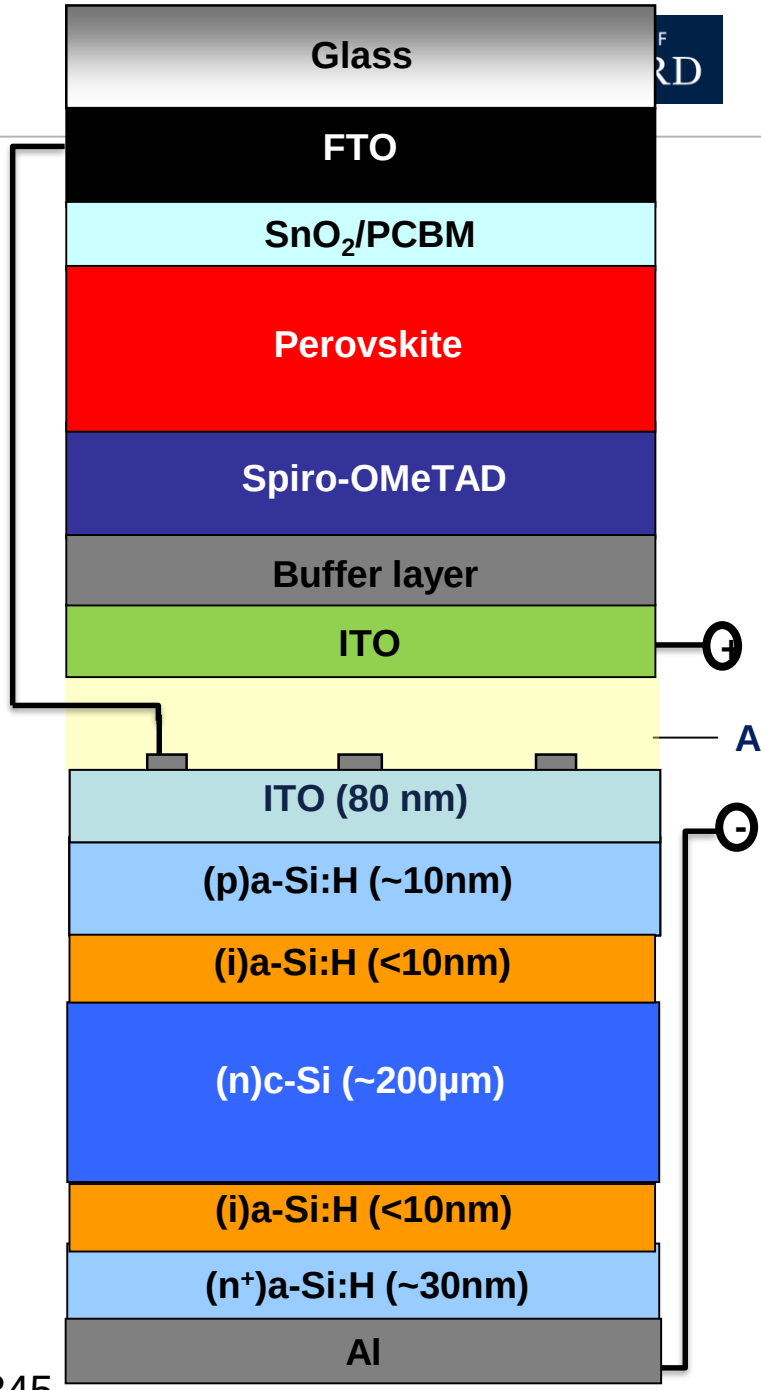
Perovskite on Si

Eg. See papers by Baliff et al and McGehee et al,



Simple 4-T configuration

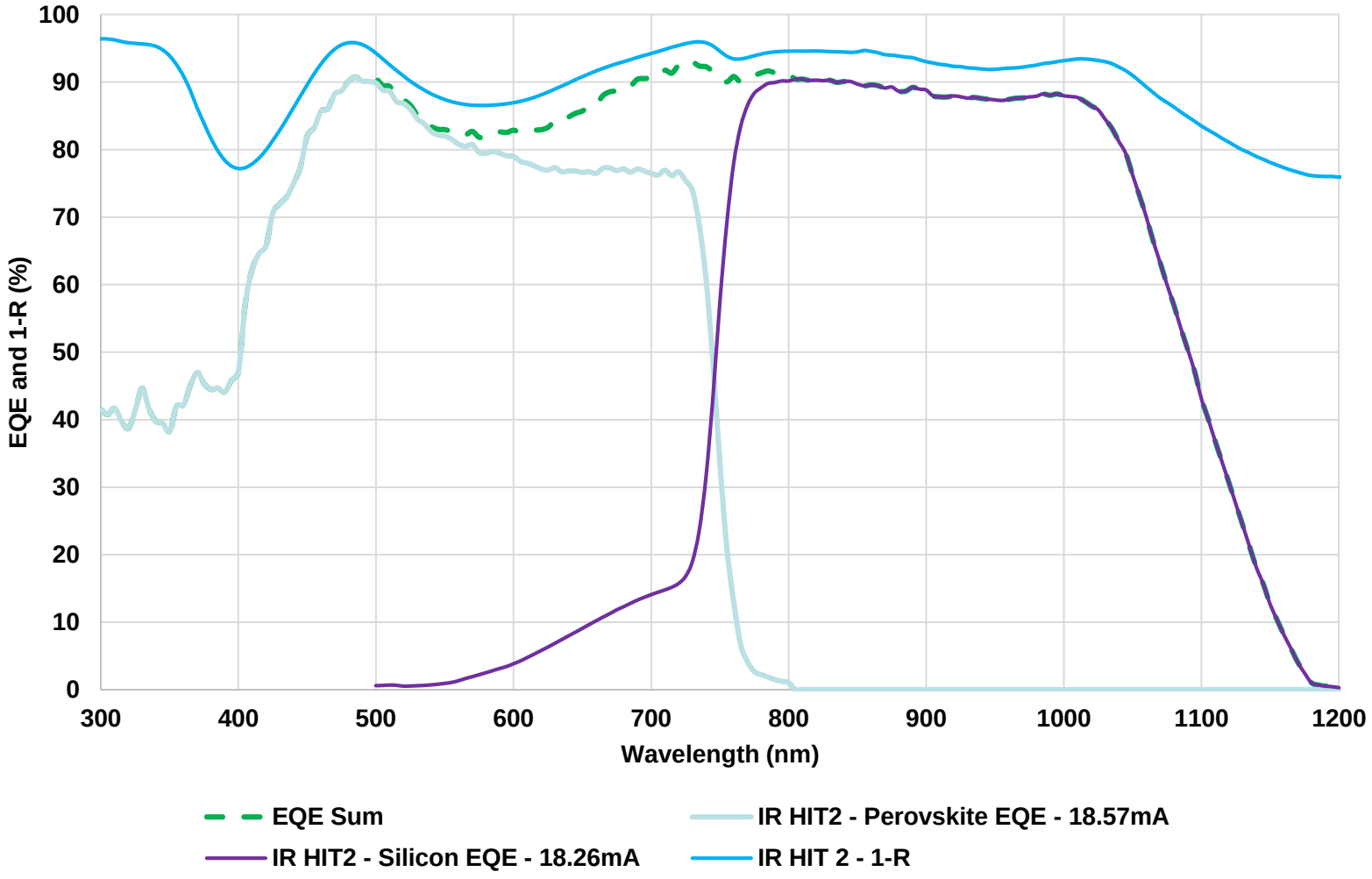




Demonstrates Feasibility for > 25% efficiency

D. McMeekin et al. *Science* 2016 DOI 10.1126/science.aad5845

Perovskite-on-Si Tandem EQE and 1-R



In collaboration with m. McGehee et al. in Stanford University

23.6%-Efficient Monolithic Perovskite/Silicon Tandem Solar Cells with Improved Stability

Kevin A. Bush[†1], Axel F. Palmstrom[†1], Zhengshan J. Yu[†2], Mathieu Boccard[2], Rongrong Cheacharoen[1], Jonathan P. Mailoa[3], David P. McMeekin[4], Robert L. Z. Hoye[3], Colin D. Bailie[1], Tomas Leijtens[1], Ian Marius Peters[3], Maxmillian C. Minichetti[1], Nicholas Rolston[1], Rohit Prasanna[1], Sarah Sofia[3], Duncan Harwood[5], Wen Ma[6], Farhad Moghadam[6], Henry J. Snaith[4], Tonio Buonassisi[3], Zachary C. Holman*[2], Stacey F. Bent[1], and Michael D. McGehee*[1]

[1] *Stanford University, Stanford, 94305, USA.*
[2] *Arizona State University, Tempe, 85281, USA.*
[3] *Massachusetts Institute of Technology, Cambridge, 02139, USA.*
[4] *University of Oxford, Oxford, UK.*
[5] *D2 Solar LLC, San Jose, 95131, USA.*
[6] *SunPreme, Sunnyvale, 94085, USA.*

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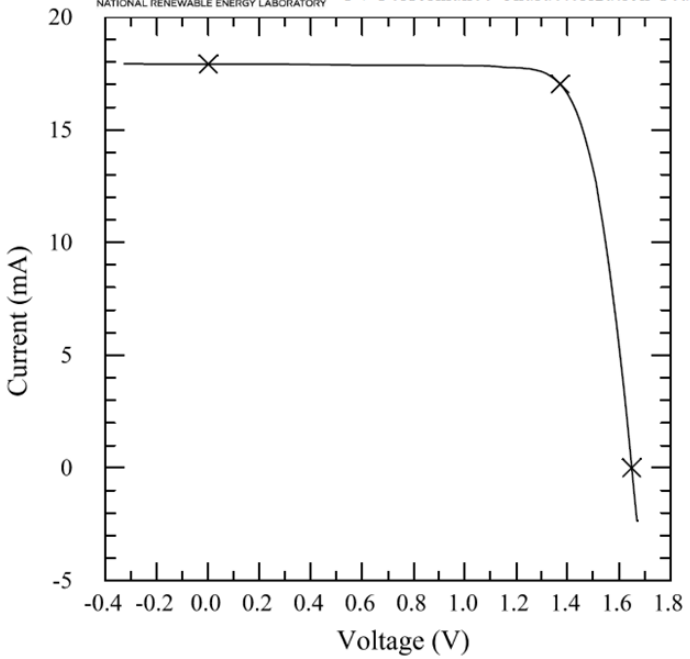
Stanford

Perovskite/HIT tandem Cell

Device ID: HIT4
2:16 PM 8/9/2016
Spectrum: ASTM G173 global

Device temperature: 25.0 ± 1.0 °C
Device area: 0.990 cm^2 ± 0.1%
Irradiance: 1000.0 W/m^2

NREL NATIONAL RENEWABLE ENERGY LABORATORY
OSMSS IV System
PV Performance Characterization Team

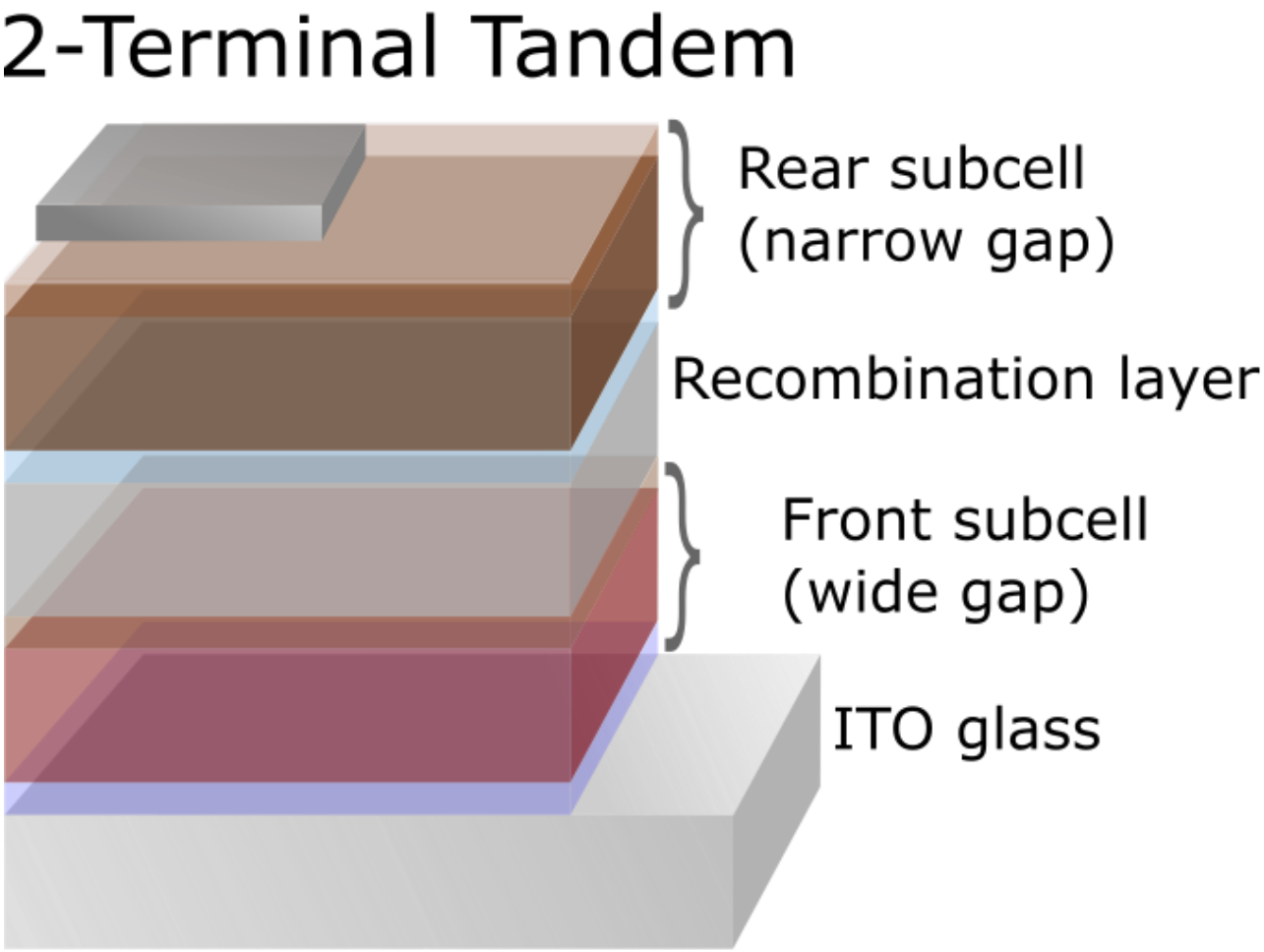


V_{oc} = 1.6506 V ± 0.6%
I_{sc} = 17.910 mA ± 1.3%
J_{sc} = 18.093 mA/cm^2 ± 1.3%
Fill Factor = 79.0 % ± 0.3%

I_{max} = 17.023 mA ± 1.3%
V_{max} = 1.3712 V ± 0.6%
P_{max} = 23.342 mW ± 1.4%
Efficiency = 23.58 % ± 1.4%

10.0 seconds per data point

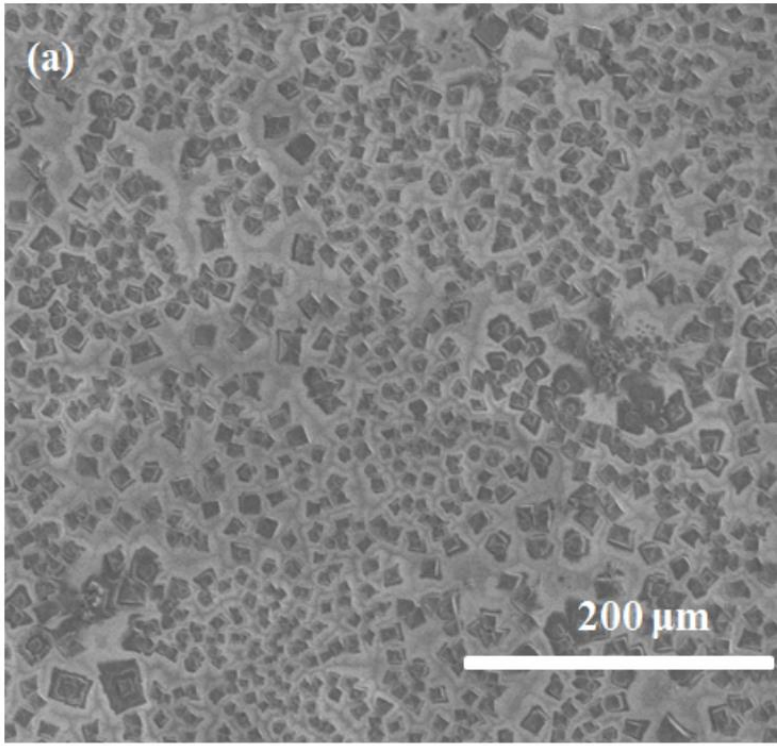
Can we go to “All-Perovskite” tandem



We need a low band gap perovskite cell

1.2eV planar devices?

1:1 MAI:SnI2 in DMF?

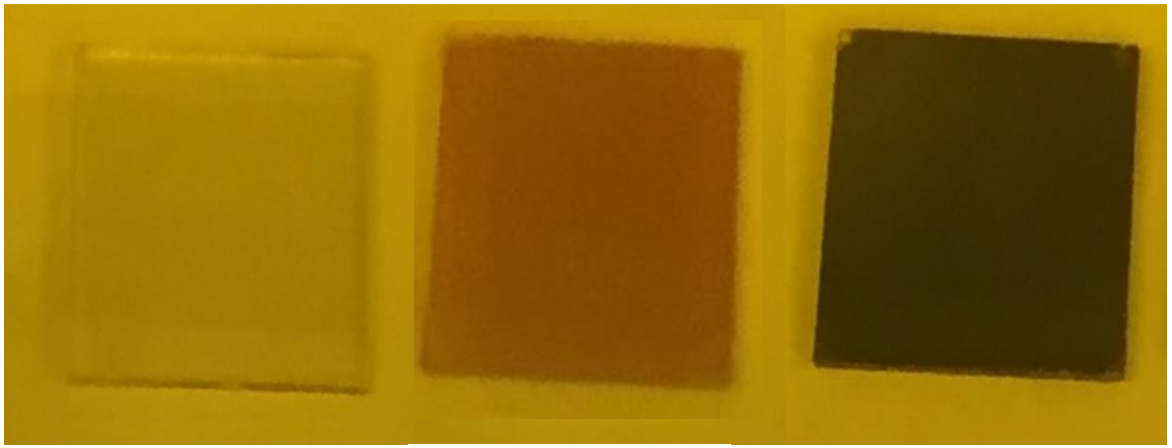


…not so promising morphology.

Tin-based materials seem to crystallise very rapidly, during spin-coating

Noel et al, EES 2014

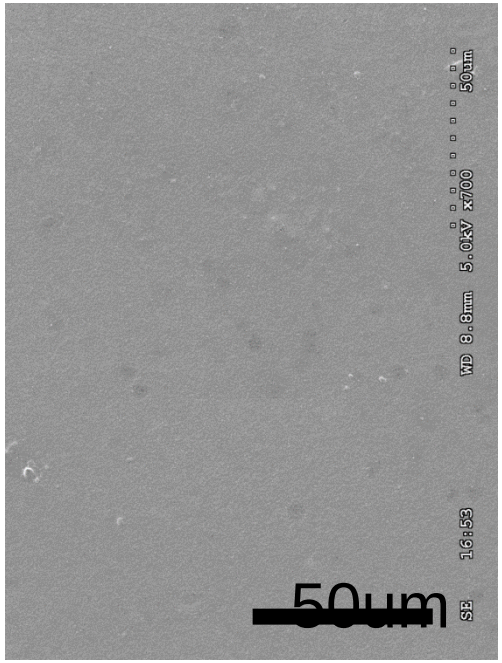
Precursor-phase Antisolvent Immersion for high quality films

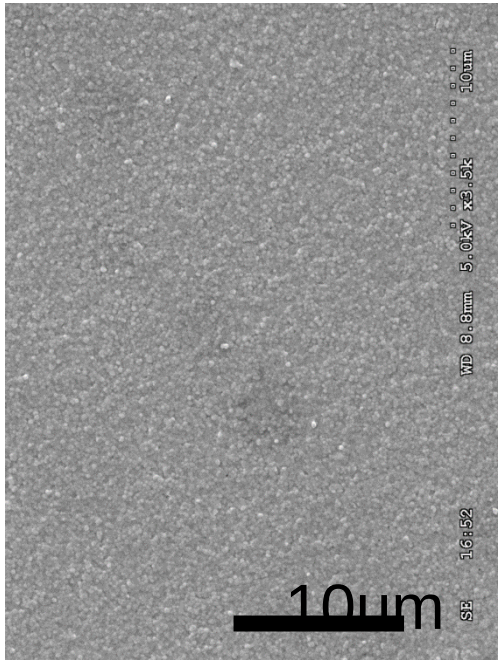


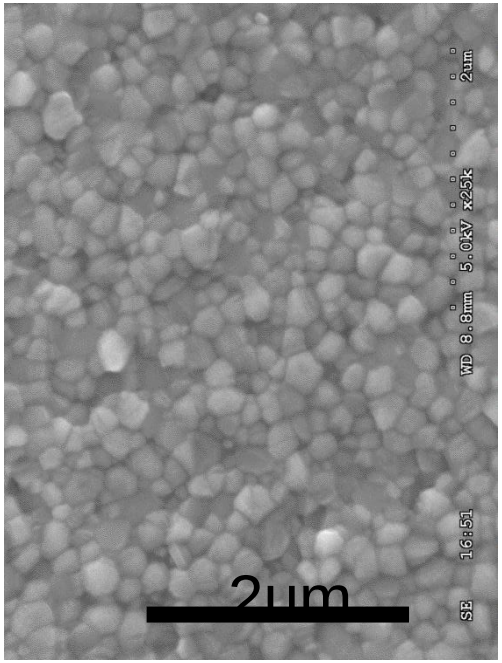
1. After spin-coating

2. After immersion in anisole bath

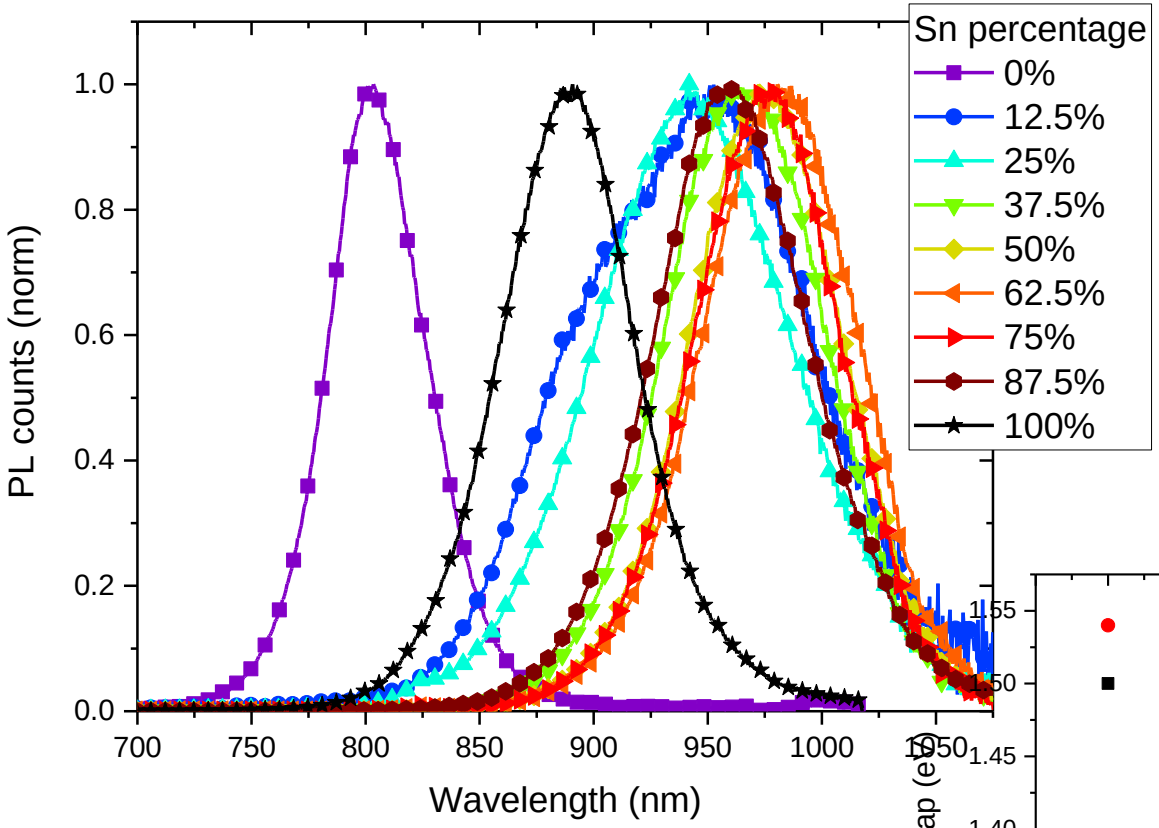
4. After annealing.

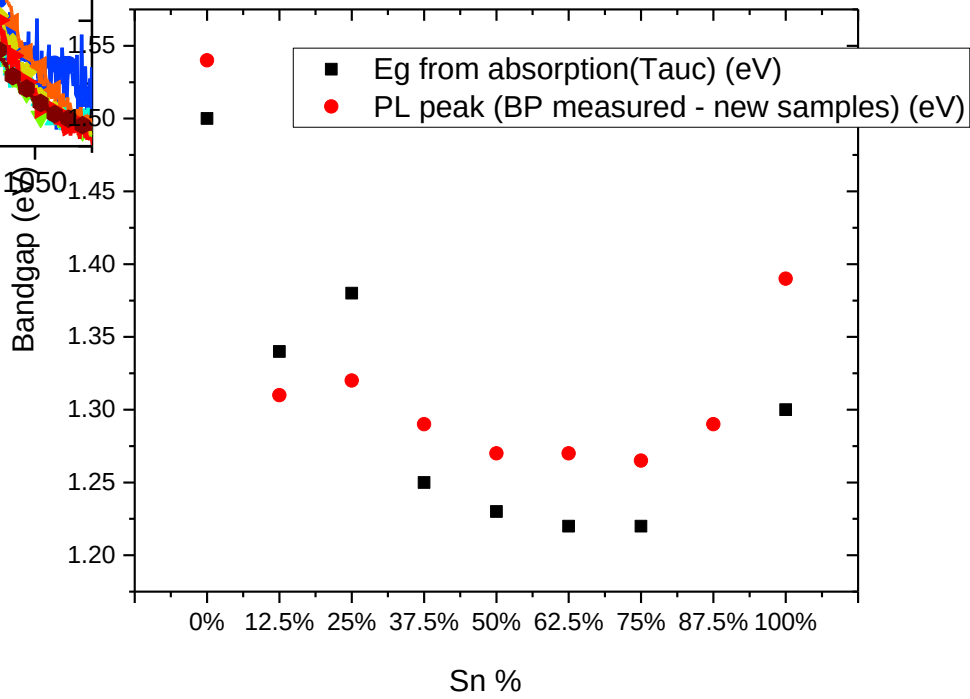




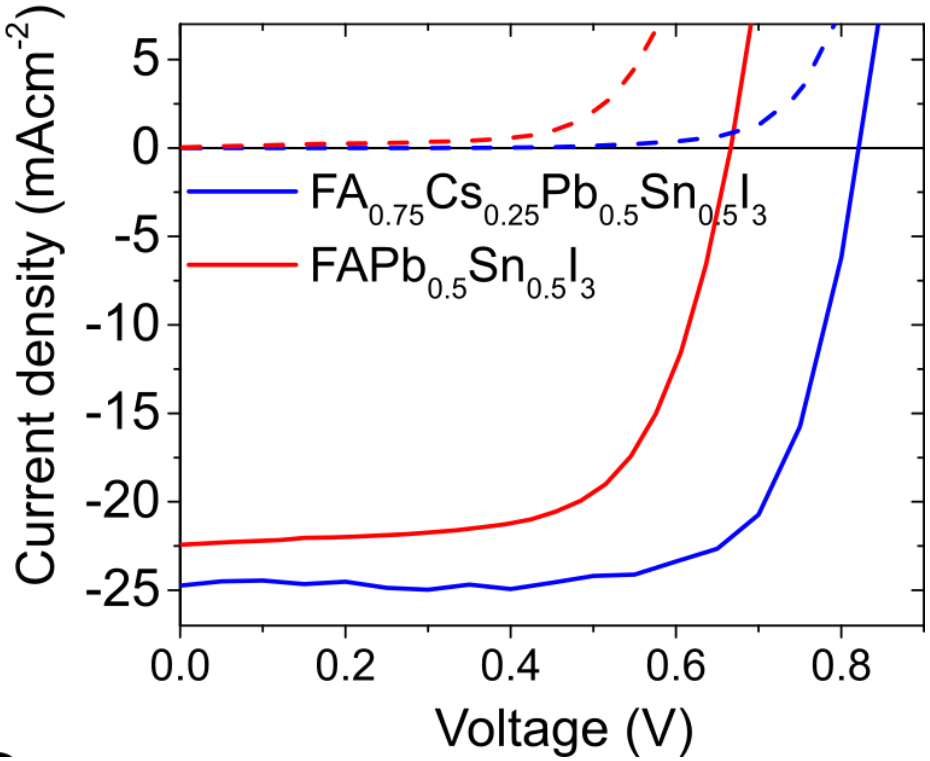


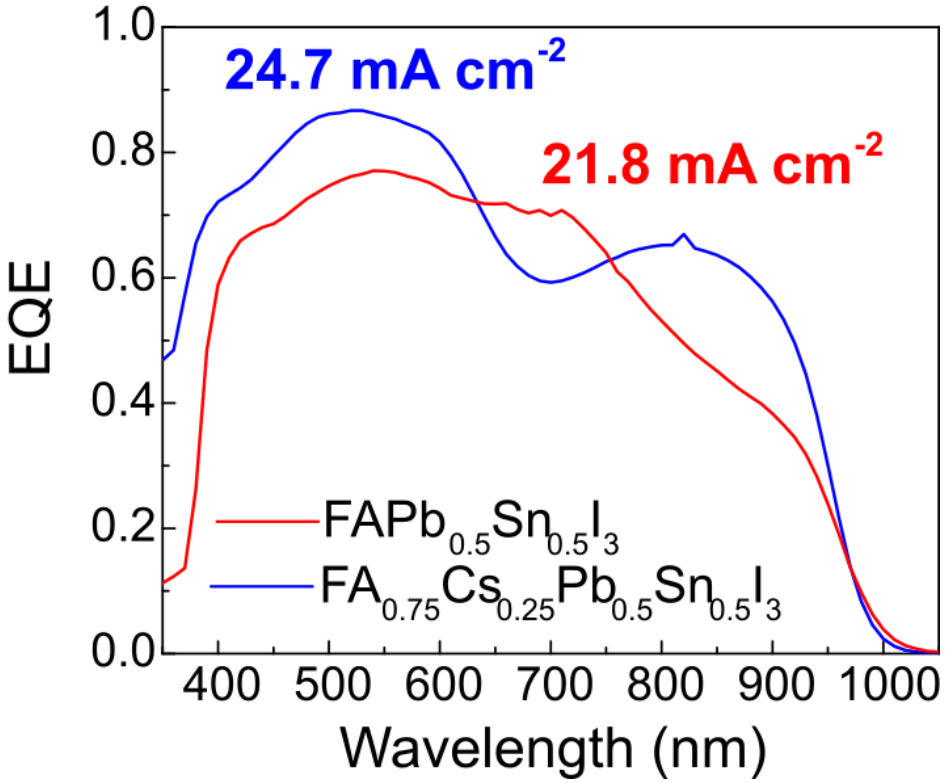
$FAPb_{1-x}Sn_xI_3$: Photoluminescence





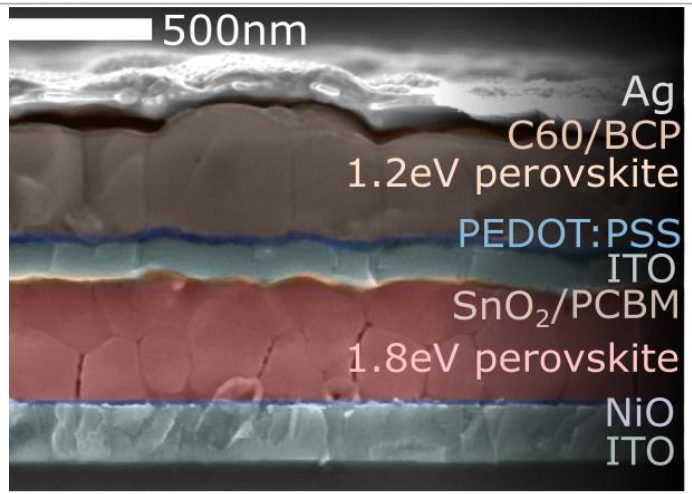
Cs addition enables a very high V_{OC} for a 1.2 eV band gap material

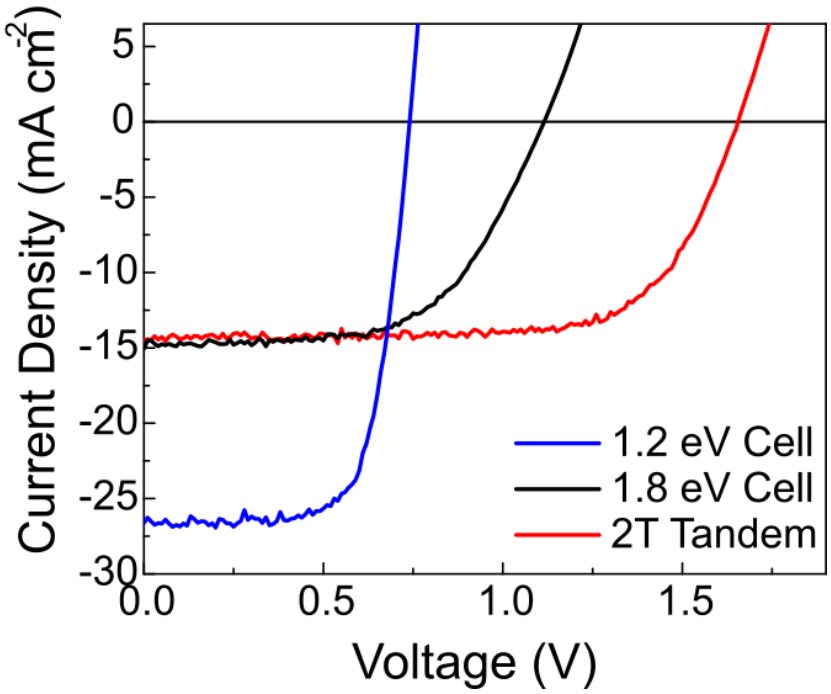


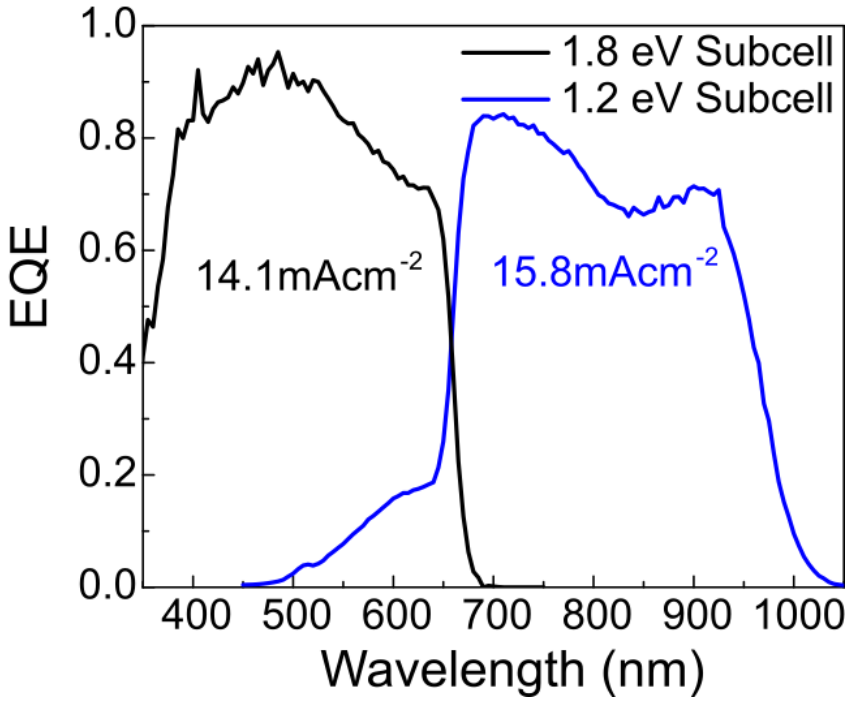


G. Eperon et al. Science 2016

All perovskite tandems

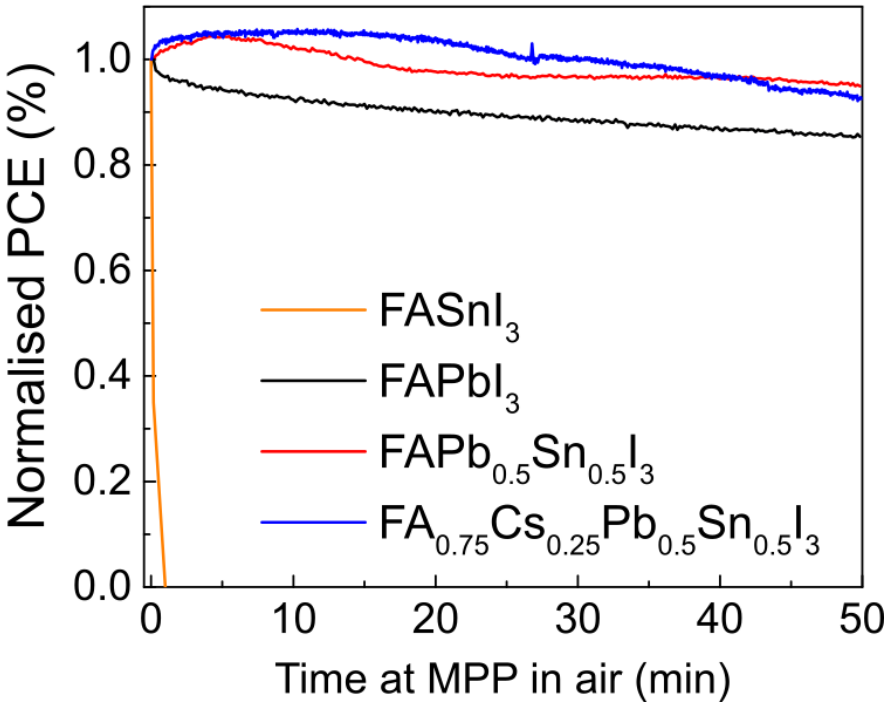


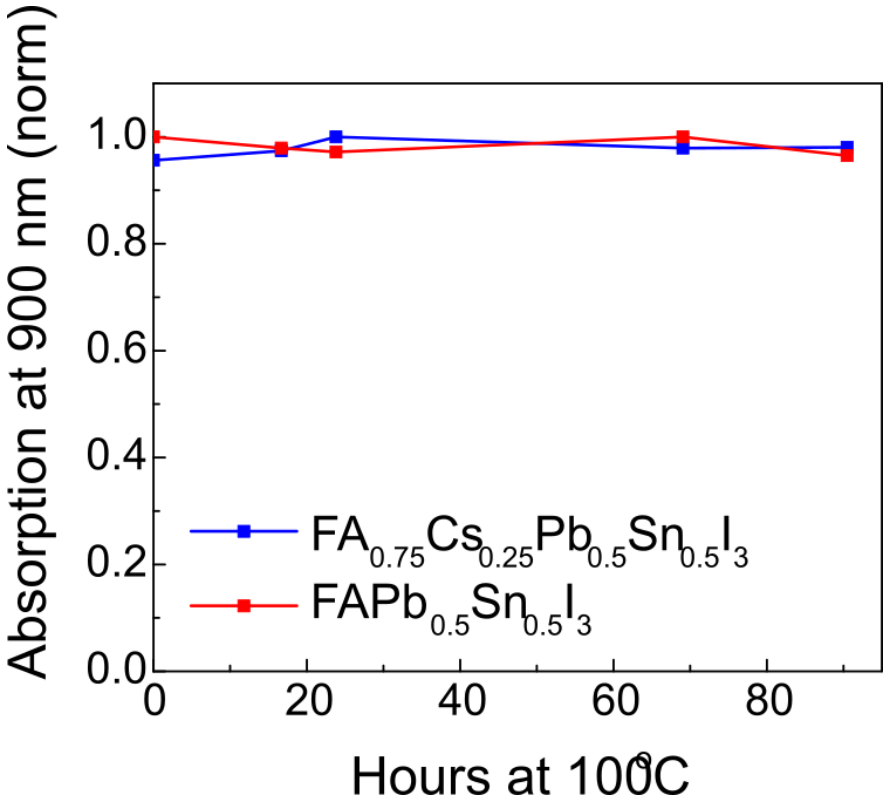




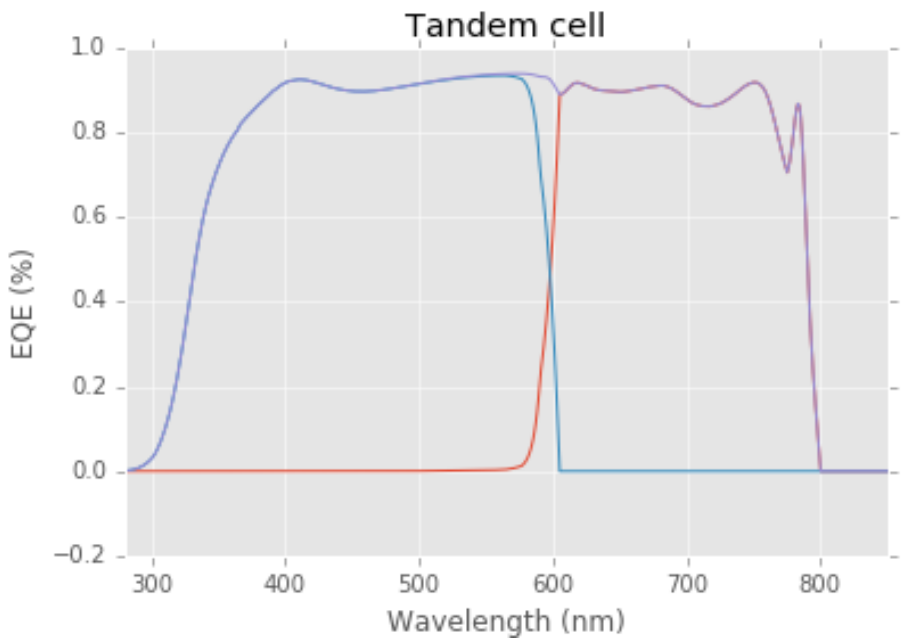
G. Eperon et al. Science 2016

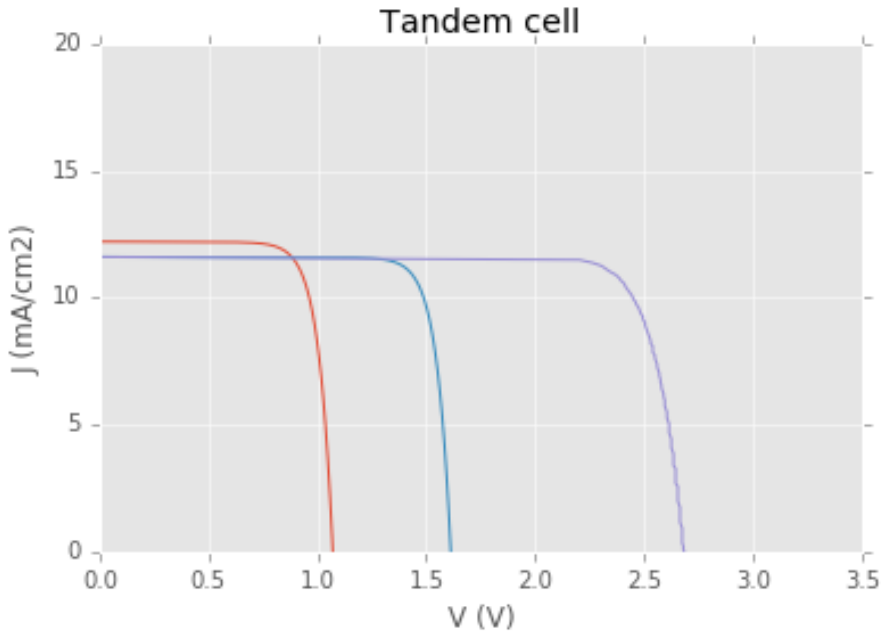
Sn-Pb devices show unprecedented stability





Is it worth “going tandem” without the low gap perovskites?



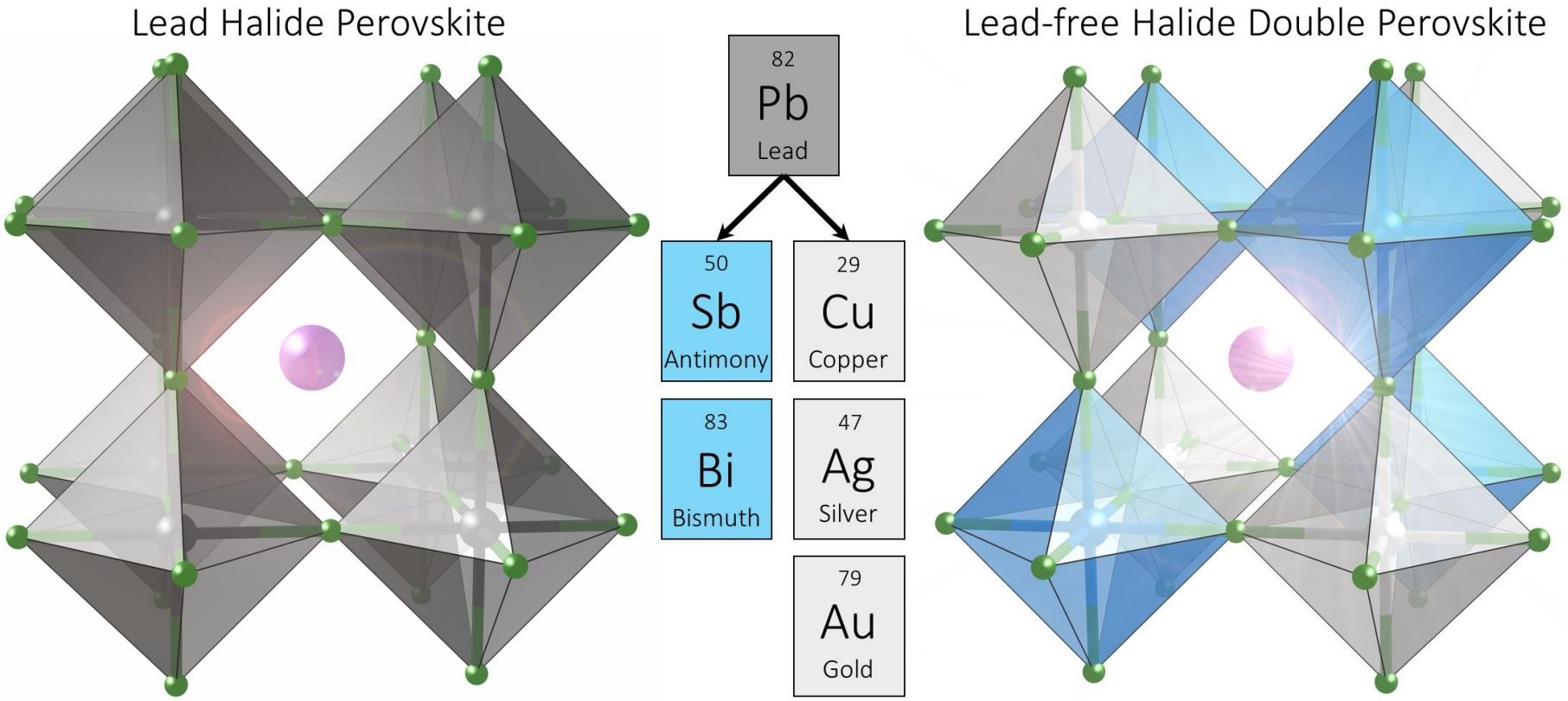


Calculated EQE and JVs assuming KRICT record cell parameters

PCE	FF	Voc	Jsc	Jmpp	Vmpp
25.94	0.83	2.69	11.61	11.26	2.30

A **22.1%** $APbX_3$ single junction becomes a **25.9%** $APbX_3/APbX_3$ tandem
Target: cell with a band gap of 2.06eV and V_{oc} of 1.59V
On Silicon, a **30.1%** hybrid-tandem becomes a **33.6%** “triple junction” (+ 0.7V Voc due to Si rear, and FF boost to 0.85)

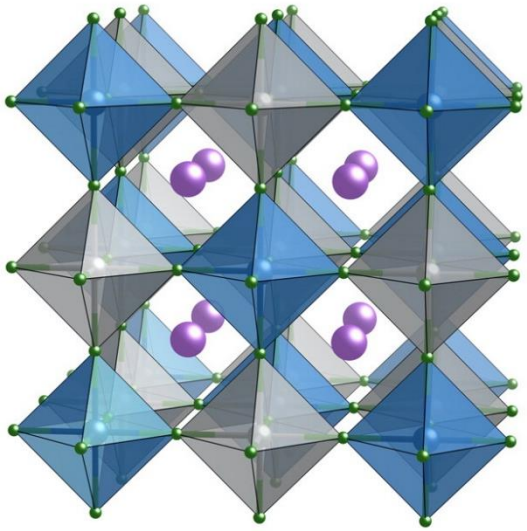
Beyond Group XIV elements:



G. Volonakis et al. JPCL 2016
ALSO See: Slavney, A. H et al. JACS 2016
McClure, E. T. et al. Chem. Matter. 2016

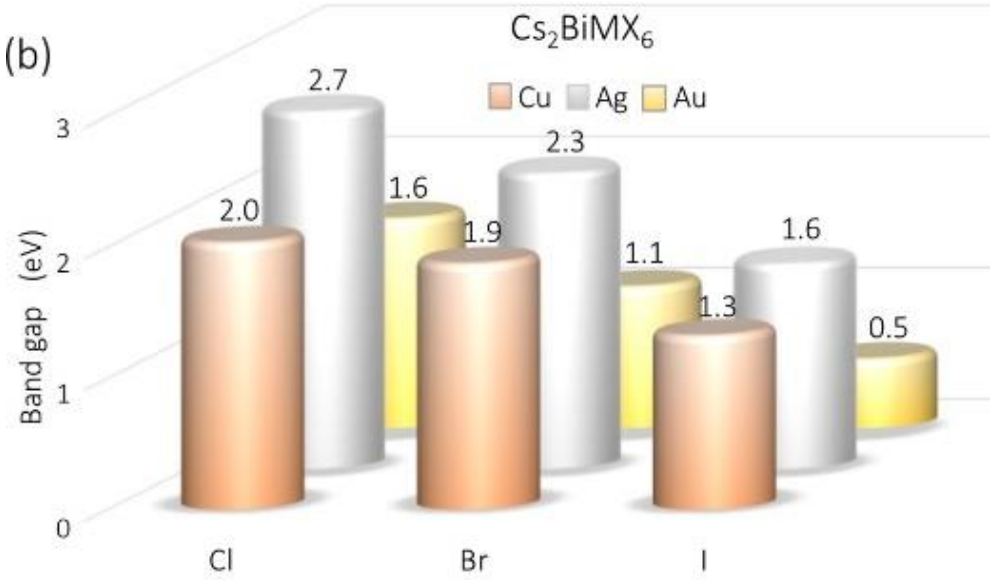
Calculated Band-gaps and effective mass

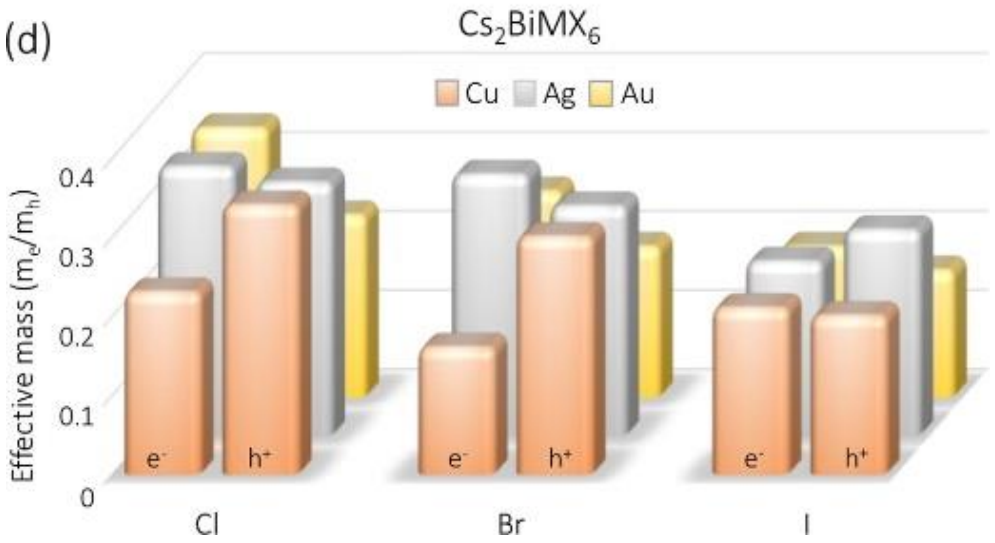
Conventional Cell



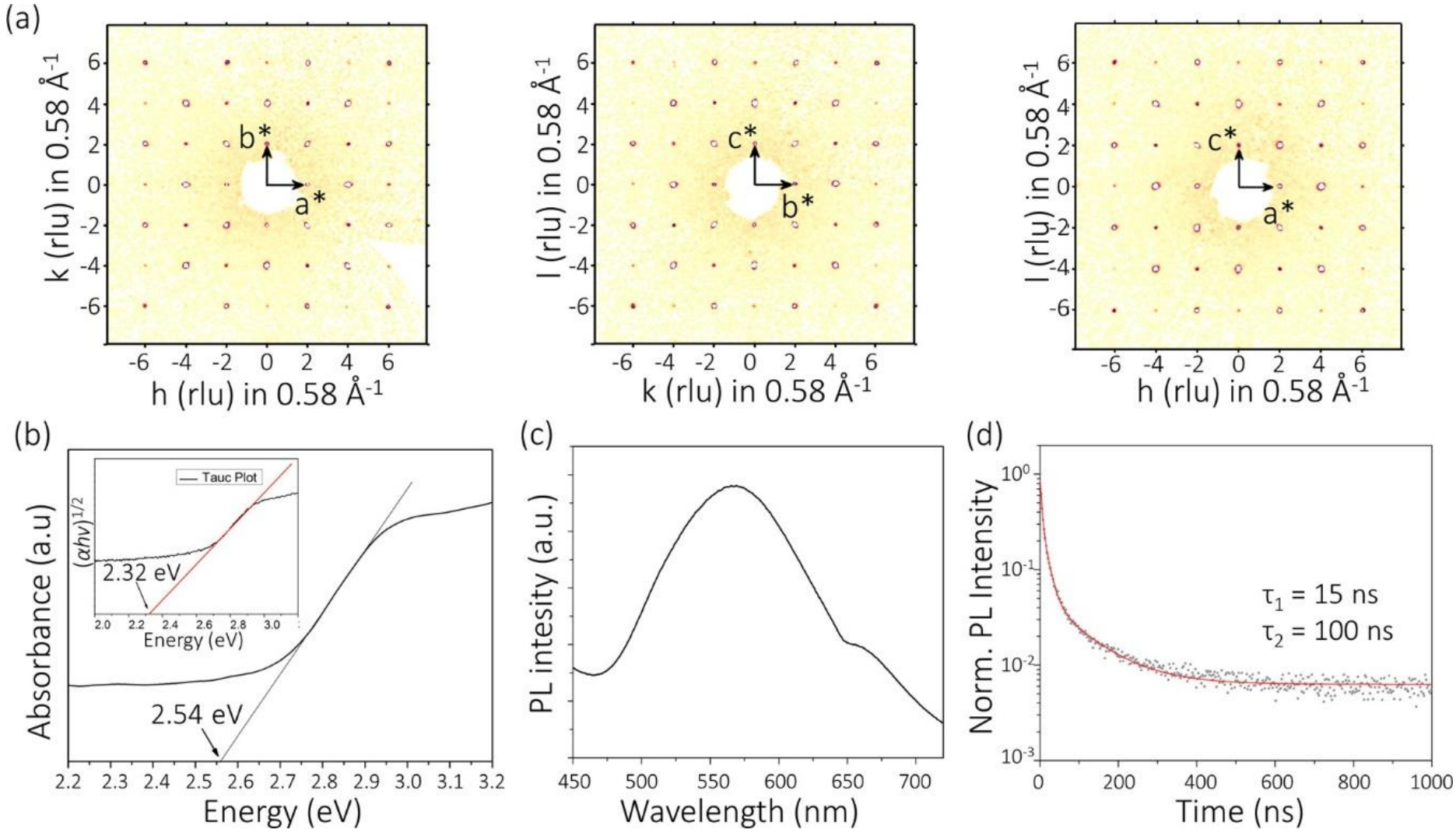
$Cs_2B'B''X_6$

B': Cu, Ag, Au
B'': Sb, Bi
X: Cl, Br, I





Single Crystal Data



G. Volonakis et al. JPCL 2016

Commercialisation

Device and mini-module development

Present Target:

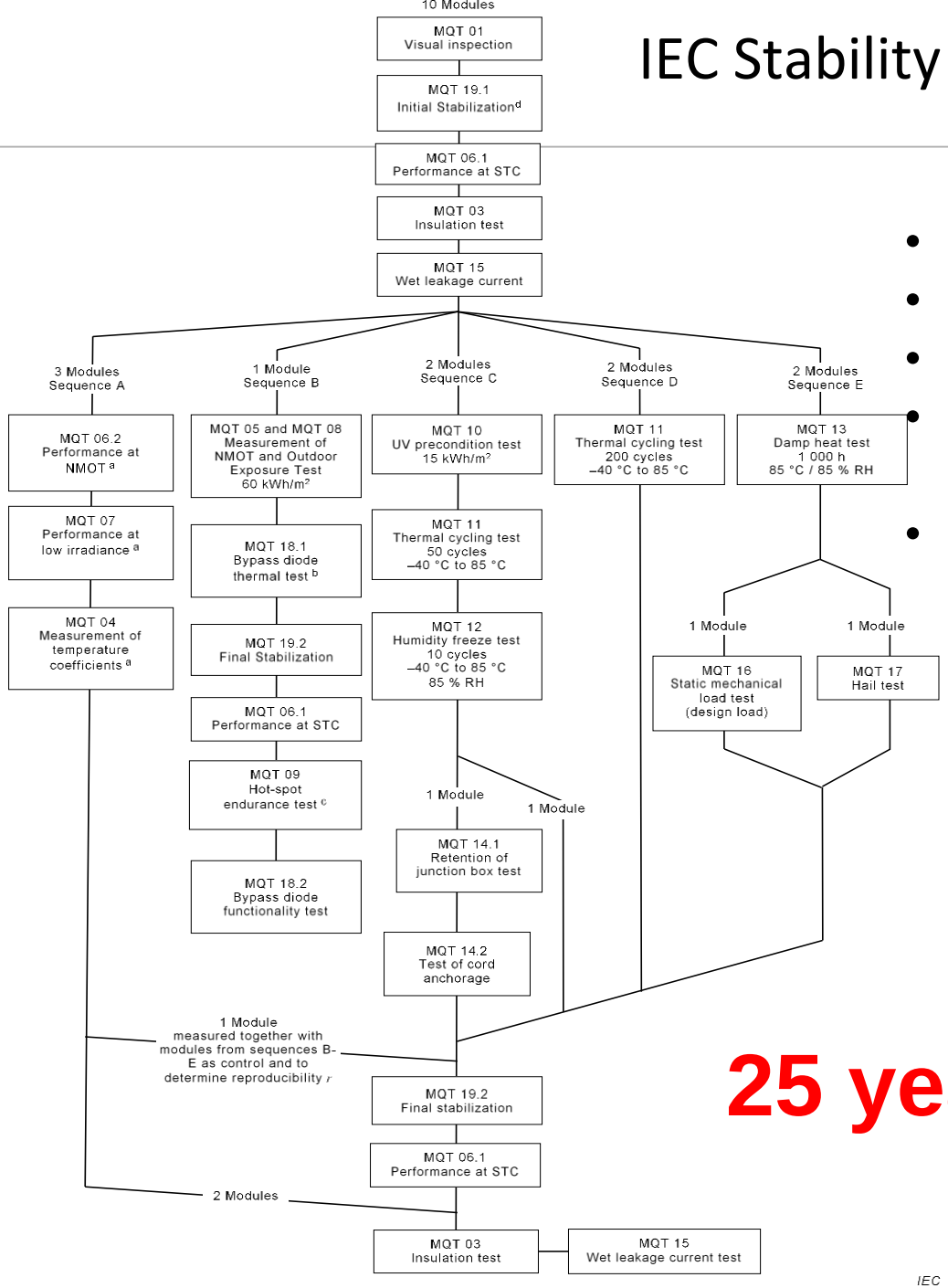
- Develop stable and efficient materials stack
- Develop processing methodology to deliver Efficient perovskite/Silicon tandem cells at high yield
- Partner with existing Si-PV industry to manufacture

Test and reliability laboratory

Requirements:

- Climatic testing to IEC61646
- -85℃/85% RH >1000hrs
- +85 to -40℃ cycling >200 cycles
- “Full Spectrum” Light soaking to AM1.5G 3000hrs (not IEC)
- High UV exposure
- Etc etc etc

IEC Stability testing



- 85℃ for 1000's of hrs
- 85℃ 85% RH for 1000's hrs
- High levels of UV light exposure
- Thermal Cycling from -40 to +85℃
- Full sun light exposure at 60 to 85C

Important note:

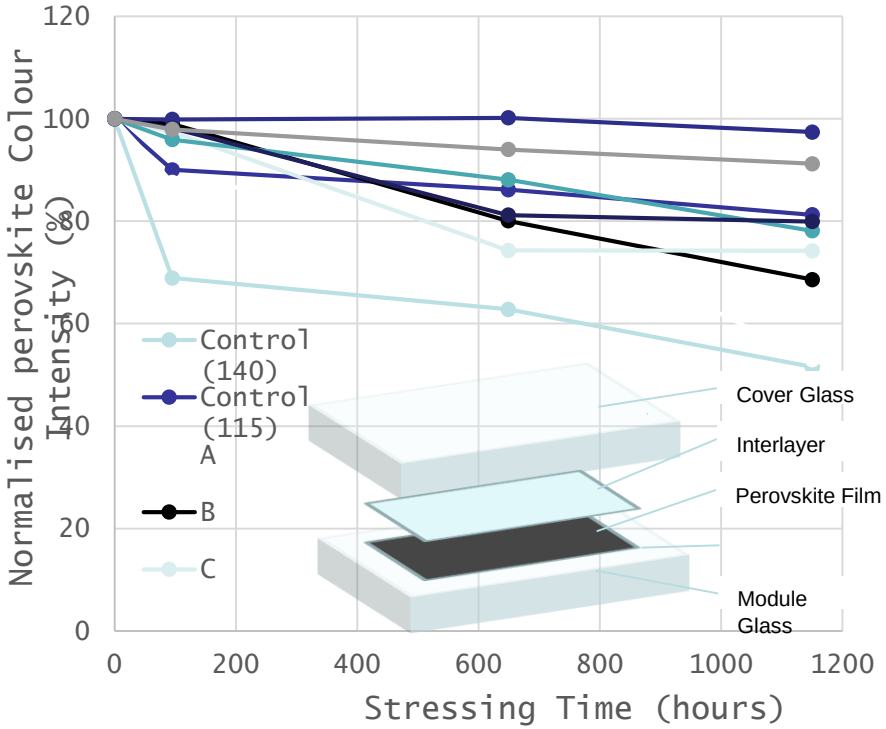
IEC = 1000hrs

25 years = 218,850 hrs

IEC

Proper Encapsulation of Cells

Encapsulation selection using 1000hr 85°C/85% baseline



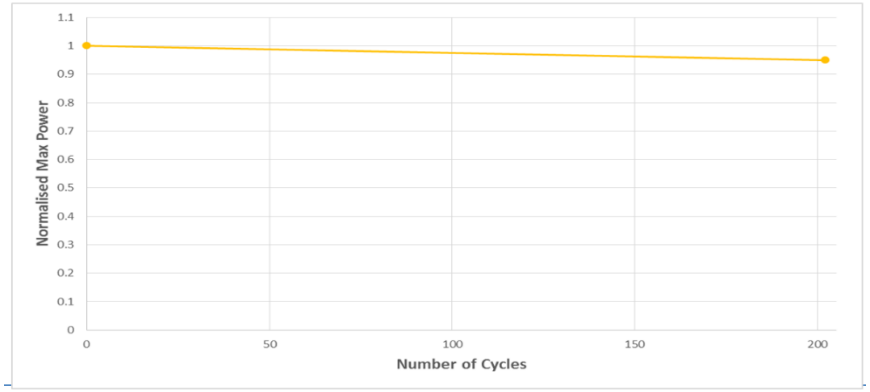
Moisture ingress accelerates degradation

Perovskite layer degradation by moisture ingress after early lamination failure

OXFORD PV

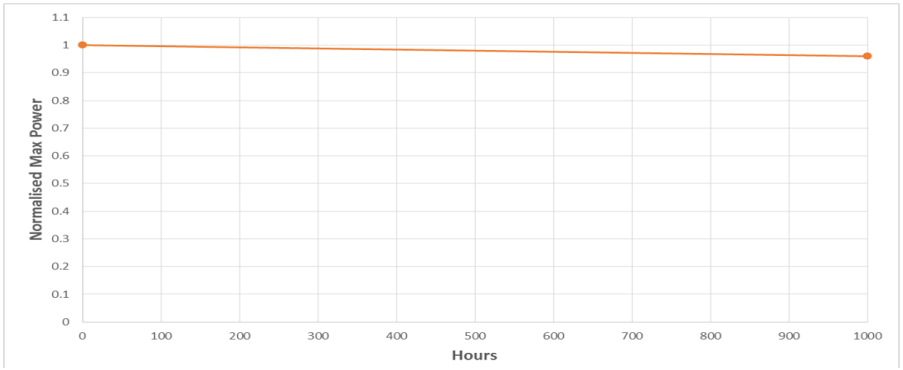
Stability: IEC61646 Results

200 thermal cycles (-40°C to +85°C) with < 5% drop achieved



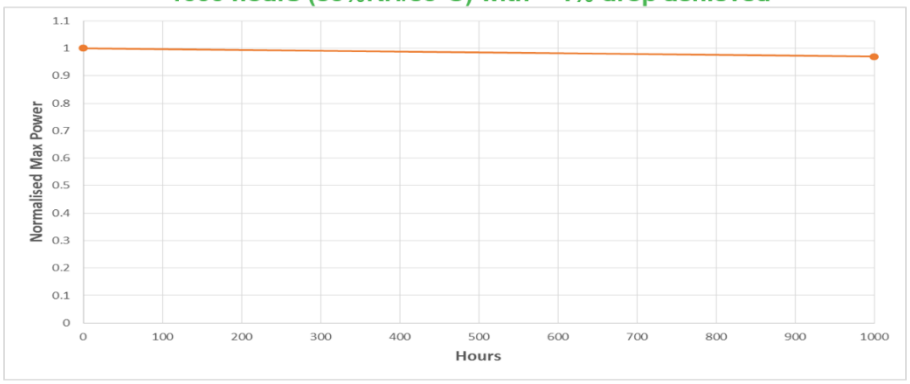
Thermal Cycling: Pass

1000 hours (60°C light soak) with < 5% drop achieved



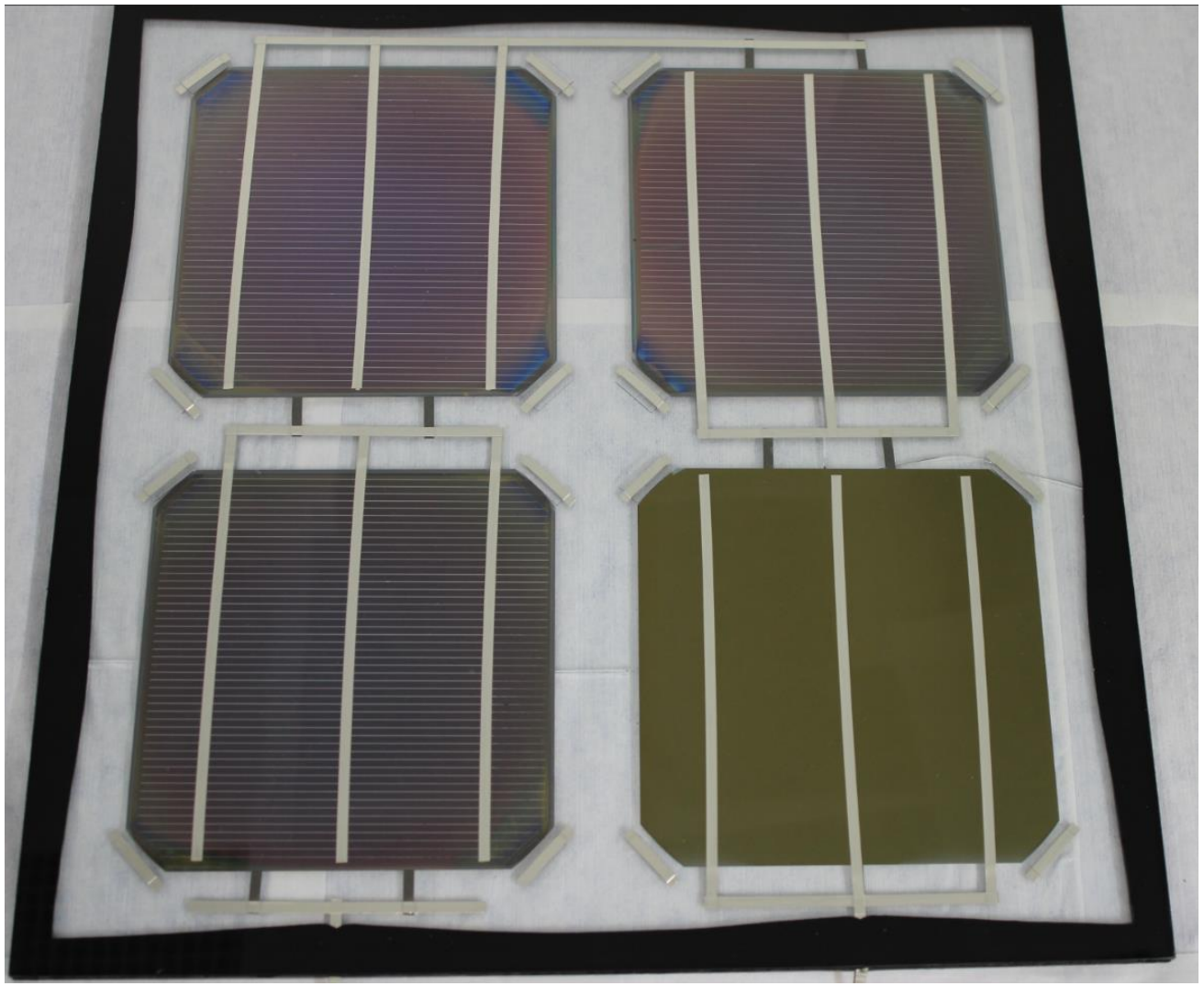
Full sun light soaking: Pass

1000 hours (85%RH/85°C) with < 4% drop achieved



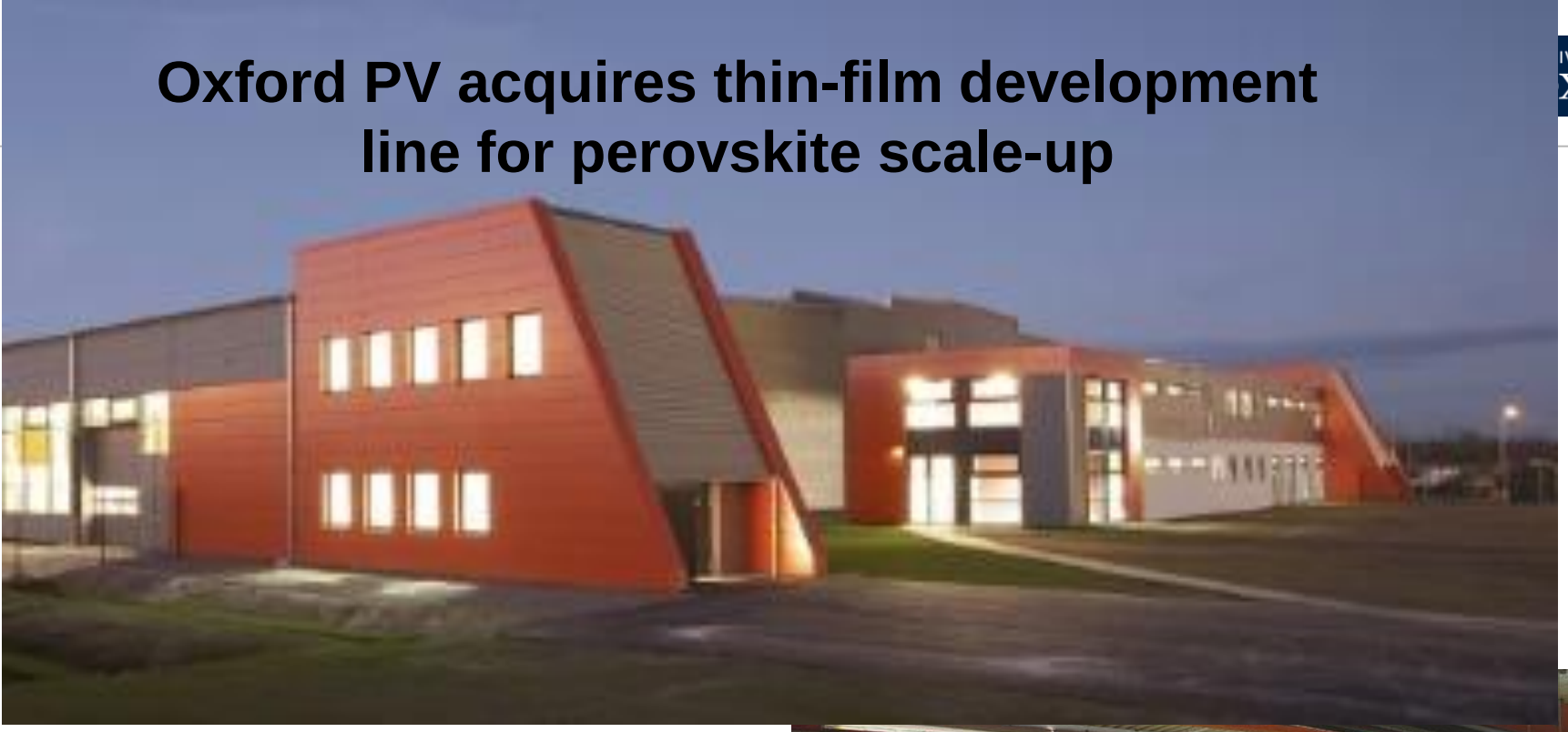
Damp heat: Pass

Next Steps: Development Through to Manufacturing



OXFORD PV

Oxford PV acquires thin-film development line for perovskite scale-up



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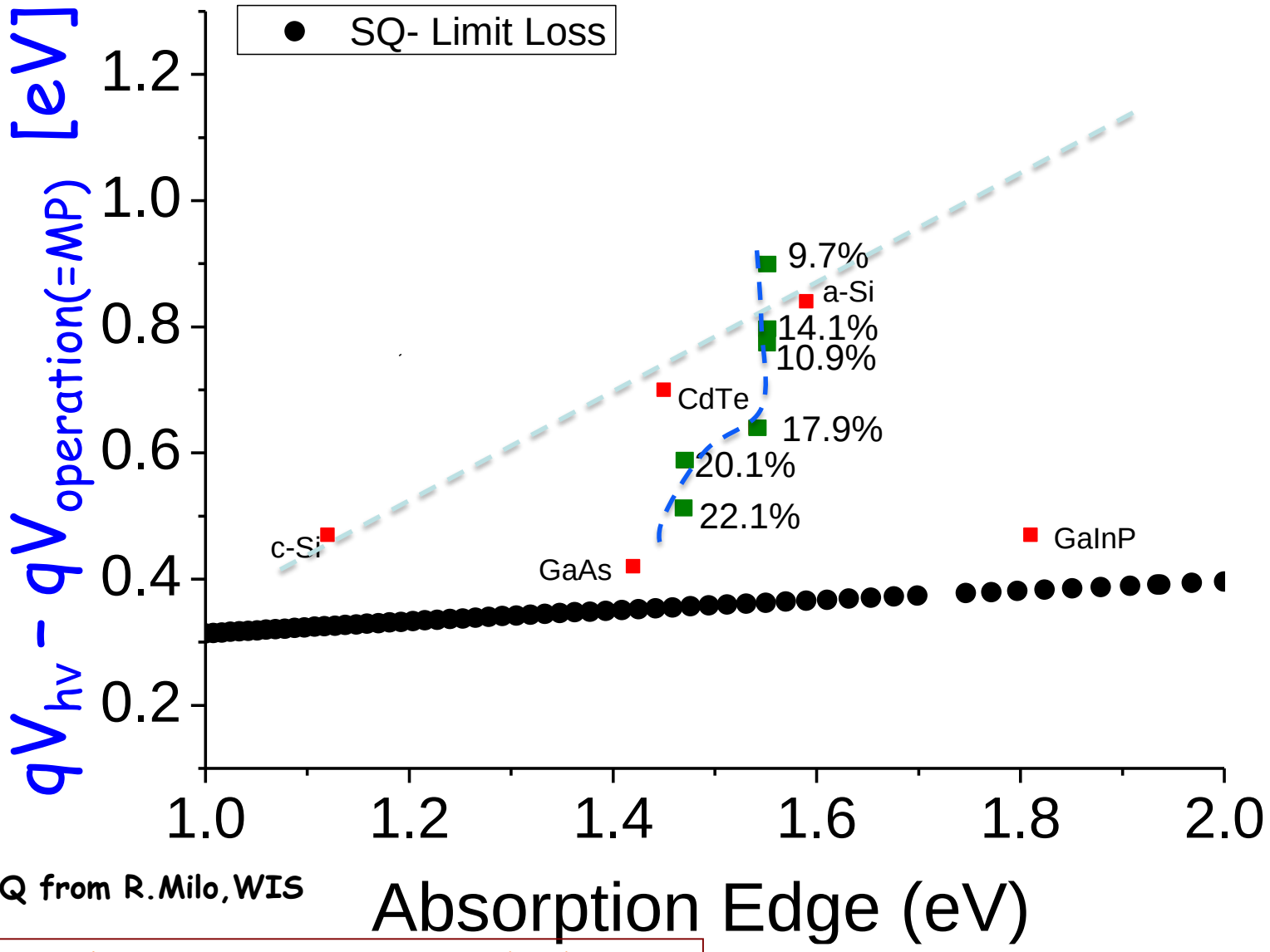
OXFORD PV

It has acquired the production site previously operated by Bosch Solar CISTech GmbH. The site, located in Brandenburg an der Havel, Germany, will be equipped to provide modern, pilot-scale capacity to scale-up Oxford PV's perovskite technology to industry-standard wafer size and to perfect the manufacturing processes necessary for commercial deployment.

Evolution of Operational loss in perovskite cells

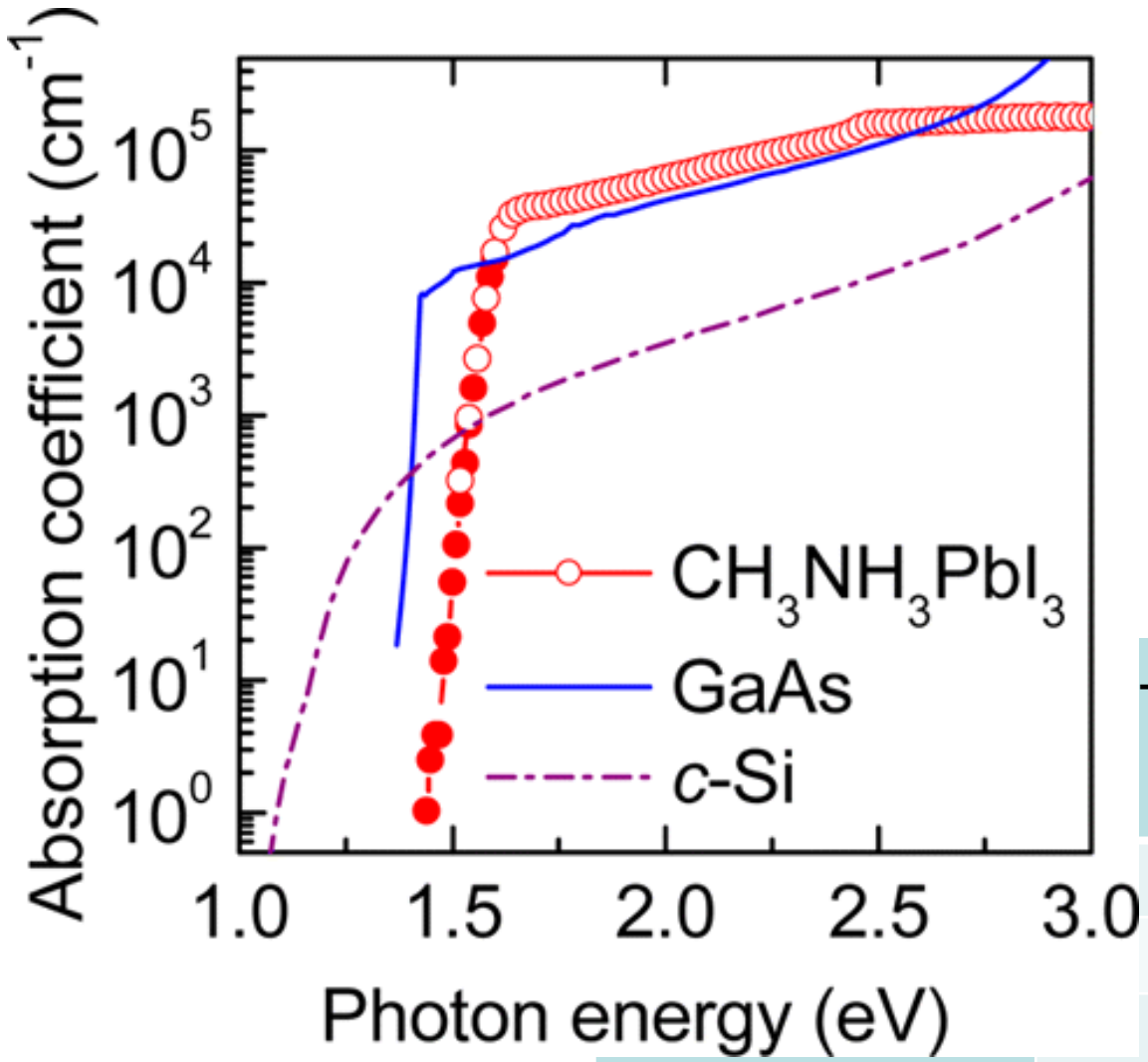


S-Q from R.Milo,WIS

Nayak et al. *Adv. Mater.*, 5-2011,3-2014; updated 09-2016

Why are metal halide perovskites such good solar cell materials???

Sharp and strong absorption edge



Urbach energy as low as 13 meV

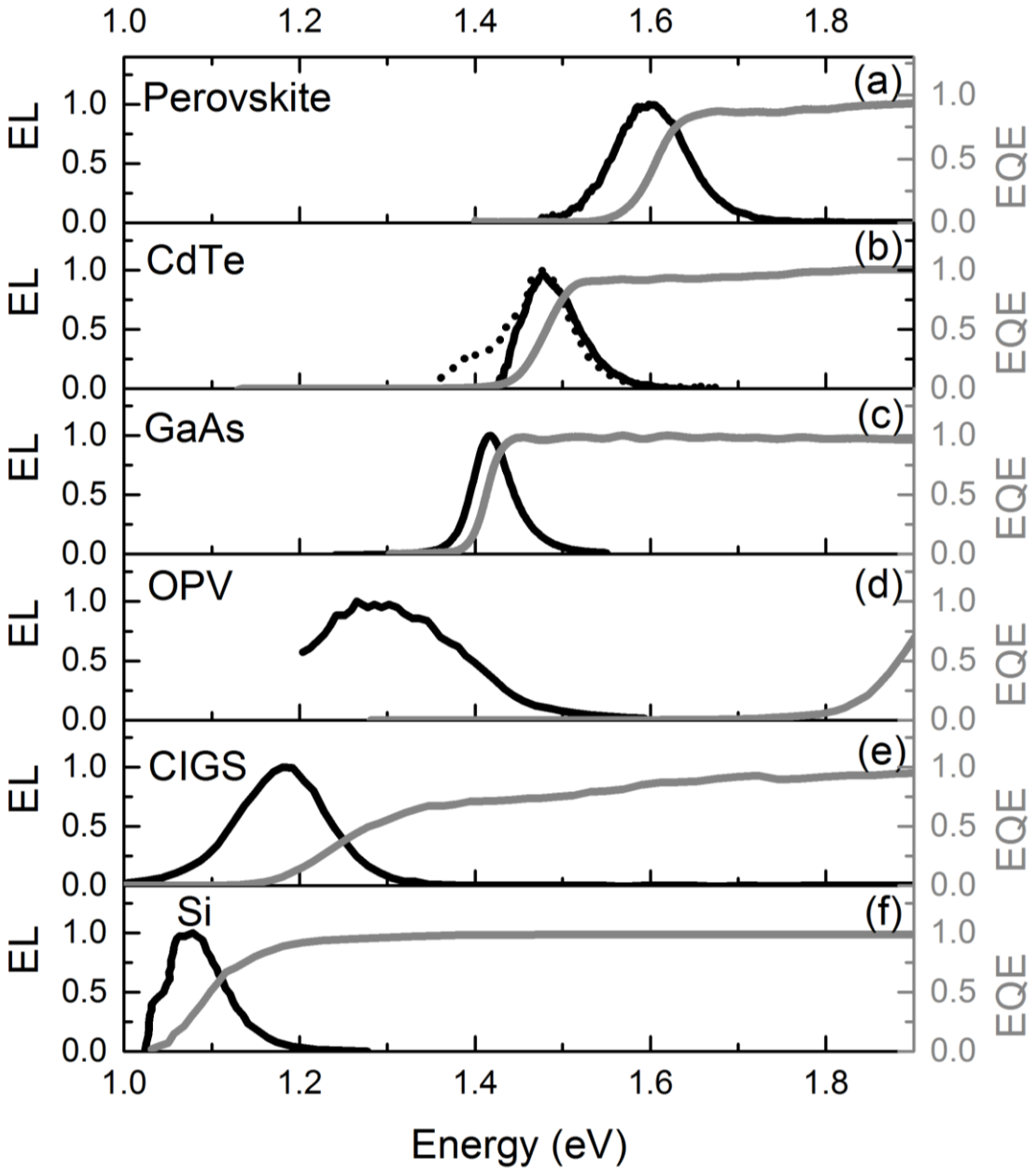
Steepness of absorption edge depicts quality of semiconductor

Steeper = lower disorder = higher voltage

Technology	Urbach Energy (meV)
GaAs	7
c-Si	11
Perovskite	15
CIGS	25
Organics	25-50

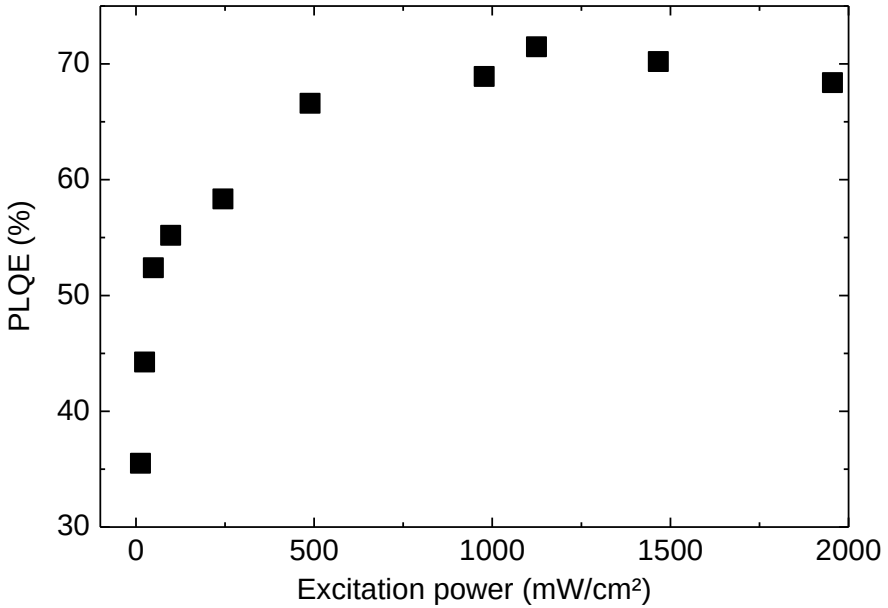
Christoph Baliff and co workers JPCL 2014 5 (6), pp 1035–1039

Electroluminescence vs Absorption onset.

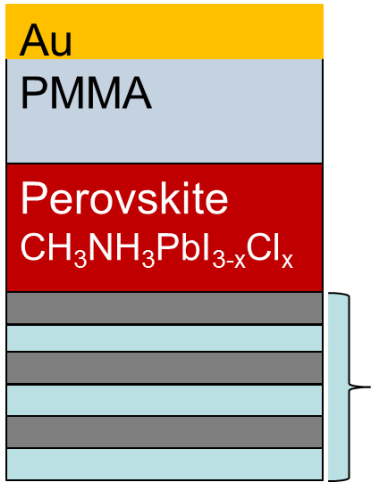


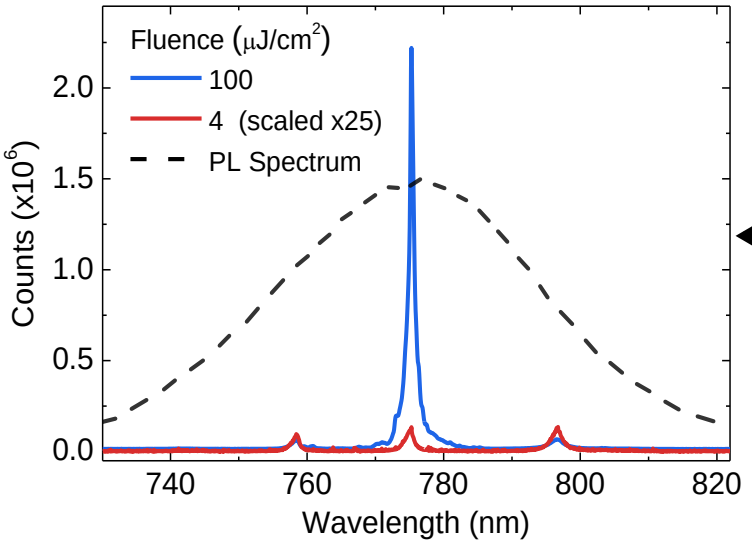
PLQE and lasing!!

Very High **Photo Luminescent quantum yield** → Negligible non-radiative decay



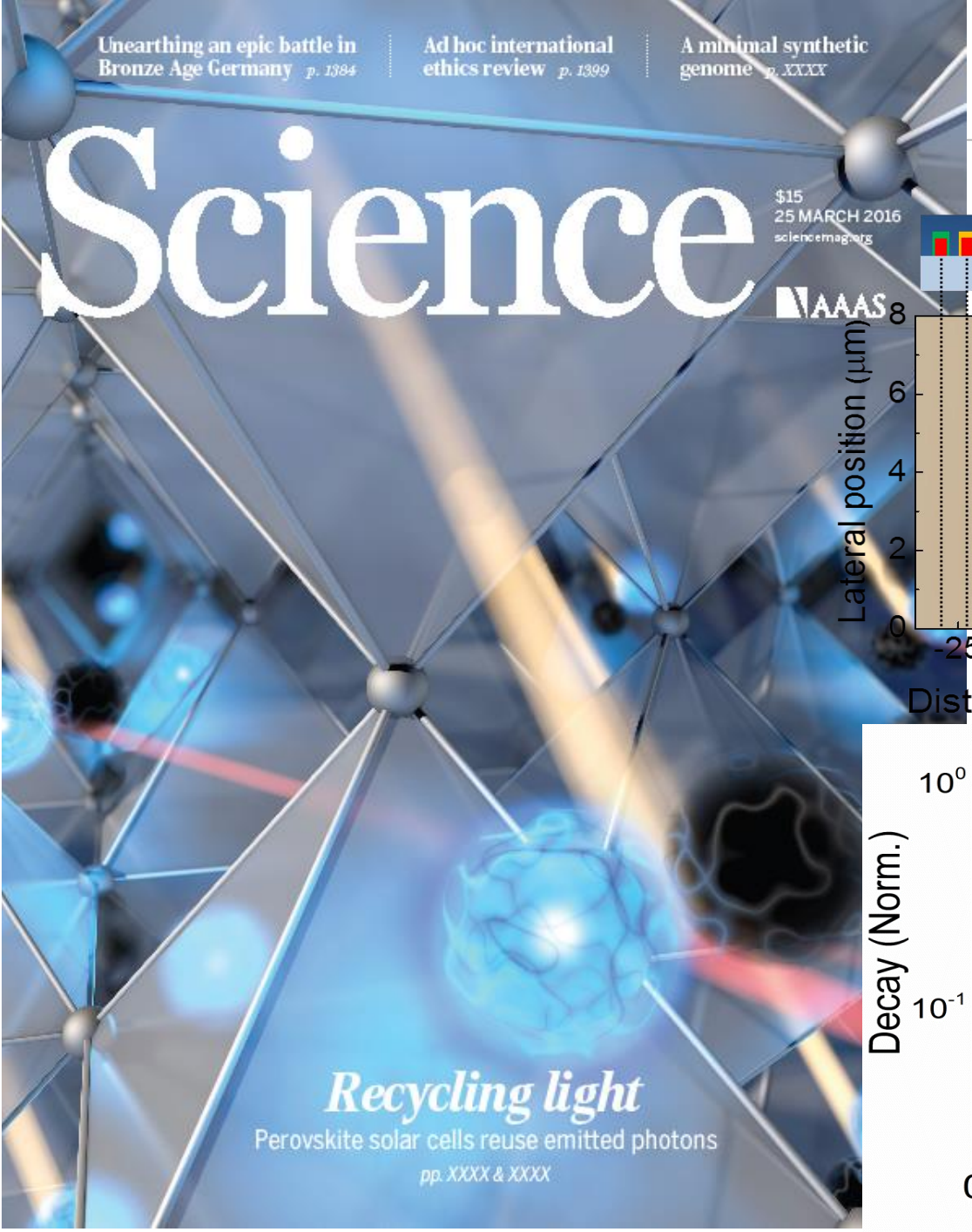
Micro-cavity





Even **room temperature lasing** of as cast films within a cavity

Felix Deschler et al. JPCL 2014



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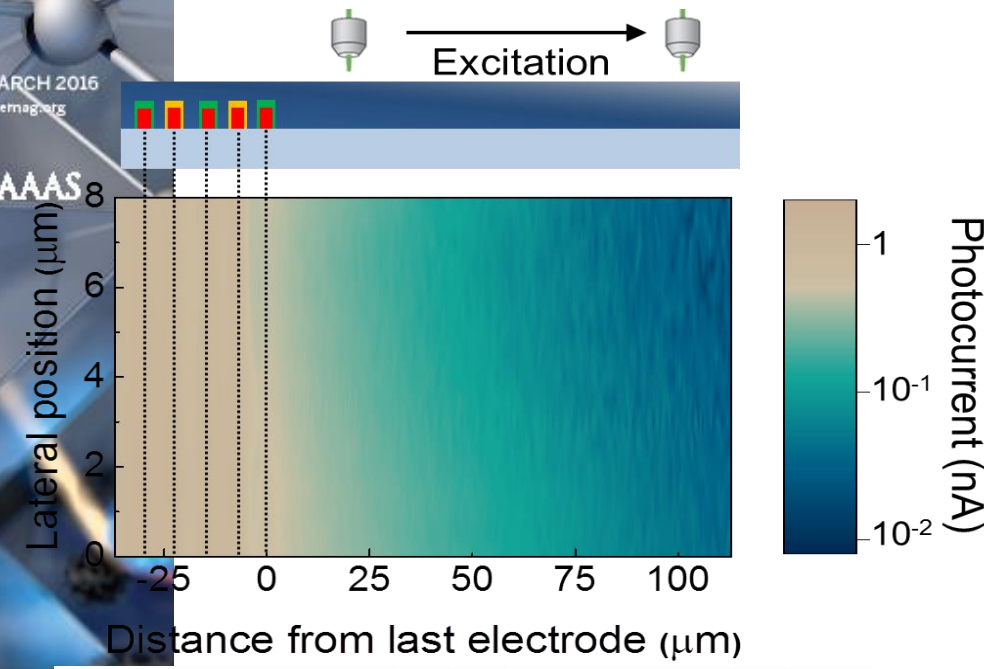

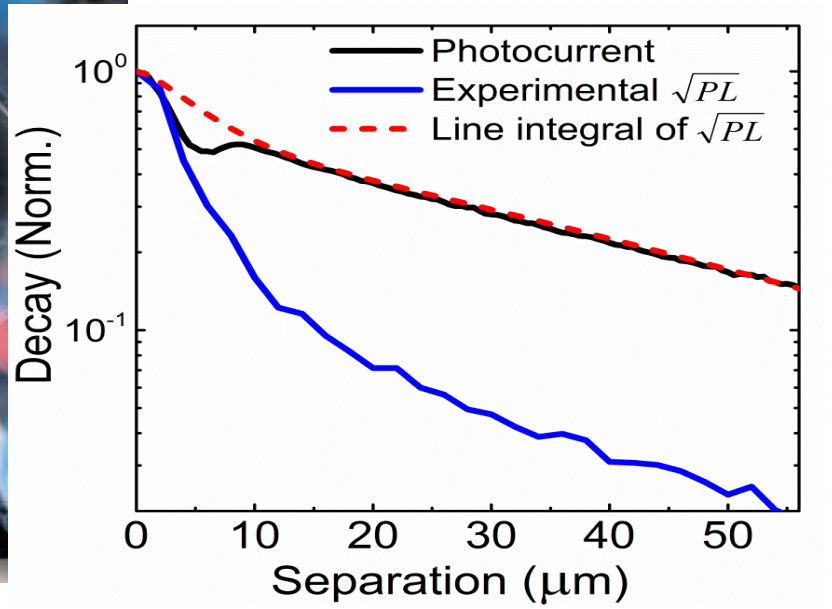

Acknowledgements

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Oxford: Laura Herz, Michael Johnston, Robin Nicholas, Moritz Reide

Cambridge: Richard Friend and co-workers

Stanford: M. McGehee et al.

GT: Seth Marder et al.

Bordeaux: Guillaume Wantz et al.

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