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INSTYTUT METALURGII I INŻYNIERII MATERIAŁOWEJ
im. Aleksandra Krupkowskiego
Polskiej Akademii Nauk

Photovoltaic systems – theory and practice

Part 4

Marek Lipiński

Kraków 2020

Projekt nr WND-POWR.03.02.00-00-IO43/16
Międzynarodowe interdyscyplinarne studia doktoranckie z zakresu nauk o materiałach z wykładowym językiem angielskim
Program Operacyjny Wiedza Edukacja Rozwój 2014-2020, Działanie 3.2 Studia doktoranckie

Cours description

1. Introduction to photovoltaics

Basic information about the solar energy and photovoltaic Energy conversion

2. Technology of solar cells

The industrial technology of silicon solar cells and thin films solar cells will be presented

3. **Emerging photovoltaics**

Emerging materials and devices including dye-sensitized solar cell, organic solar cell, perovskite solar cell and quantum dot solar cell

4. Photovoltaic systems

Technology, applications, economics of photovoltaic systems

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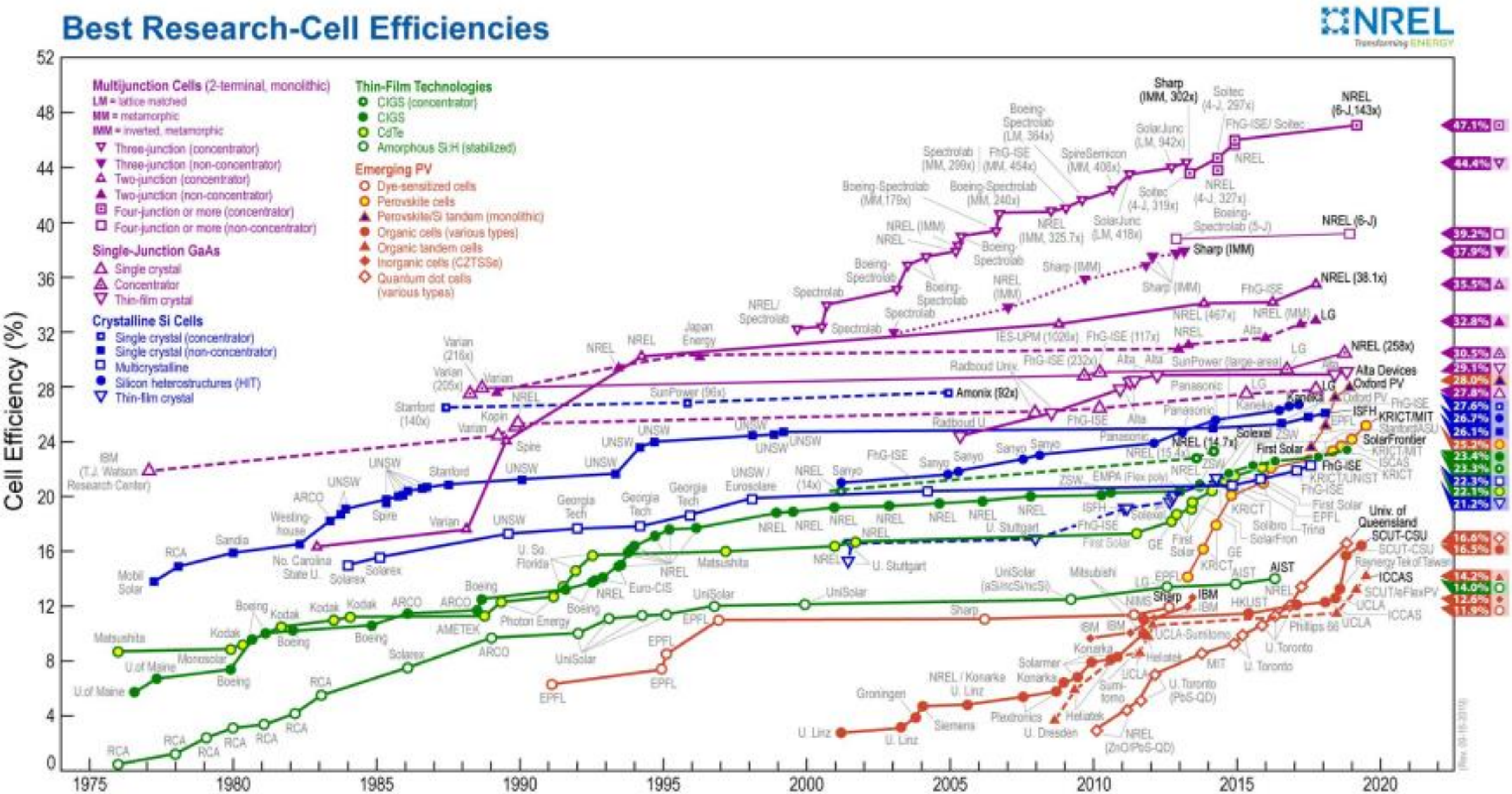
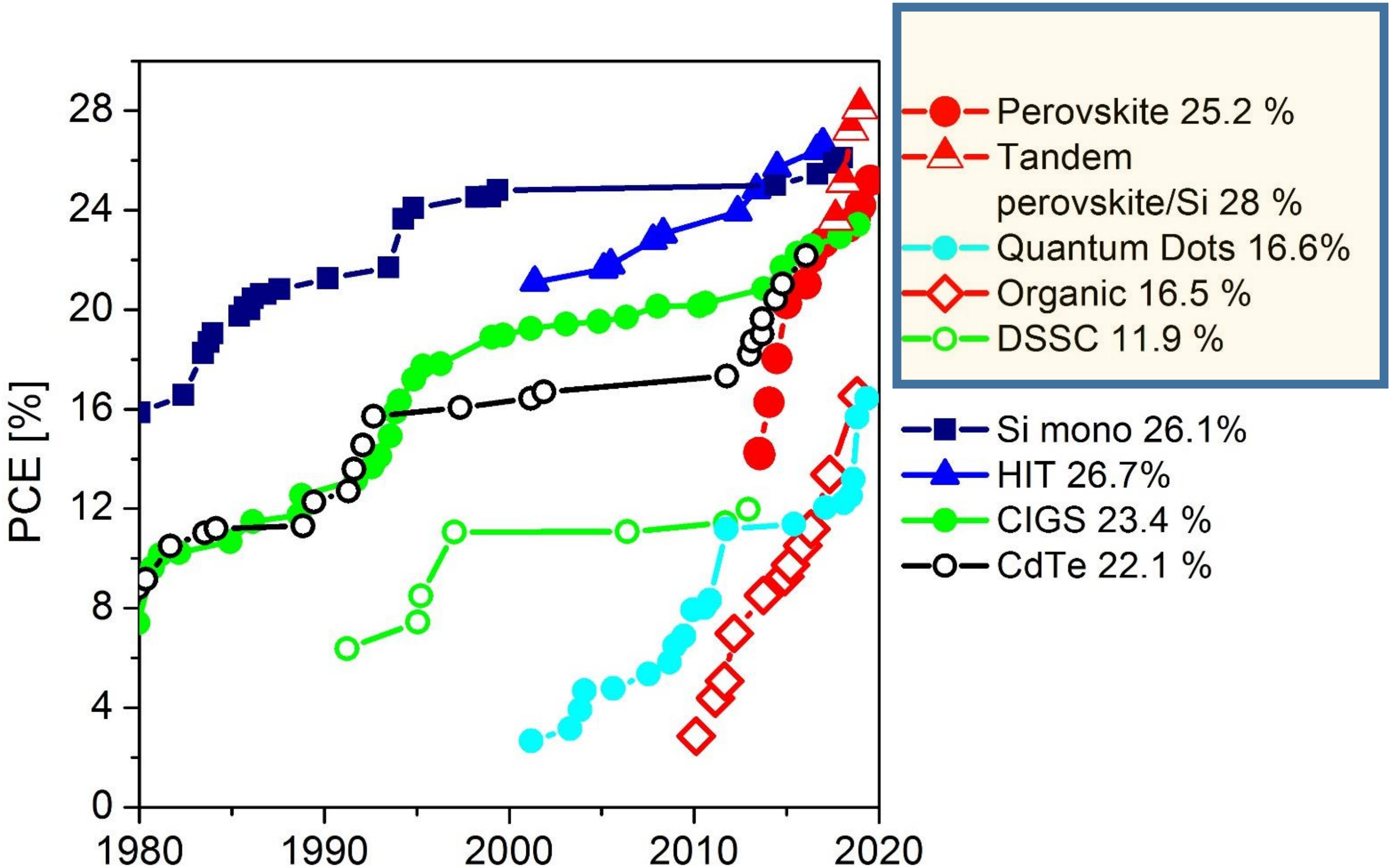

Best Research-Cell Efficiencies
NREL
Transforming ENERGY
Multijunction Cells (2-terminal, monolithic)
LM = lattice matched
MM = metamorphic
IMM = inverted, metamorphic
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal (concentrator)
Single crystal (non-concentrator)
Multicrystalline
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
CIGS (concentrator)
CIGS
CdTe
Amorphous Si:H (stabilized)
Emerging PV
Dye-sensitized cells
Perovskite cells
Perovskite/Si tandem (monolithic)
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells (various types)
Cell Efficiency (%)
52
48
44
40
36
32
28
24
20
16
12
8
4
0
1975
1980
1985
1990
1995
2000
2005
2010
2015
2020
47.1%
44.4%
39.2%
37.9%
35.5%
32.8%
30.5%
29.1%
28.0%
27.8%
27.6%
26.7%
26.1%
25.2%
23.4%
23.3%
22.3%
22.1%
21.2%
16.6%
16.5%
14.2%
14.0%
12.6%
11.9%

Emerging PV



PCE [%]
28
24
20
16
12
8
4
0
1980
1990
2000
2010
2020
Perovskite 25.2 %
Tandem perovskite/Si 28 %
Quantum Dots 16.6%
Organic 16.5 %
DSSC 11.9 %
Si mono 26.1%
HIT 26.7%
CIGS 23.4 %
CdTe 22.1 %

QD solar cells

In a semiconductor crystallite whose size is smaller than twice the size of its exciton Bohr radius (a_b), the excitons are squeezed, leading to quantum confinement.

https://en.wikipedia.org/wiki/Quantum_dot

Material properties and Bohr radii a_B of various bulk semiconductors

		E_g (eV)	m_e^*/m_0	m_h^*/m_0		Electron a_B (nm)	Hole a_B (nm)	Exciton a_B (nm)
II–VI	CdS	2.48	0.25	0.6	5	1	<1	2
	CdSe	1.73	0.12	0.9[a]	6	3	1[a]	4
	CdTe	1.48	0.09	0.8[a]	7	4	1[a]	5
III–V	InP	1.34	0.073	0.45[a]	11	7	1	8
	InAs	0.35	0.023	0.57[a]	12	27	2	29
	InSb	0.17	0.012	0.44[a]	16	59	2	61
IV–VI	PbS[c]	0.42	0.087[b]	0.083[b]	17	10	11	21
	PbSe[c]	0.28	0.047[b]	0.041[b]	23	26	29	55
	PbTe[c]	0.31	0.034[b]	0.032[b]	33	56	48	104

$a_B = \varepsilon\, m_0/m^*\, a_0$

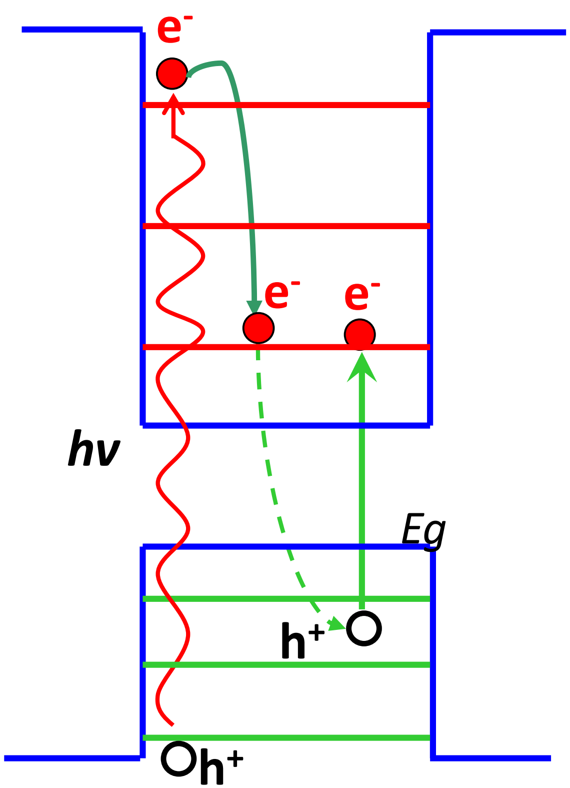
a_0 Bohr radius $a_0 \approx 0.53$ nm
ε semiconductor dielectiric constant
m^* effective mass of electron of hole
or for exciton reduced mass ($m_{exe}^{*-1} = m_e^{*-1} + m_h^{*-1}$

[1] O. Madelung , Semiconductors: Data Handbook. Berlin:Springrer-Verlag,2004.
[2] T. D. Krauss and J. J. Peterson in Colloidal Quantum Dot Optoelectronics and Photovoltaics, edited by G. Konstantatos and E. H. Sargent

QD solar cells

Semiconductor	Size (nm)	Eg (eV)
PbSe	∞	0.27 i
PbSe	5.4	0.73
PbSe	4.7	0.82
PbSe	3.9	0.91
PbS	∞	0.41 i
PbS	5.5	0.85
PbTe	∞	0.31 i
PbTe	5.5	0.91
Si	∞	1.12
Si	2	1.7

QD solar cells



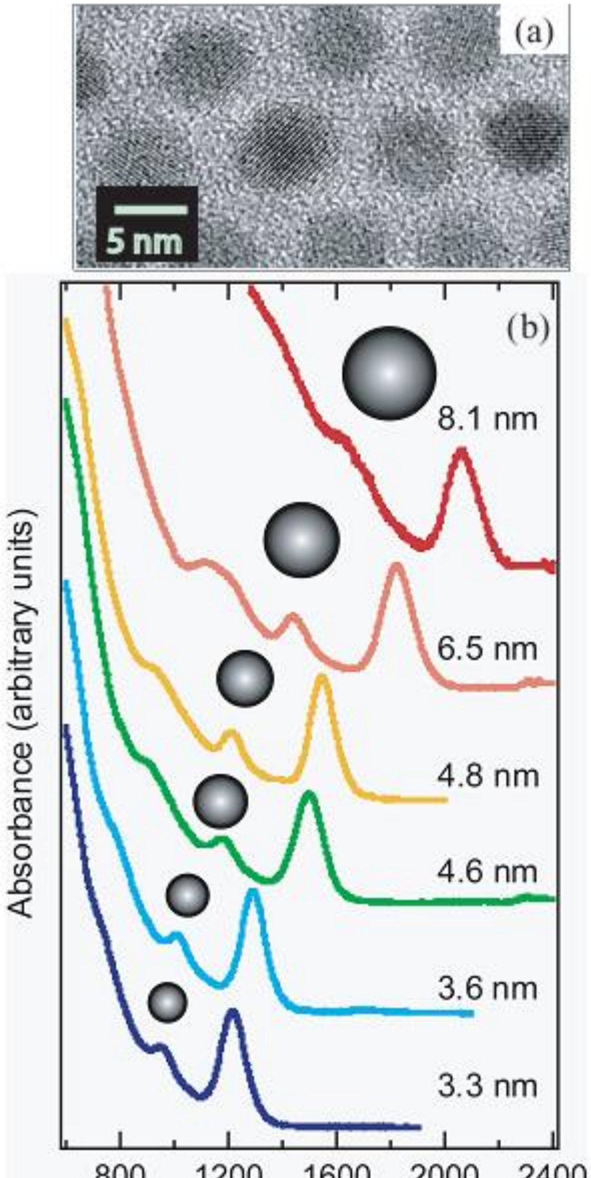
One photon two pairs e-h

The effects of quantum confinement in quantum dots

- Slowing down the cooling of excitons, strengthening the Auger process,
- There is no request to maintain the crystalline momentum
- One photon can generate many e-h pairs. Crash ionization multi-exciton generation by high energy photons
- Expanding the energy gap

- A.J. Nozik / Physica E 14 (2002) 115
- A. Luque, A. Marti, and A.J. Nozik, MRS Bulletin Vol. 32 (2007) 236

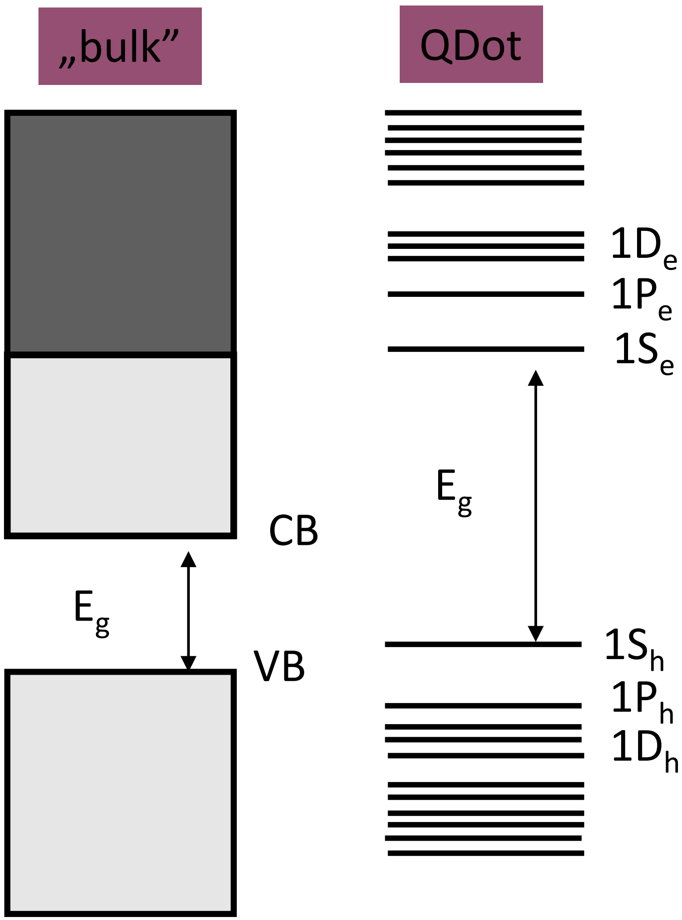
QD solar cells



(a) TEM image showing PbSe NCs with average diameter of 5.2nm. (b) Linear absorption spectra of a series of PbSe NCs with average diameter ranging from 3.3nm to 8.1nm. Strong excitonic absorption and a blue-shift of the onset are signatures of quantum confinement in NCs.

https://onlinelibrary.wiley.com/doi/pdf/10.1002/lpor.200810013

QD solar cells



Quantum dot fluorescence (Q-dots) CdSe of various sizes when exposed to UV light

https://onlinelibrary.wiley.com/doi/pdf/10.1002/lpor.200810013

QD solar cells

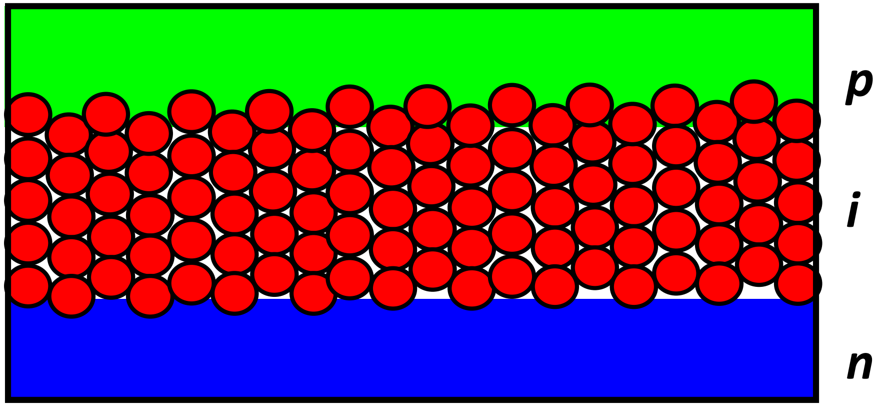
Solar cell configurations with quantum dots:

1. Photoelectrodes from QDs "arrays„ (super-lattice)
2. Nanocrystalline TiO_2 sensitized QDs
3. QDs immersed in a polymer blend ("e" and "h")

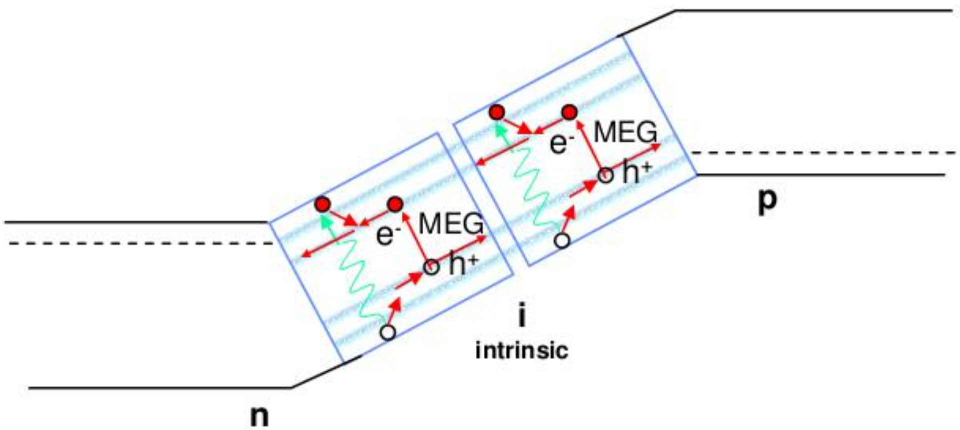
A.J. Nozik / Physica E 14 (2002) 115

QD solar cells

1. Quantum super-lattice – p-i-n structure.



Quatum super-lattice - (QDs)

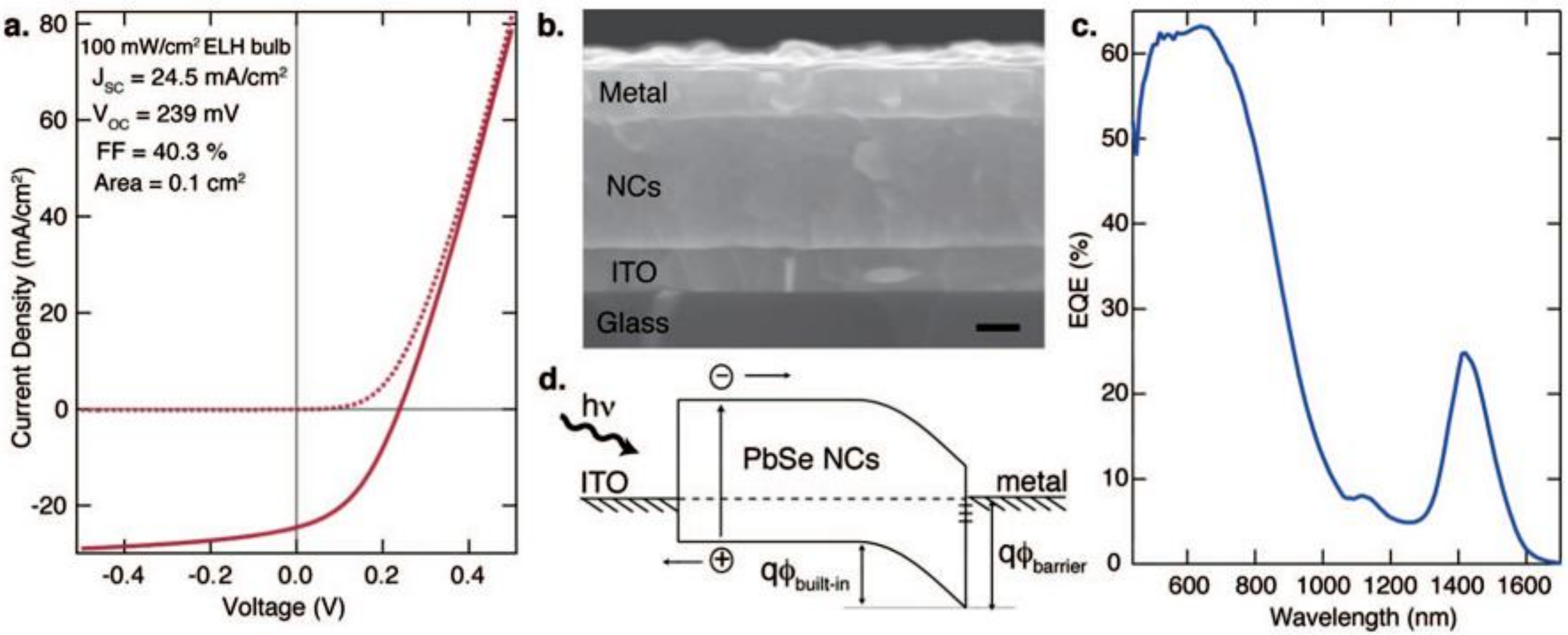


Slow down cooling process, transport and collection of hot carriers in p and n contacts - higher voltage or larger photocurrent as a result of MEG

A. Luque, A. Marti, and J. Nozik, MRS Bulletin Vol. 32 (2007) p. 236

QD solar cells

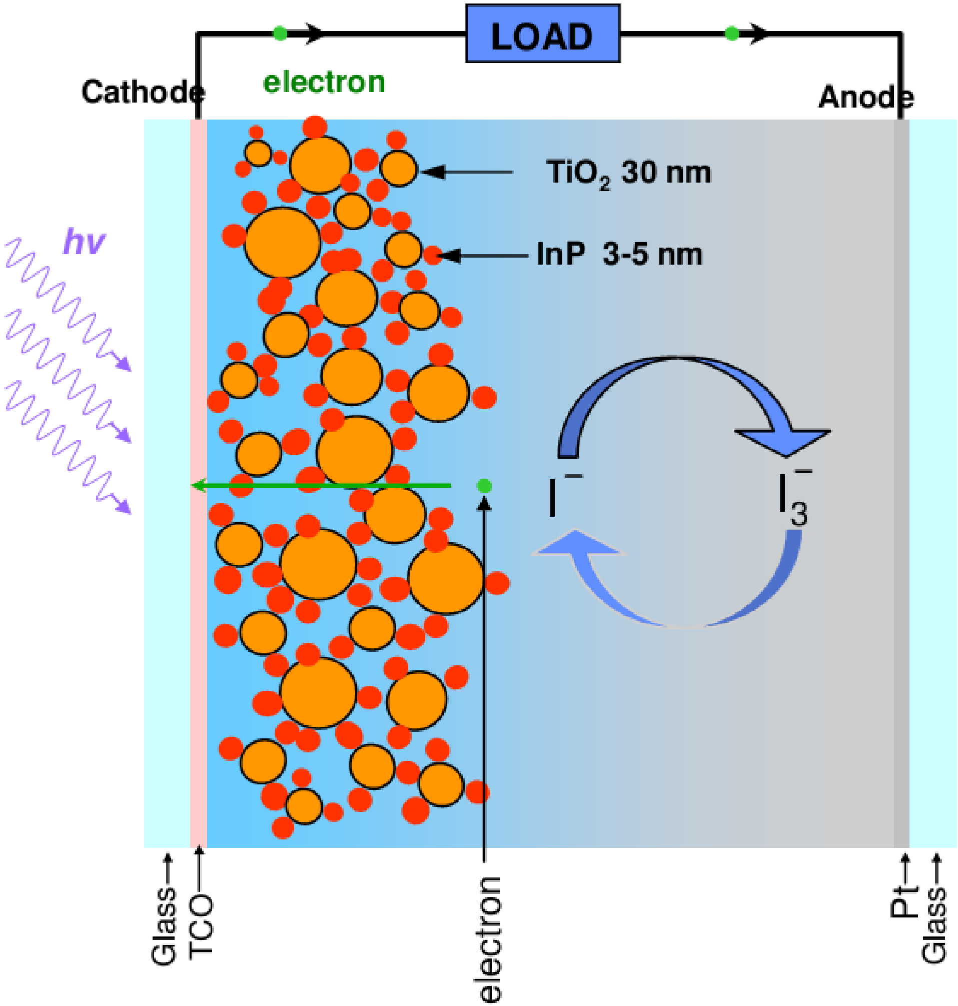
Qunatum super-lattice– Structure with a Schottki diode



NCs layer– deposited by „layer – by layer (LBL) dip coating", 60 nm thickness

J. M. Luther, M. Law, M. C. Beard, Q., M.O. Reese, R. J. Ellingson, and A. J. Nozik, Nano Lett.,Vol. 8, No. 10,2008, p.3488.

2. QDs DSSC



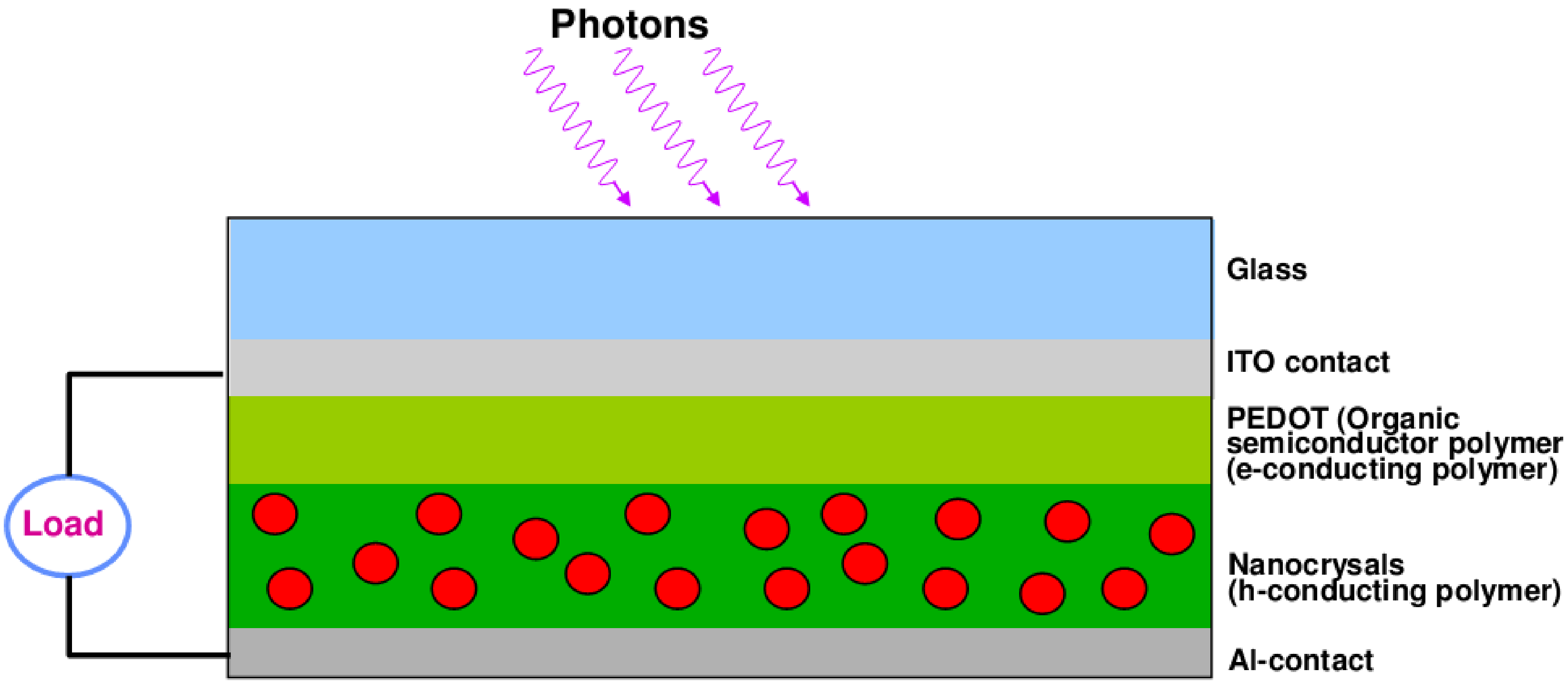
1. Electrons of QD are excited by solar energy adsorption
2. Electron transfer from QD to TCO via TiO_2
3. Electrons get to the counter electrode after working at external load
4. ½ I_3^- - e^- → 3/2 I^- at counter electrode
5. 3/2 I^- → ½ I_3^- + e^- at QD

TiO_2 : QD-sensitized negative charge carrier
Electrolyte: iodine-triiodide redox couple
QD: InP, CdSe, CdTe, PbS, etc.
TCO: Transparent conducing oxide
Pt : Catalyst

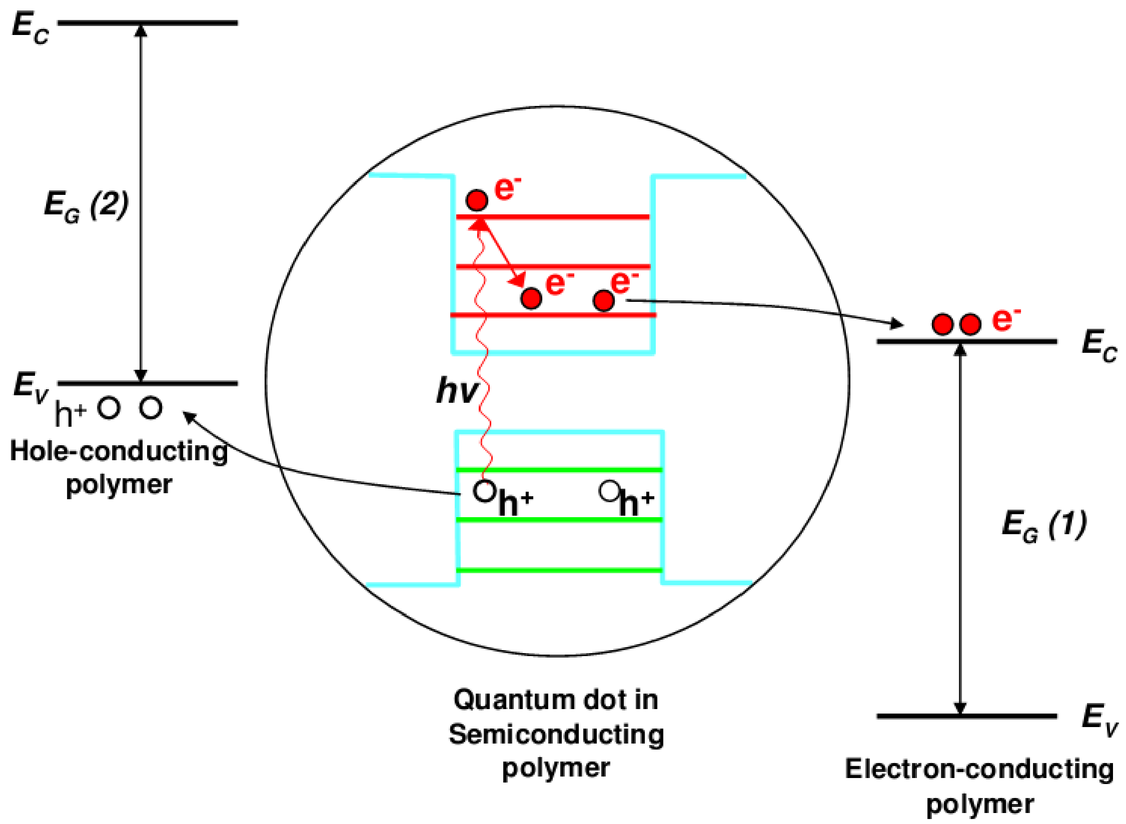
A. Luque, A. Marti, and J. Nozik, MRS Bulletin Vol. 32 (2007) p. 236

Barwnik w ogniwach DSSC zastąpiony jest przez QDs.

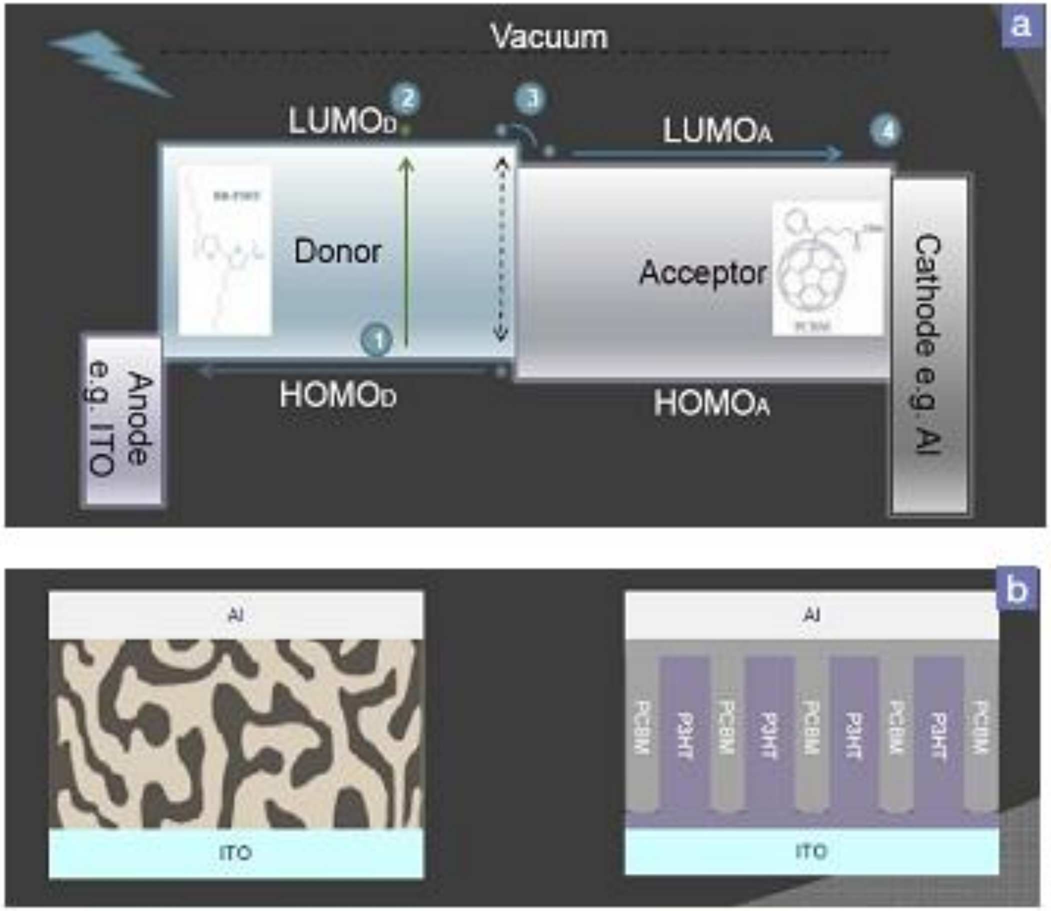
QDs immersed in a polymer blend



QDs immersed in a polymer blend



QDs immersed in a polymer blend



The schematic band energy structure of bulk-heterojunction organic cell used to produce the results (b)(left) a schematic showing random distribution of donor (P3HT) and acceptor (PCBM) regions in the blended bulk-heterojunction organic solar cell, (right) a schematic diagram of systematic alignment of donor and acceptor layers

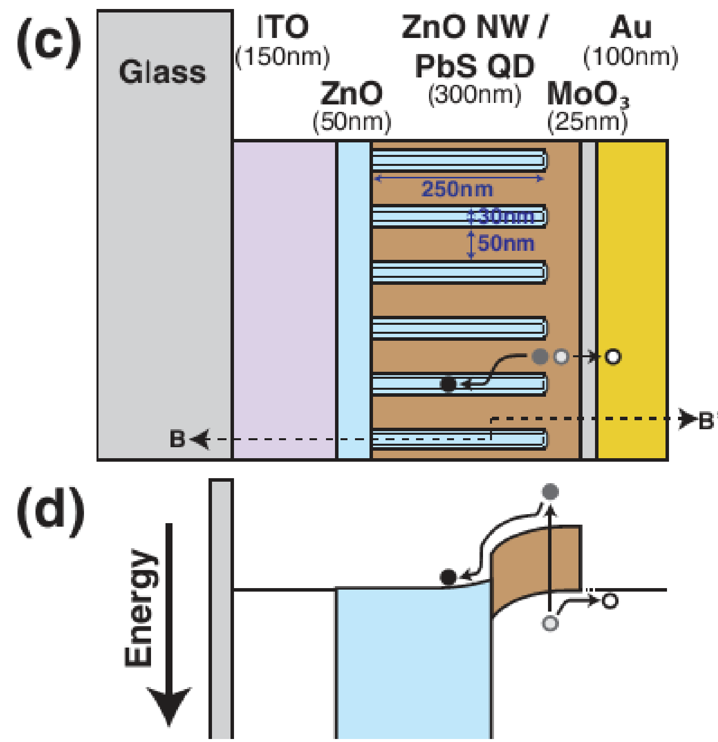
QDs immersed in a polymer blend

Materials Views
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

ZnO Nanowire Arrays for Enhanced Photocurrent in PbS Quantum Dot Solar Cells

*Joel Jean, Sehoon Chang, Patrick R. Brown, Jayce J. Cheng, Paul H. Rekemeyer, Moungi G. Bawendi, Silvija Gradečak, and Vladimir Bulović**



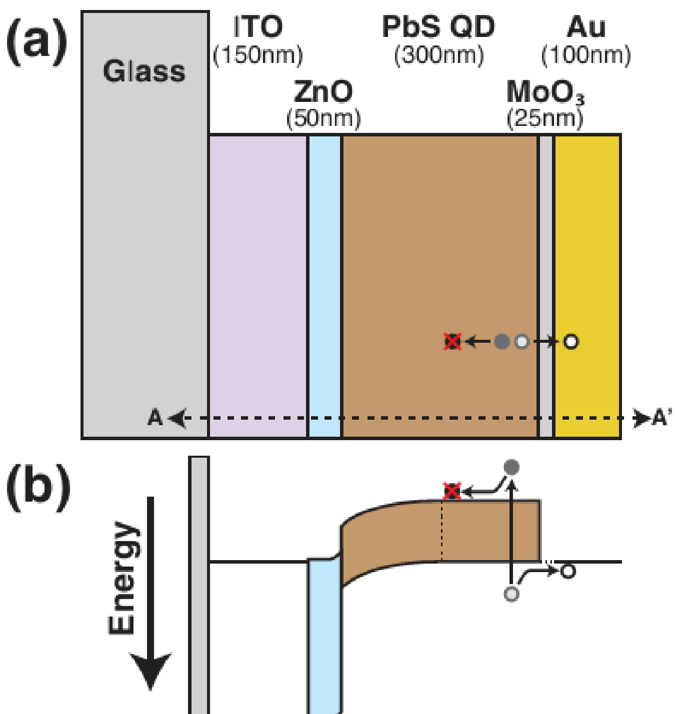


Figure 1. (a) Schematic and (b) energy band diagram at short-circuit (cross-section along A-A') of a planar QDPV device with parallel light absorption and carrier collection pathways. By incorporating solution-processed ZnO nanowires, an ordered bulk heterojunction (BHJ) architecture – shown here by: (c) schematic and (d) energy band diagram (cross-section along B-B') – can decouple absorption from collection, extending the effective depletion width throughout a thick QD film.

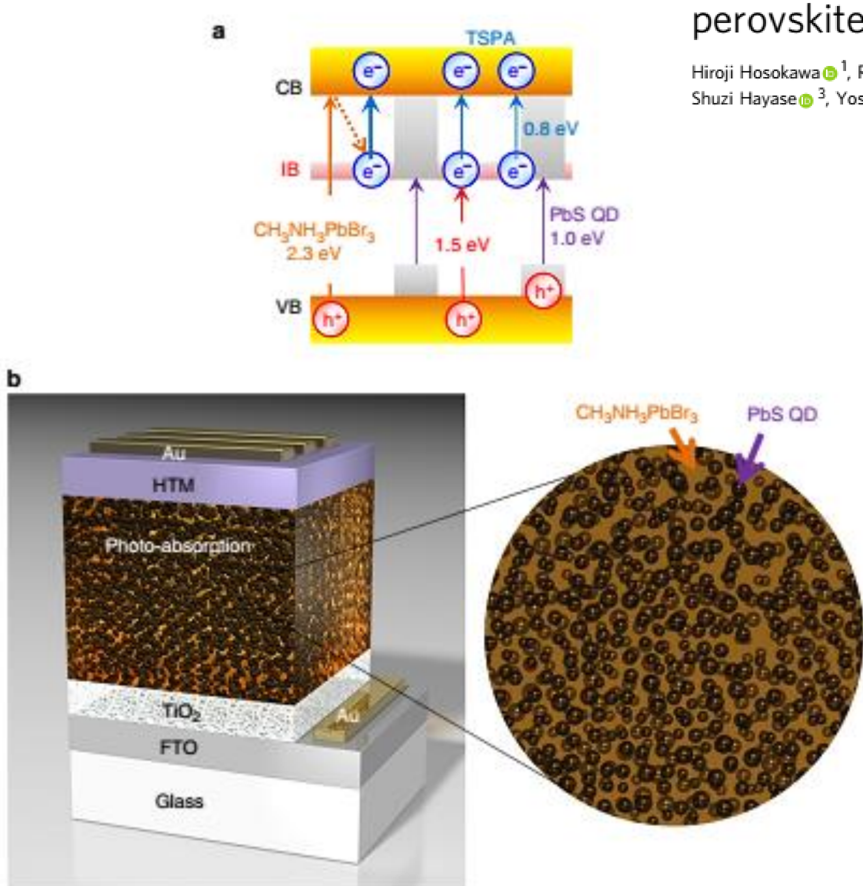
IBSC cells from colloidal solutions of quantum dots

Nature Comunications (2019)

ARTICLE
DOI: 10.1038/s41467-018-07655-3 OPEN

Solution-processed intermediate-band solar cells with lead sulfide quantum dots and lead halide perovskites

Hiroji Hosokawa[1], Ryo Tamaki[2], Takuya Sawada[1], Akinori Okonogi[1], Haruyuki Sato[1], Yuhei Ogomi[3], Shuzi Hayase[3], Yoshitaka Okada[2] & Toshihiro Yano[1]



IBSC made from solutions. PbS quantum dots (4 nm) immersed in $MAPbBr_3$ perovskite

Silicon Quantum dots for III generation solar cells

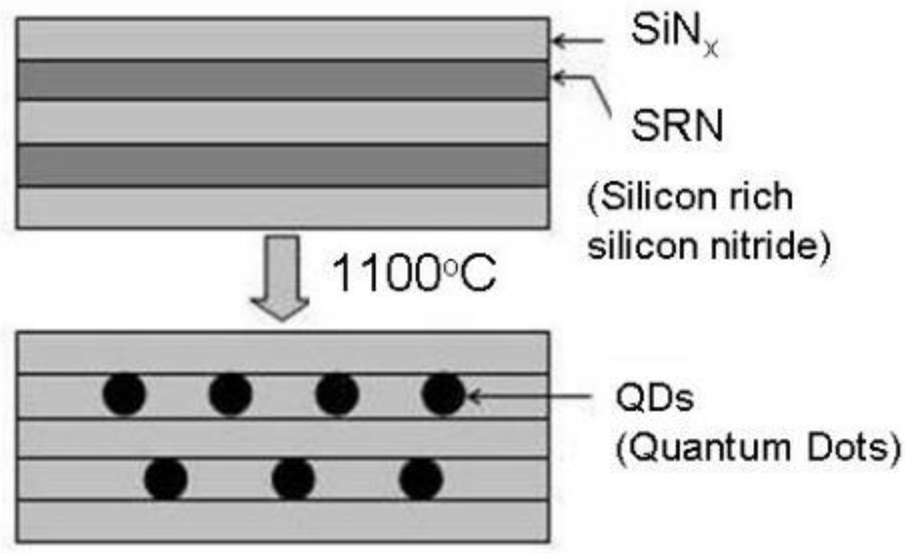
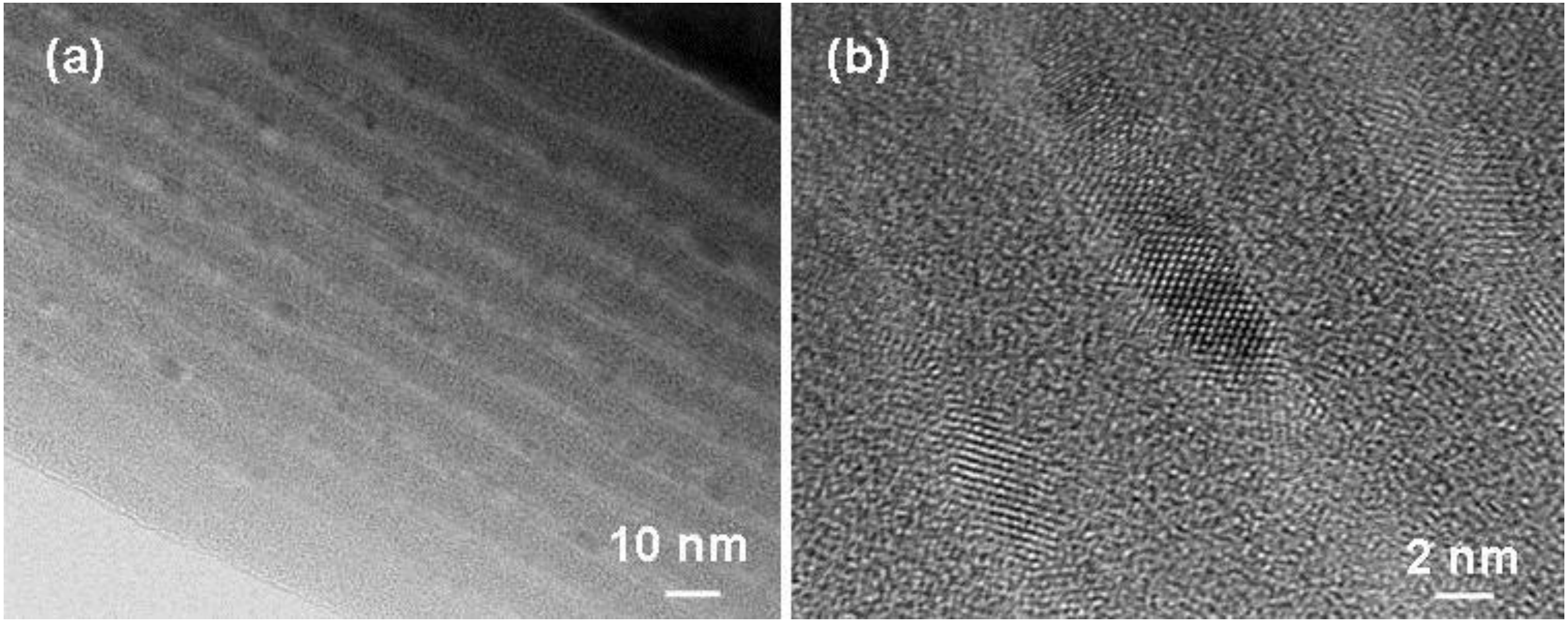


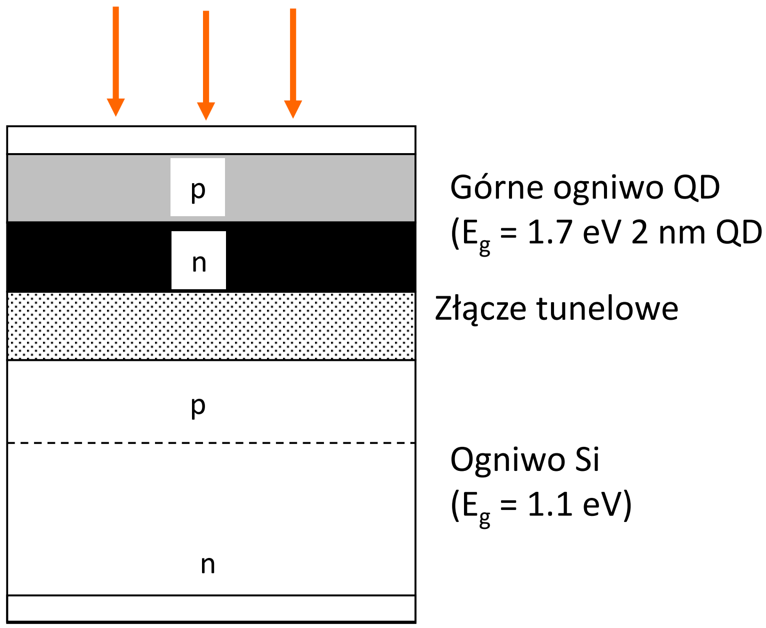
Fig. 1. Scheme of formation of quantum dots (QDs) in silicon nitride multilayer according to Zacharias and Green (M. Lipiński in *Archives of Materials Science and Engineering*, 46 (2010) 69-87).

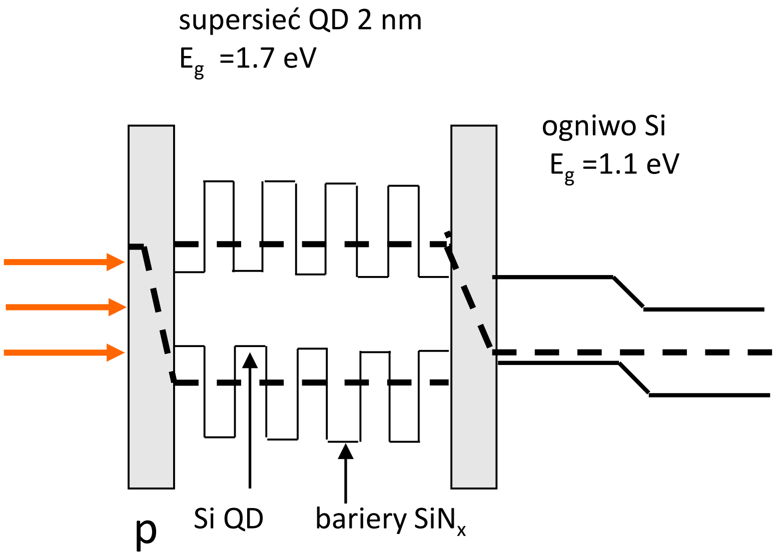
Silicon Quantum dots for III generation solar cells



Cross-sectional TEM images of the multilayer (a) low and (b) high magnification. The sample was annealed at 1100^{o}C (M. Lipiński in Archives of Materials Science and Engineering, 46 (2010) 69-87).

Tandem silicon solar cells using Si Qdots





a) Scheme of a two-junction silicon cell. The upper cell is made of a silicon superlattice quantum dots with an energy gap of 1.7 eV, the bottom cell is a classic silicon link. These cells are connected with each other by a tunnel junction [1].

b) Scheme of the band structure of a two-junction cell [2].

[1] E.-C. Cho, M.A.Green, G. Conibeer et al., *Silicon quantum dots in a dielectric matrix for all-silicon tandem solar cells*, Hindwai Publishing Corporation, Advances in OptoElectronics (2007) 1-11

2] G. Coniber, Third-generation photovoltaics, Materials Today 10 (2007) 42-50.

Light converter from perovskite nanoparticles

STUDYING OF PEROVSKITE NANOPARTICLES IN PMMA MATRIX USED AS LIGHT CONVERTER FOR SILICON SOLAR CELL

Arch. Metall. Mater. **62** (2017), 3, 17331-1739

M. LIPIŃSKI*#, R.P. SOCHA**, A. KĘDRA**, K. GAWLIŃSKA*, G. KULESZA-MATLAK*,
Ł. MAJOR*, K. DRABCZYK*, K. ŁABA***, Z. STAROWICZ*, K. GWÓŹDŹ****, A. GÓRAL*, E. POPKO****

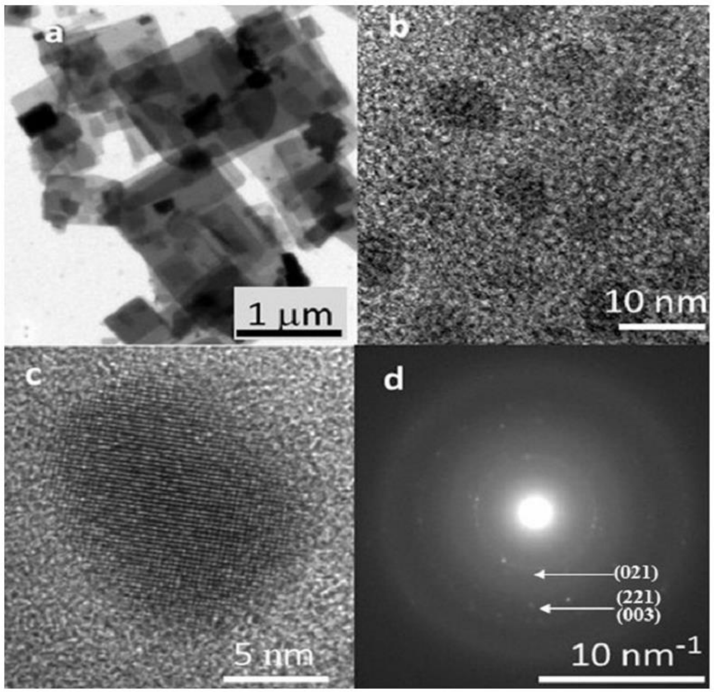
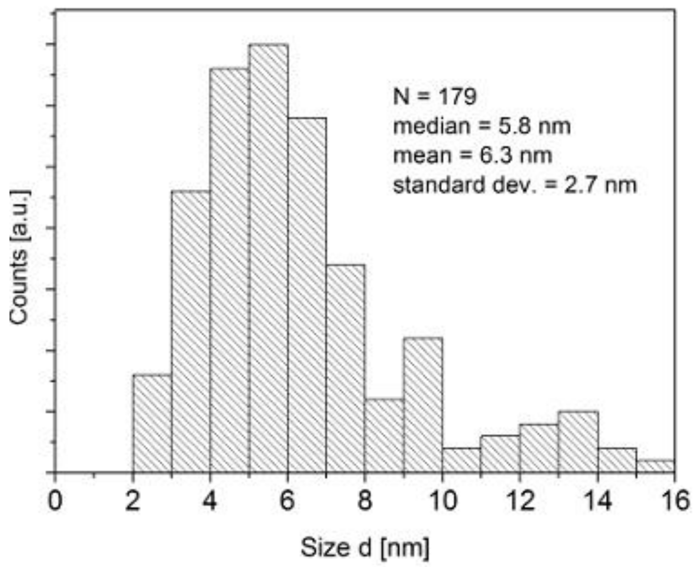
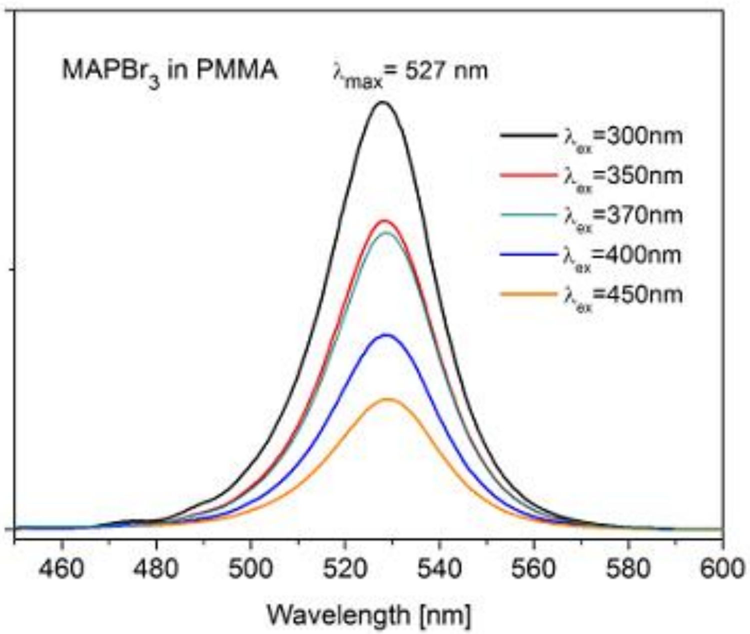


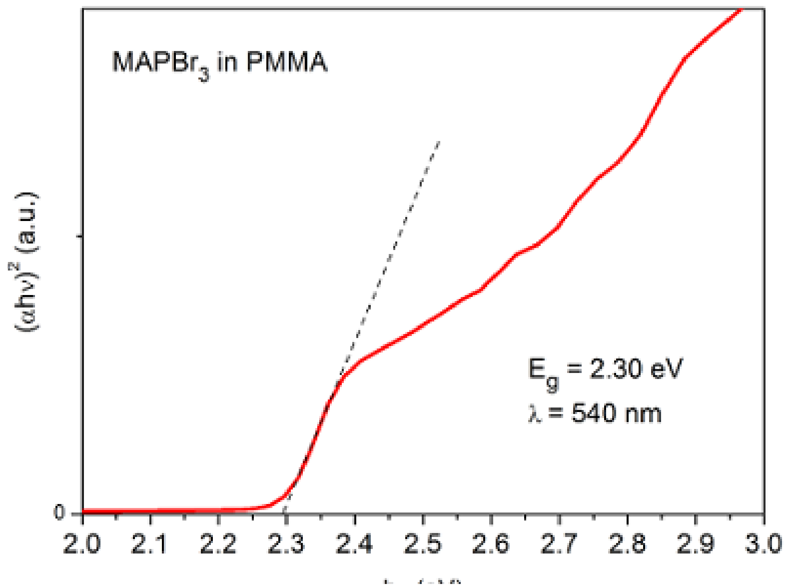
Fig. 1. The TEM image of the $CH_3NH_3PbBr_3$ perovskite morphology (a), High Resolution TEM images (b,c) and electron diffraction pattern with two rings corresponded to (021), (221) and (003) faces of cubic phase according to ref. [27] (d) of the nanoparticles



Nanoparticles $MAPbBr_3$

Light converter from perovskite nanoparticles





Light converter from perovskite nanoparticles

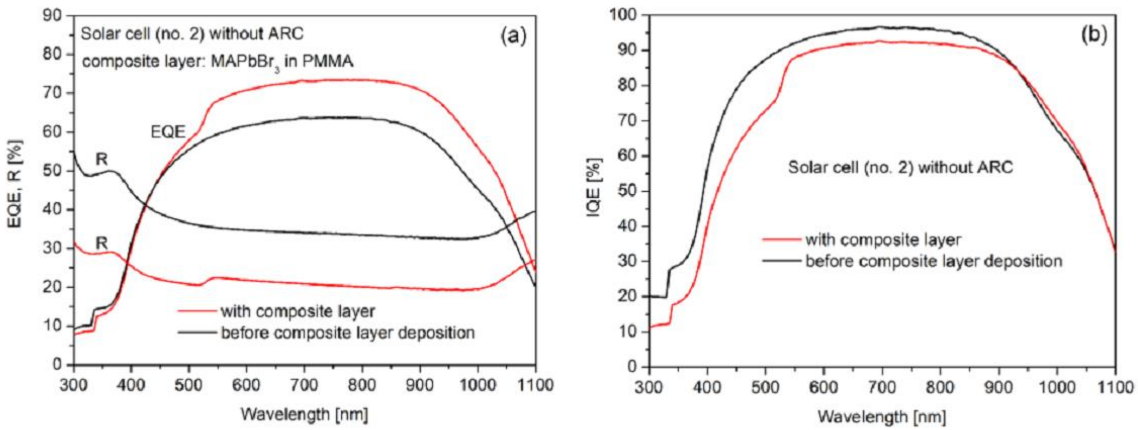
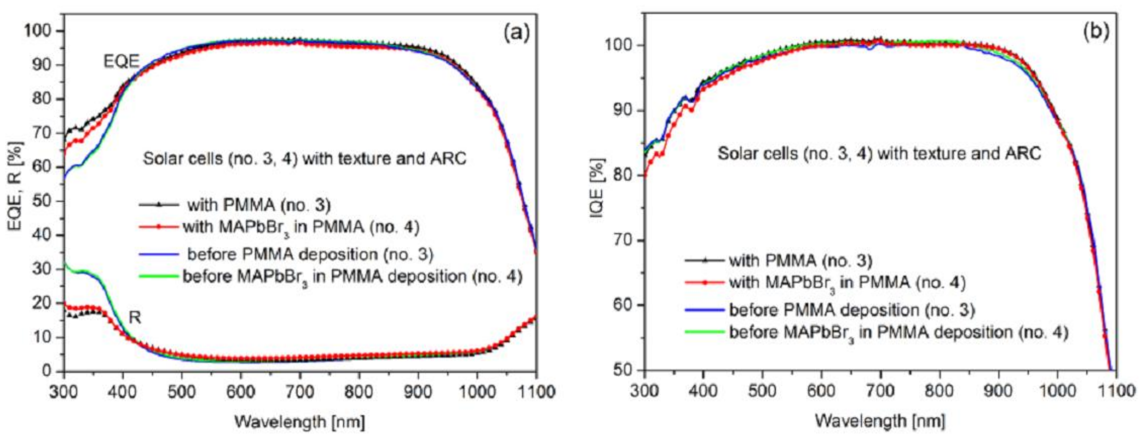
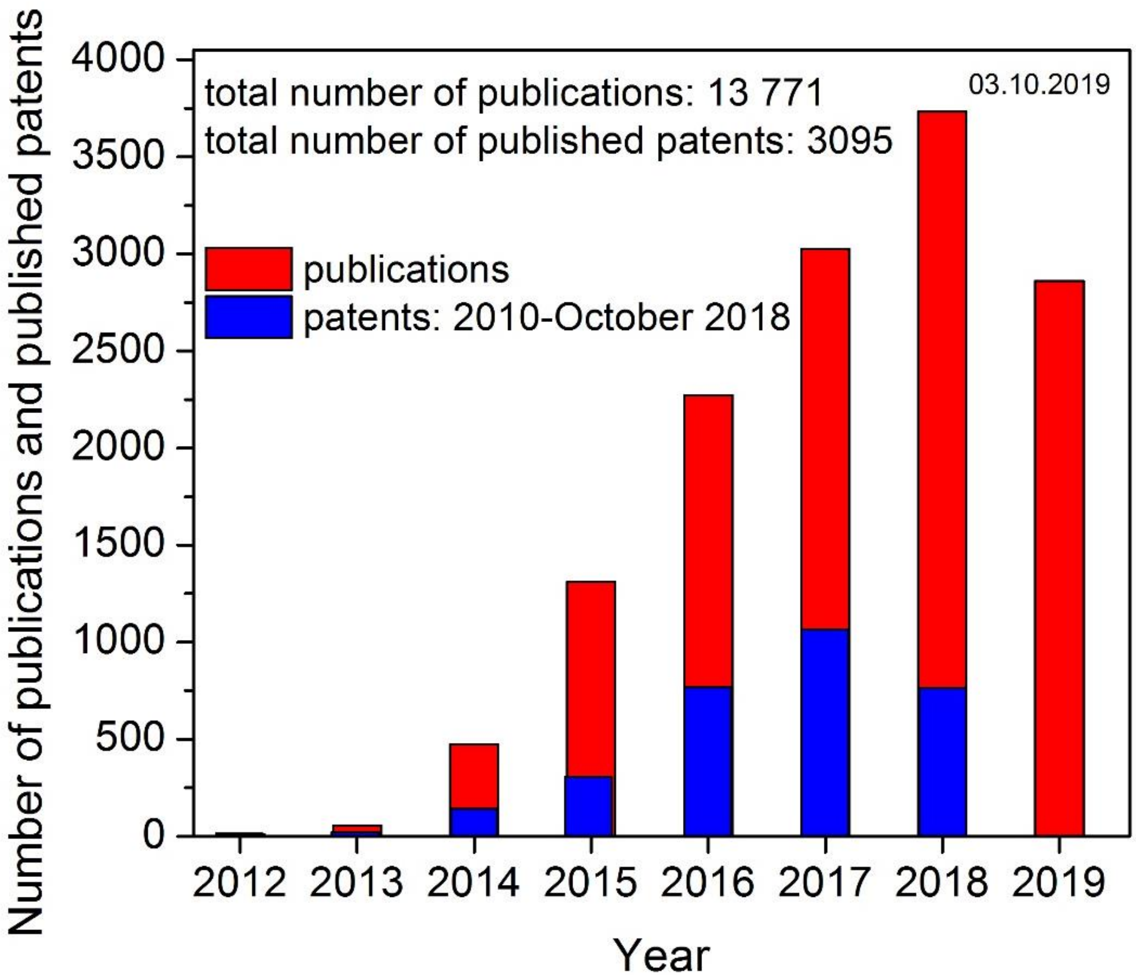


Fig. 8. The external EQE (a) and internal IQE (b) quantum efficiencies of the solar cell with and without the composite ($MAPbBr_3$ in PMMA) layer. The solar cell is without ARC. The difference between the IQE curves is caused by absorption of the composite layer



Perovskite solar cells

Progress in perovskite solar cells

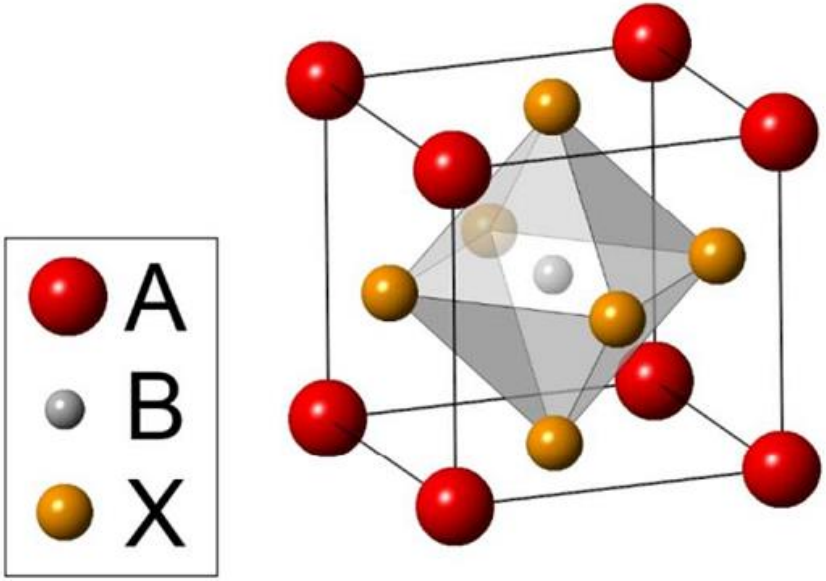


Source: Web of Science. Topic: Perovskite solar cells
A review of the patent landscape. Cintelliq https://go.nature.com/2IGsIR9 (2018).

Perovskite ABX_3

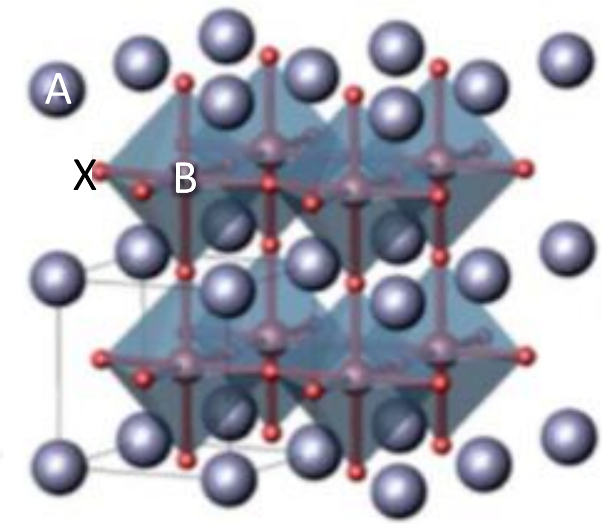
Perovskite - Calcium titanium oxide $CaTiO_3$ was discovered in the Urals Mountains in 1838 by Gustav Rose and named after Russian mineralogist Lev Perovski
All materials with the crystallographic structure of calcium titanium oxide $CaTiO_3$ are named perovskites

The general chemical formula for pure perovskite compounds is ABX_3, where 'A' and 'B' are two cations of very different sizes, and 'X' is an anion that binds to both.



Ideal crystal structure of cubic perovskite

Halide perovskite ABX_3



Perowskite crystalline system (ABX_3)

Halide perovskite ABX_3
A^{I} (Li^+, K^+, Cs^+, $CH_3NH_3^+$)
B^{II} (Pb^{2+}, Mg^{2+}, Ca^{2+}, Sn^{2+}, Ba^{2+}, Zn^{2+})
X (F^-, Cl^-, Br^-, I^-)

Oxide perovskite ABO_3
A^{II} (Mg^{2+}, Ca^{2+}, Ba^{2+})
B^{IV} (Ti^{4+}, Si^{4+})

Organo-metal halide perovskite

Alkali-halide perovskite

Peng Gao et al., Organohalide lead perovskites for photovoltaic applications, *Energy & Enviromental Science*, 2014

1892 r : First article on halide perovskites

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.

Halide perovskite ABX_3

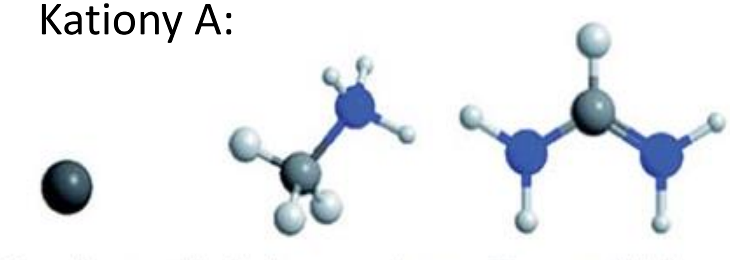
X = F, Cl, Br, I
A = organic cation: MA ($CH_3NH_3^+$) , FA ($CH_3(NH_2)_2^+$) or Cs^+
B = inorganic cations (Pb, Sn)

A	R_A [nm]
MA	0,18
FA	0,19-0,22
Cs	0,17
Rb	0,15

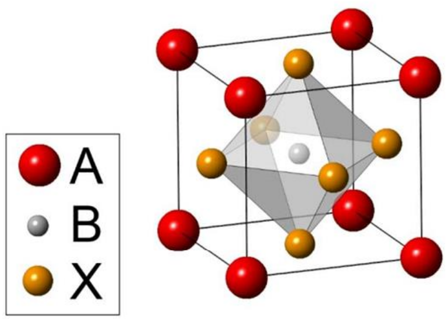
X	R_A [nm]
I	0.220
Br	0.196
Cl	0.181

B	R_B [nm]
Pb	0.119
Sn	0.110

Kationy A:



Cs^+ (cezu) MA (metyloamoniowy) FA (formamidinowy)



Goldschmidts tolerance factor *t* :

$t = (R_B+R_X)/\{\sqrt{2}(R_B+R_X)\}$

R_A, R_B, R_X ionic radii

For halide perovskites:
$0{,}81 < t < 1{,}11$

t = 0,89–1.0 cubic structure
dla t < 0,89 tetragonal or orthorhombic

M. A. Green, A. H-Bailie, and **H. J. Snaith**, Nature Photonics, **8**, 2014

Halide perovskite ABX_3

	t	phase, color	Phase after annealing	Eg	PCE
$MAPbI_3$	0,89	Tetragonal, black	Tetragonal	1,5	20,3
$FAPbI_3$	1,02	Hexagonal, yellow	regular	1,49	17
$CsPbI_3$	0,79	Rhombic, yellow	Rhombic, yellow	1,72	10,77

$FAPbI_{3-x}Br_x$, E_g =1.48 – 2.23 eV

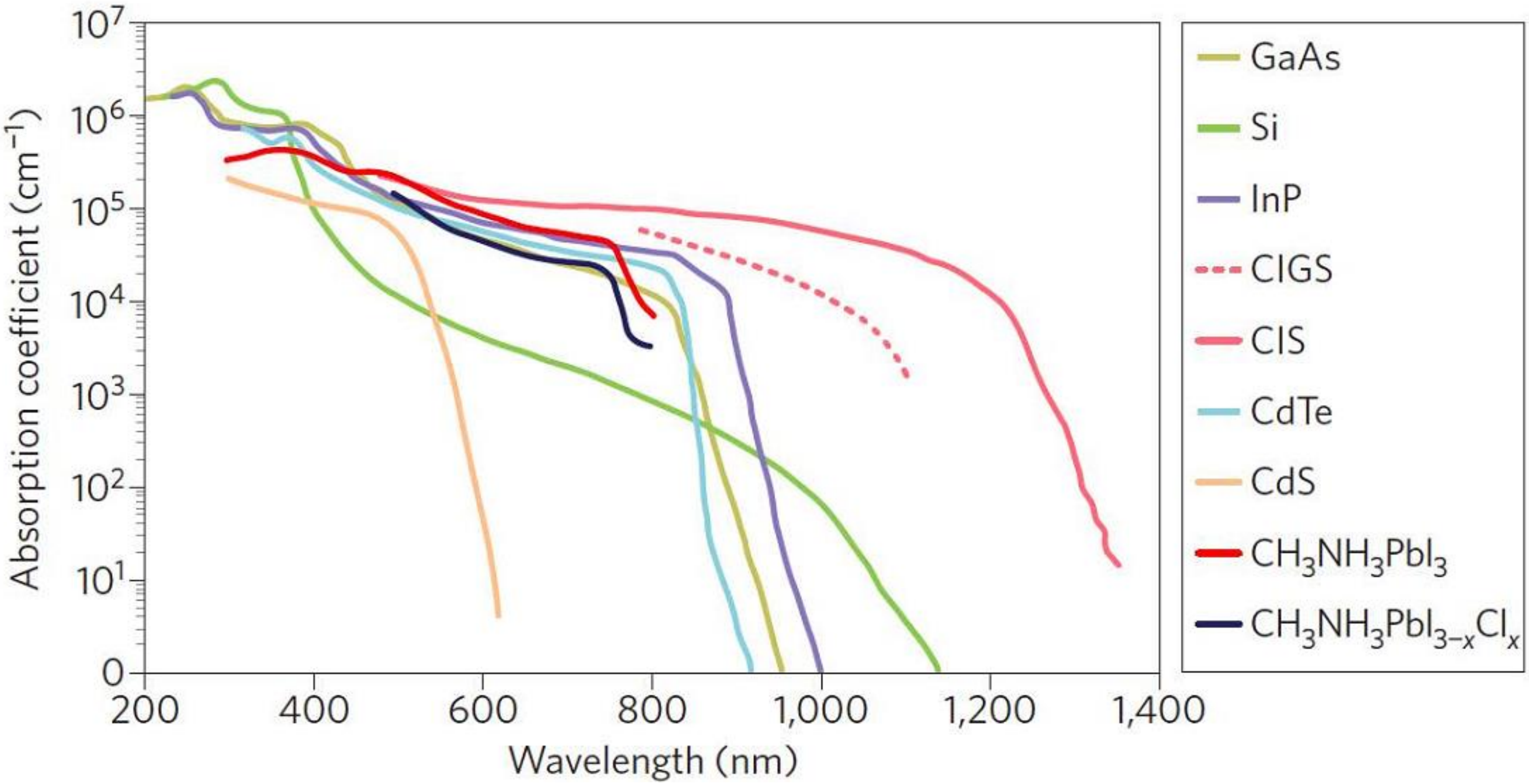
Electronic properties of perovskites

Perovskit	Cariers	D(cm^2s^{-1})	L_D(nm)
$CH_3NH_3PbI_{3-x}Cl_x$	electron	0.042±0.016	1069±204
	hole	0.054±0.022	1213±243
$CH_3NH_3PbI_3$	electron	0.017±0.011	129±41
	hole	0.011±0.007	105±32

D diffusion coefficient
L_D diffusion length

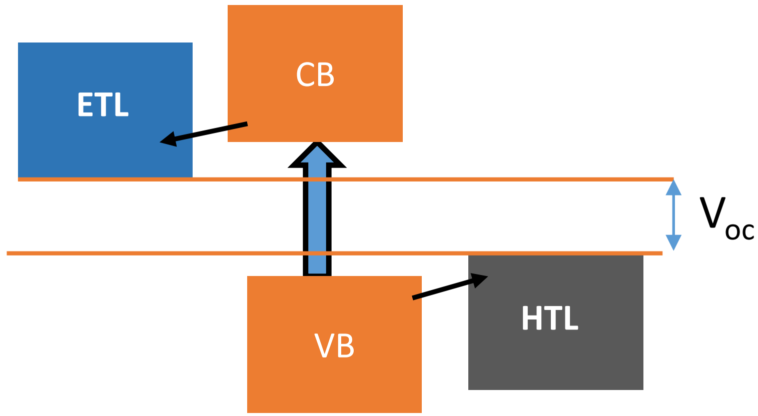
H.J. Snaith i współp.: *Science 342* (2013) 341

Optical properties of perovskites



M. A. Green, A.H-Baillie and H. J. Snaith, NATURE PHOTONICS **8,** 2014, 506.

Perovskite solar cells



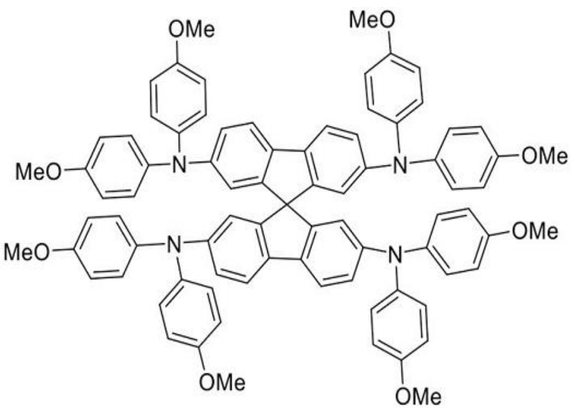
Absorber –
Perowskit halogenkowy

ETL: TiO_2 , SnO_2,….

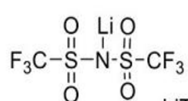
HTL: spiro-MeOTAD , PTAA

spiro-MeOTAD =
2,2 *0*,7,7 *0*-tetrakis-(*N*,*N0*-di-*p*-methoxyphenylamine)- 9,9 *0*-spirobifluorene)
LITFSI (lithium bis(trifluoromethanesulfonyl)imide) + TBP

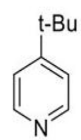
PTAA - poly(triaryl amine)



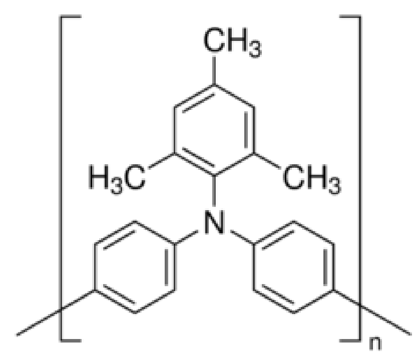
Spiro-OMeTAD



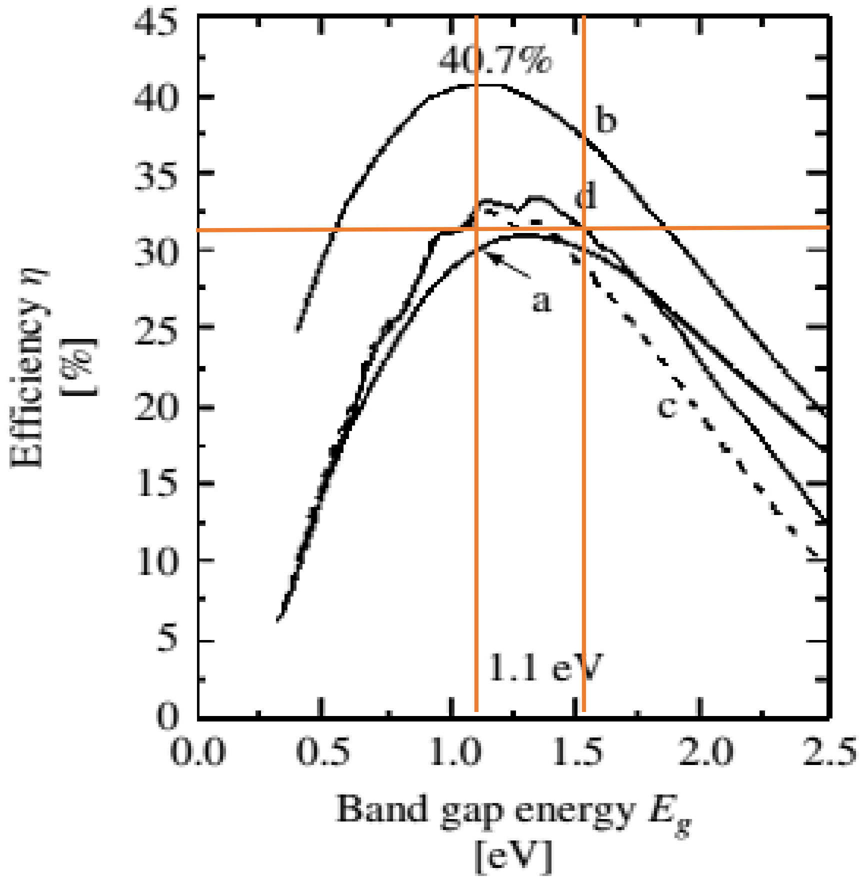
LiTFSI



TBP



Shockley - Queisser efficiency limit

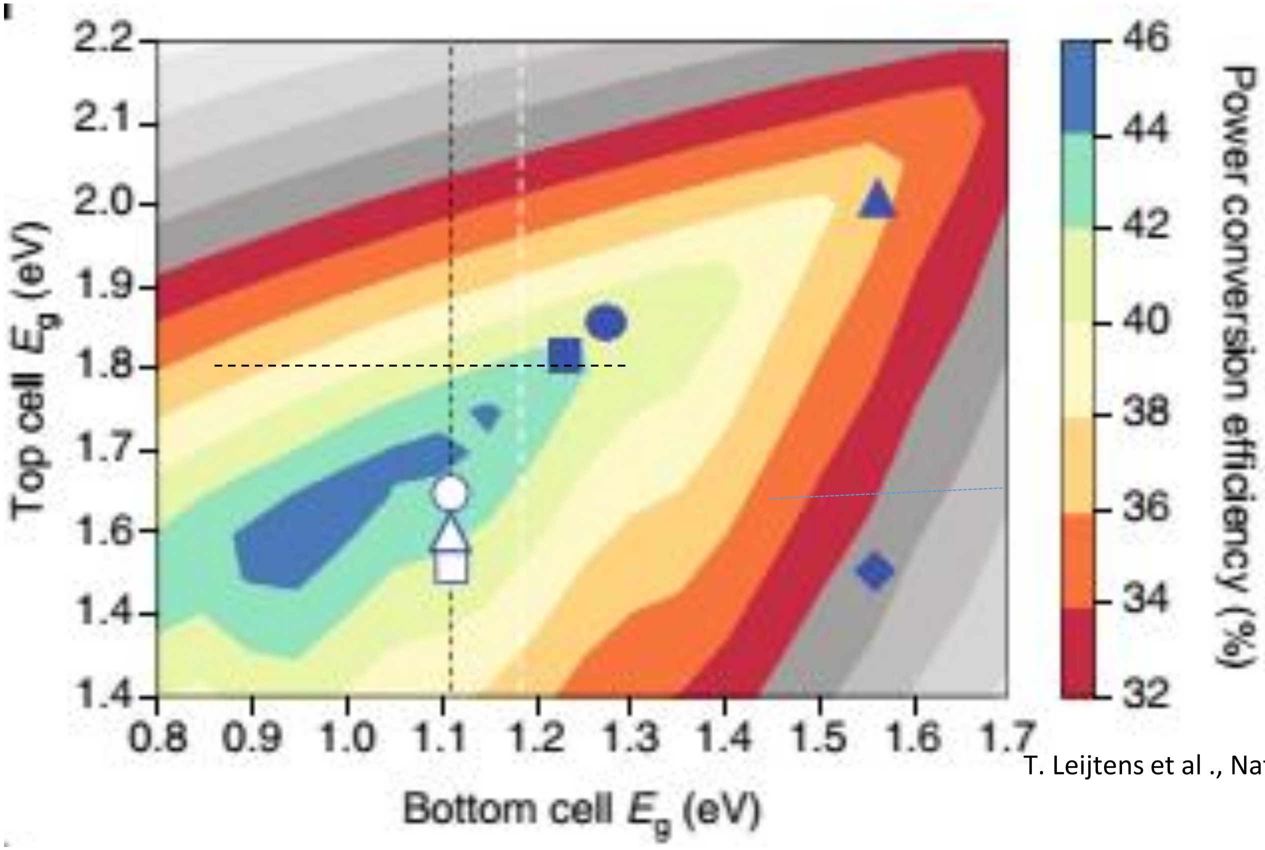


Handbook of Photovoltaic Science and Engineering, Ed: A. Luque and S. Hegedus , J. Wiley, 2003.

E_g = 1.55 eV for $MAPbI_3$

Shockley - Queisser efficiency limit for an ideal solar cell versus band gap energy for: (a) unconcentrated 6000 K black body radiation (1595.9 Wm^{-2}); (b) full concentrated 6000 K black body radiation (7349.0 × 104 Wm^{-2}); (c) unconcentrated AM1.5-Direct [18] (767.2 Wm^{-2}) and **(d) AM1.5 Global (962.5 Wm^{-2})**

Theoretical limit for tandem (2-junctions)



T. Leijtens et al ., Nature Energy, 3,(2018) 828–838

Top perovskite cell: $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ E_g = 1.72 eV
botom cell Si: E_g = 1.12 eV

Advantages:

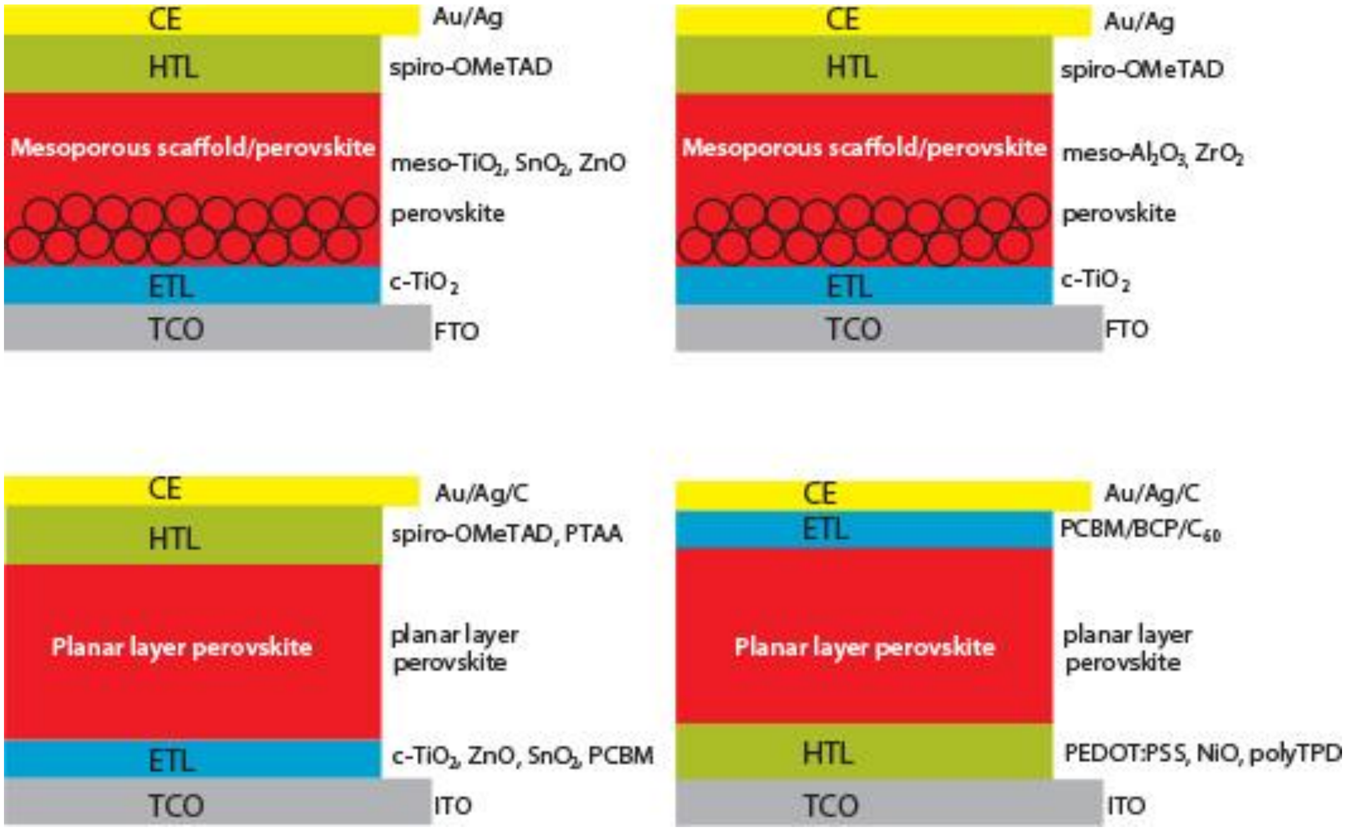
- Semiconductor with excellent opto-electronics properties,
- E_g can be changed in wide range :1.2 - 2.0 eV,
- High absorption,
- Low non-radiative carrier recombination rates,
- Excellent charge transport: diffusion of lenght > 1mm)
- Low crystallization temperature
- Simple methods of manufacturing from solutions: spin-on, ink-jet printing, spray,
- Flexibility
- Earth-abundant elements: C, N, H, Pb, I..
- High efficiency > 20%

Disadvanges:

- Low stability
- Toxicity from Pb

1. Eperon, G. E. et al. Perovskite-perovskite tandem photovoltaics with optimized bandgaps. *Science* 354, 861–865 (2016).
2. Eperon, G. E. et al. Formamidinium lead trihalide: A broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy Environ. Sci.*7, 982–988 (2014).
3. Unger, E. L. et al. Roadmap and road blocks for the band gap tunability of metal halide perovskites. *J. Mater. Chem. A* 5, 11401–11409 (2017).
5. H.J. Snaith et al., *Science 342* (2013) 341

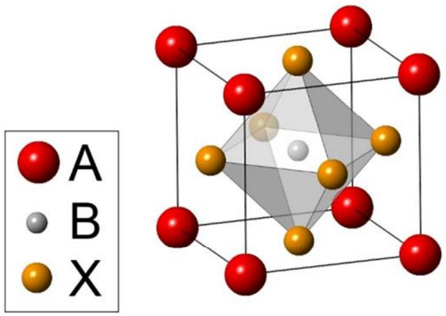
Perovskite solar cells



K. Kalyanasundaram, S. M. Zakeeruddin, M. Grätzel, *Material Matters, 2016, 11.1, 3*

Halide perovskites ABX_3 and with mixed ions

$FAPbI_{3-x}Br_x$, E_g =1.48 – 2.23 eV



(B) Sn - decreases E_g
(X) Br - increases E_g

	t	Eg	PCE
$MAPbI_3$	0.89	1.5	20.3
$FAPbI_3$	1.02	1.49	17
$CsPbI_3$	0.79	1.72	10,77
$FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$		1.62	22.1
$FA_{0.85}Cs_{0.15}PbI_3$	0.99	1.52	17.3
$FA_{0.85}Cs_{0.17}Pb(I_{0.83}Br_{0.17})_3$	1.01	1.74	20.0
$FA_{0.75}Cs_{0.25}Pb_{0.5}Sn_{0.5}I_3$		1.2	

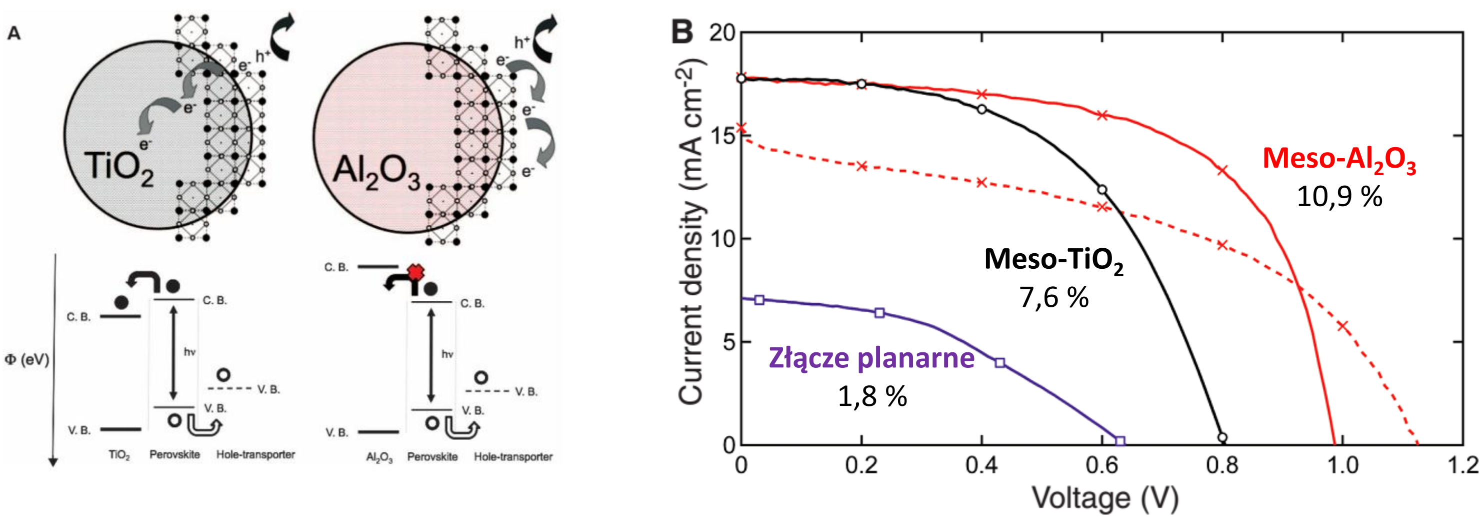
T. Leijtens et al. , J. *Mater. Chem*. A, 2017, 5,11483

Perovskite solar cells

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

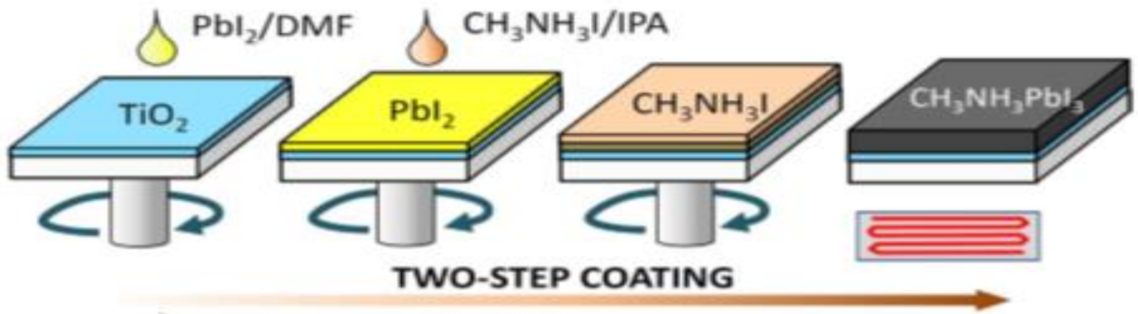
Michael M. Lee,[1] Joël Teuscher,[1] Tsutomu Miyasaka,[2] Takurou N. Murakami,[2,3] Henry J. Snaith[1]*

SCIENCE VOL 338 2 NOVEMBER 2012 643



Perovskite solar cells

Two etap method



ong-Hyeok Im i in., Morphology-photovoltaic
perty correlation in perovskite solar cells:
e-step versus two-step deposition of
$_3NH_3PbI_3$, APL Materials, 2014

PbI_2

<u>Spin – coating:</u> 3000 r. p. m, 30s

<u>Annealing:</u> 40 ° C – 2 min., 100 ° C - 5 min.

CH_3NH_3I

<u>Dippng:</u> 40 s

<u>Annealing :</u> 100 ° C, 10 min

Two-stage method - production of perovskites in mesoporous skeletal structures (TiO_x, ZnO)

Perovskite solar cells

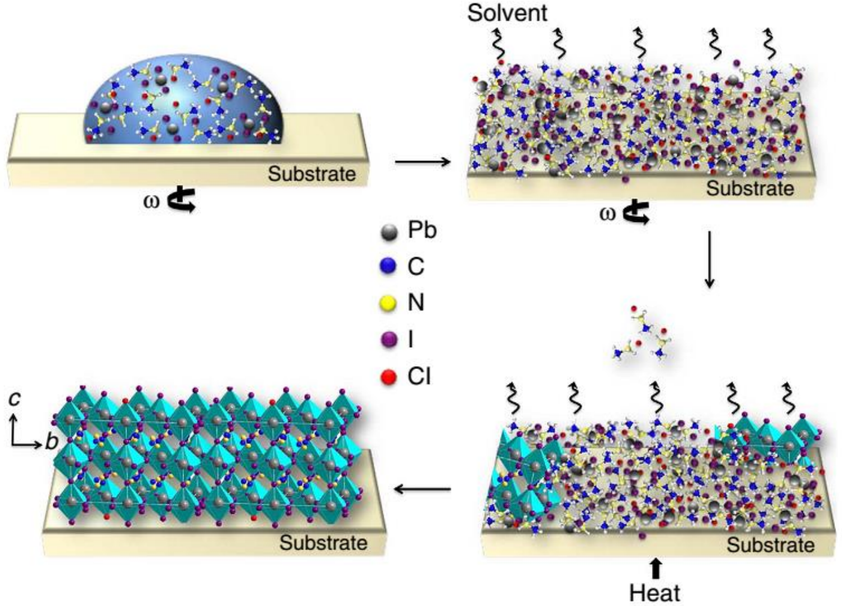
one-step method

NATURE COMMUNICATIONS 2014

Ultrasmooth organic–inorganic perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells

Wei Zhang[1], Michael Saliba[1], David T. Moore[2], Sandeep K. Pathak[1], Maximilian T. Hörantner[1], Thomas Stergiopoulos[1], Samuel D. Stranks[1], Giles E. Eperon[1], Jack A. Alexander-Webber[1], Antonio Abate[1], Aditya Sadhanala[3], Shuhua Yao[4], Yulin Chen[1], Richard H. Friend[3], Lara A. Estroff[2,5], Ulrich Wiesner[2] & Henry J. Snaith[1]

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



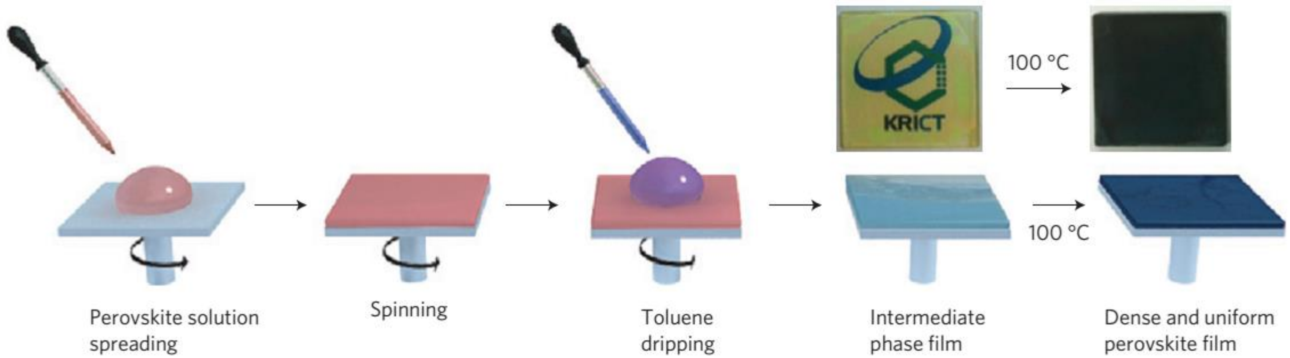
Perovskite solar cells

NATURE MATERIALS , 2014

Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells

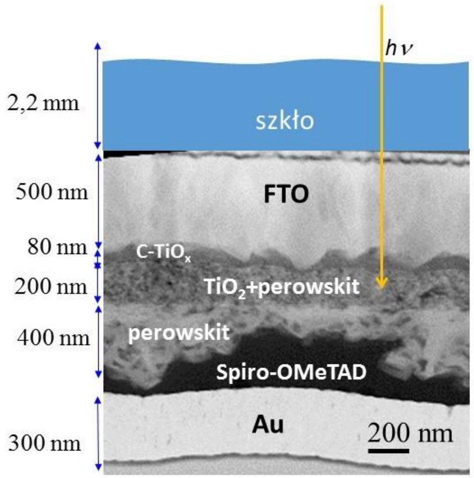
Nam Joong Jeon[1†], Jun Hong Noh[1†], Young Chan Kim[1], Woon Seok Yang[1], Seungchan Ryu[1] and Sang Il Seok[1,2*]

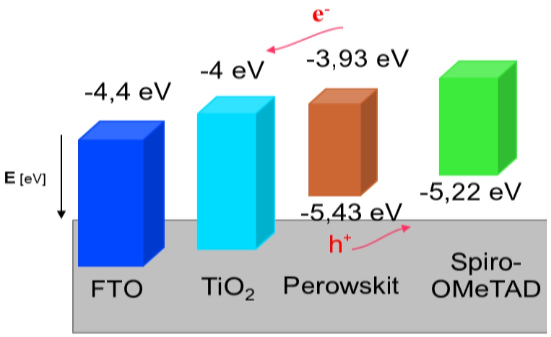
Division of Advanced Materials, Korea Research Institute of Chemical Technology, Korea,
Department of Energy Science, University, Suwon ,Republic of Korea

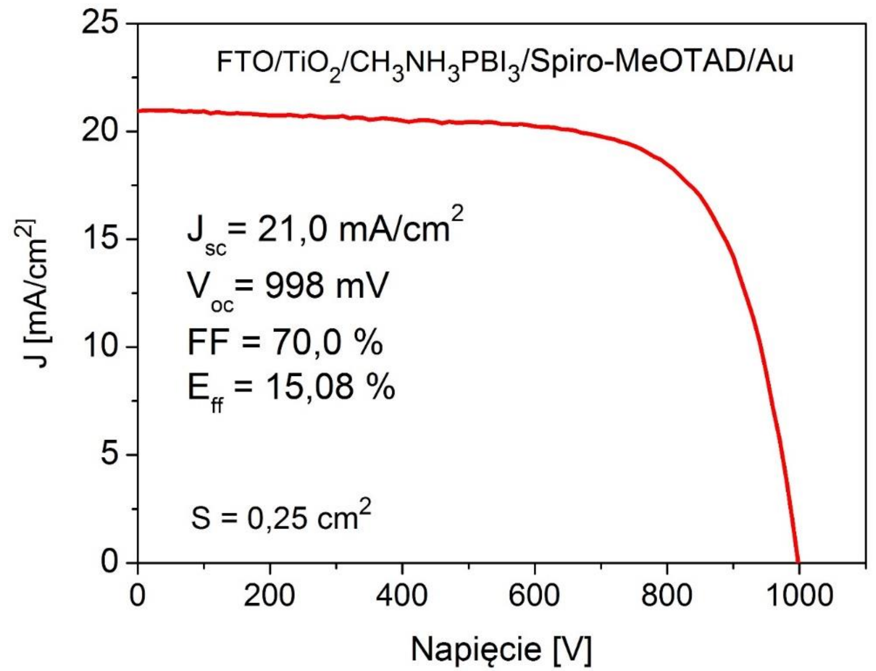


$$PbI_2 - DMSO - MAI \rightarrow MAPbI_3 + DMSO\uparrow$$

Perovskite solar cells



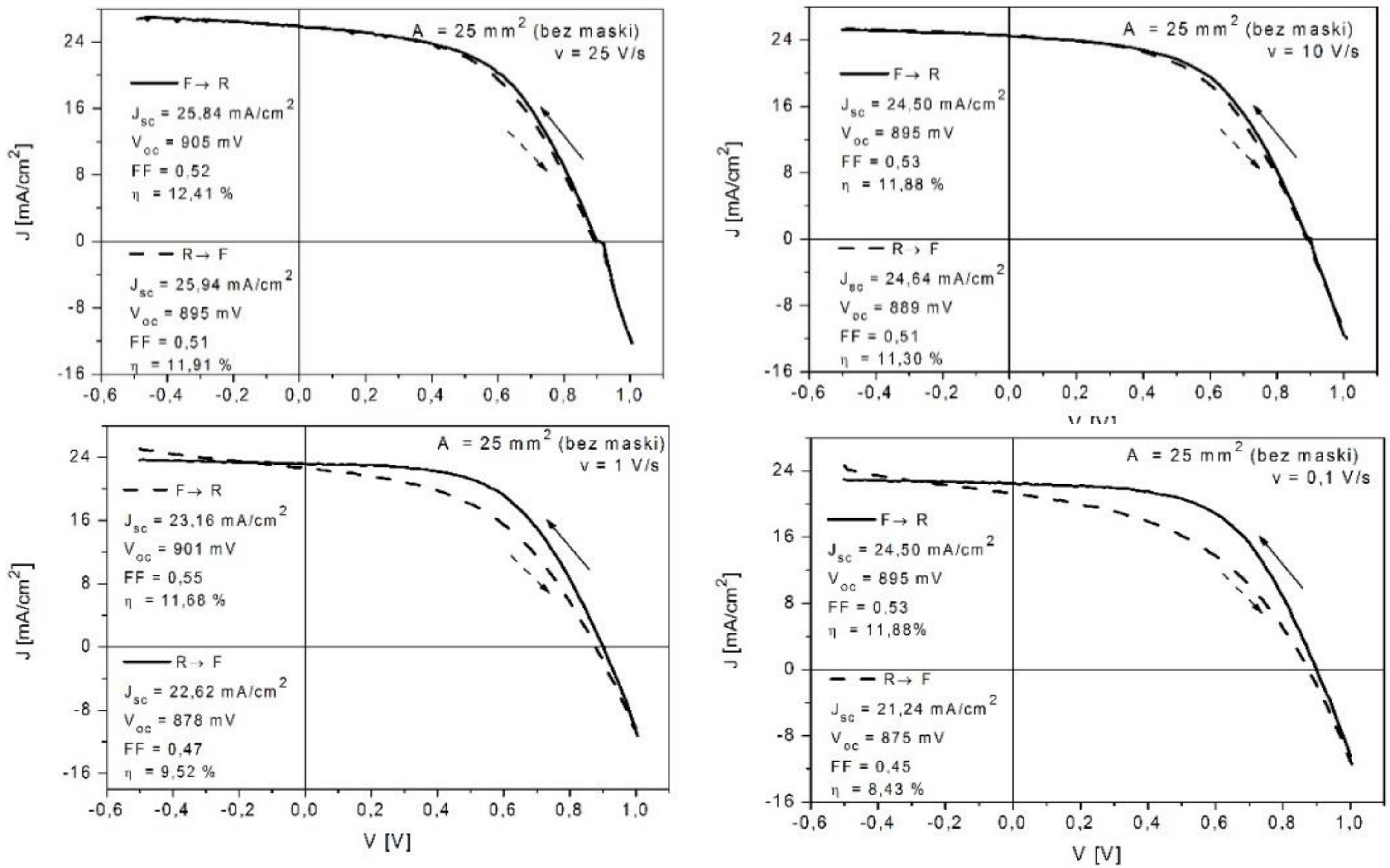




Characteristics of J-V perovskite cell made in LF IMIM PAN in Kozy

Cells developed at LF IMIM

I-V characteristic hysteresis



J-V characteristics of the perovskite cell for both scan directions for scanning speeds of 25 V / s (a), 1V / s (b) and 0.5 V/s. Cells made in LF IMIM PAN in Kozy

Stability

Opto-Electronics Review 25 (2017) 274–284

Contents lists available at ScienceDirect

Opto-Electronics Review

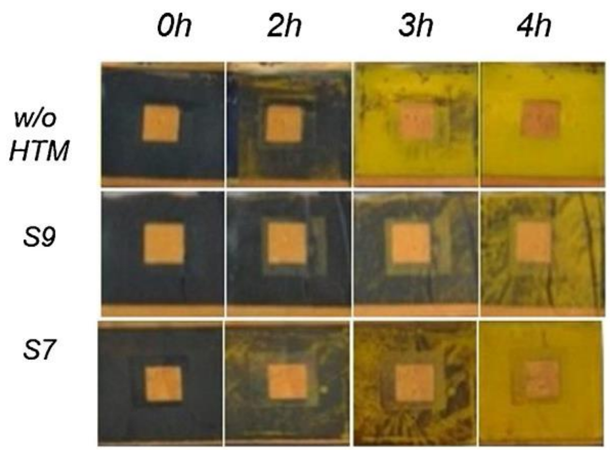
journal homepage: http://www.journals.elsevier.com/opto-electronics review

ELSEVIER

Searching of new, cheap, air- and thermally stable hole transporting materials for perovskite solar cells

K. Gawlinska[a,*], A. Iwan[b,*], Z. Starowicz[a], Grazyna Kulesza-Matlak[a], K. Stan-Glowinska[a], M. Janusz[a], M. Lipinski[a], B. Boharewicz[c], I. Tazbir[c], A. Sikora[c]

[a] Institute of Metallurgy and Materials Science, Polish Academy of Sciences, ul. Reymonta 25, 30-059 Krakow, Poland
[b] Military Institute of Engineer Technology, ul. Obornicka 136, 50-961 Wroclaw, Poland
[c] Electrotechnical Institute, Division of Electrotechnology and Materials Science, ul. M. Sklodowskiej-Curie 55/61, 50-369 Wroclaw, Poland

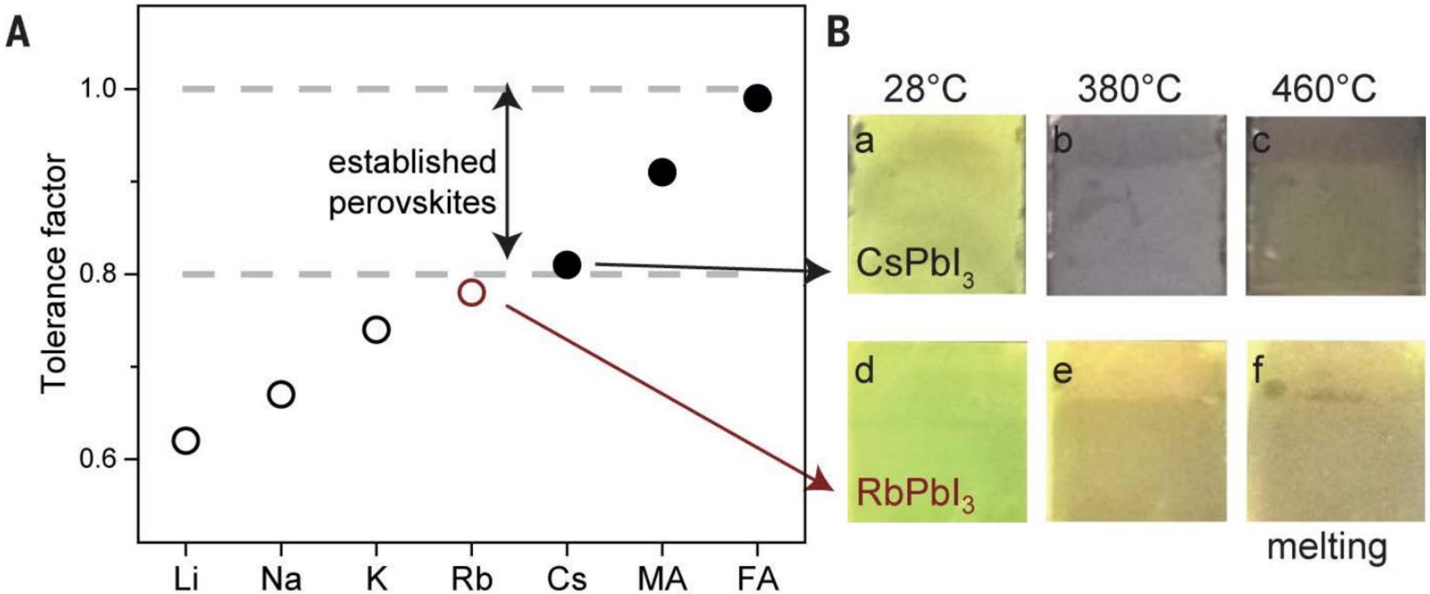


Destruction of $MAPbI_3$ perovskite in the cell (without HTM and without encapsulation). A yellow color indicates the presence of PbI2. The cell exposed to sunlight. Test of S9 and S7 polymers (polyazomethines) for encapsulation

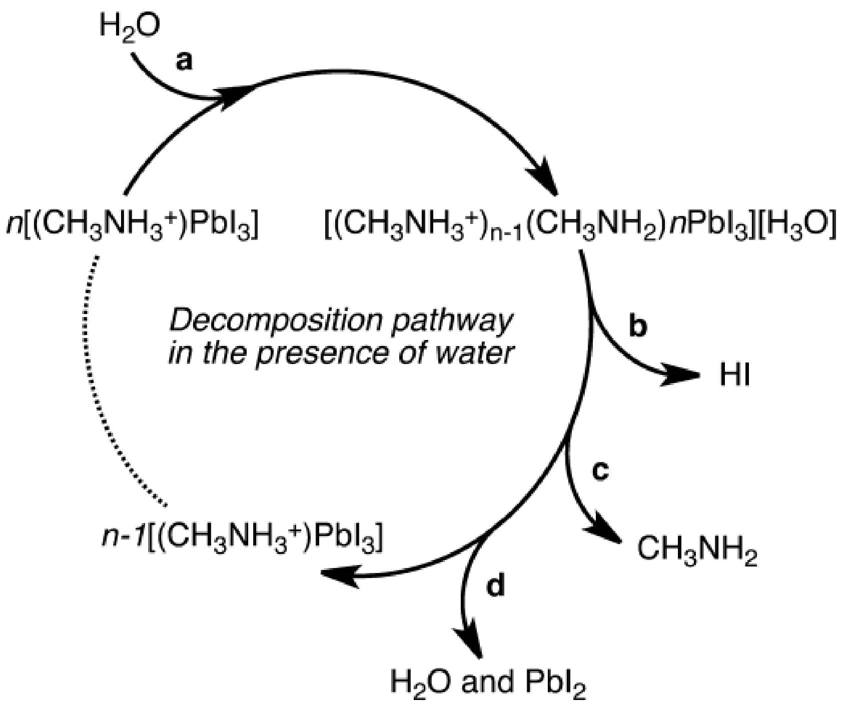
Stability

- Structure stability
- Thermal stability
- Atmospheric stability
- Oxygen interaction
- Water impact
- Stability to UV radiation

Stability



M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate and A. Hagfeldt, Incorporation of Rubidium Cations into Perovskite Solar Cells Improves Photovoltaic Performance, Science, 2016, 354(6309), 206.



$$4MAPbI_3 + 2H_2O \leftrightarrow MA_4PbI_6 \cdot H_2O + 3PbI_2$$

CH3NH2 methylamine - volatile and water-soluble HI-water-soluble 1]

Another mechanism according to [2]

1. J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. Van Schilfgaarde and A. Walsh,, Nano Lett., 2014, 14, 2584–2590
2. J. A. Christians , P. A. Miranda Herrera , P. V. Kamat ,*J. Am. Chem. Soc.* 2015 ,*137* , 1530 .

Thermal stability

Requirements:
Cell operating temperature -40 to> 85 °C. Cell operation up to 85˚C
Lamination - 150 ˚ C

MAPbX$_3$ unstable at 85°C - MA sublimates at 85 °C even in an inert atmosphere

Materials Views www.MaterialsViews.com
Adv. Energy Mater., 2015, 1500477
ADVANCED ENERGY MATERIALS www.advenergymat.de

Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite

Bert Conings, Jeroen Drijkoningen, Nicolas Gauquelin, Aslihan Babayigit, Jan D'Haen, Lien D'Olieslaeger, Anitha Ethirajan, Jo Verbeeck, Jean Manca, Edoardo Mosconi, Filippo De Angelis, and Hans-Gerd Boyen**

Institute for Materials Research
Hasselt University
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Electron Microscopy for Materials Research (EMAT)
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X-LaB, Hasselt University
Agoralaan Building D, 3590 Diepenbeek, Belgium

Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO)
CNR-ISTM, I-06123 Perugia, Italy

MAPbX$_3$ is not suitable for industrial production!

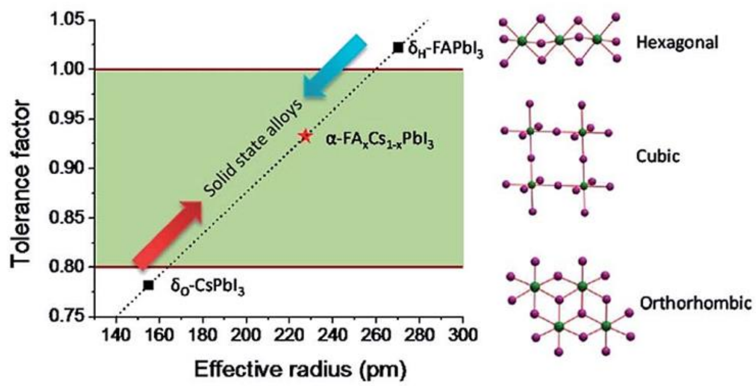
NATURE ENERGY | VOL 3 | JANUARY 2018 | 68–74 |

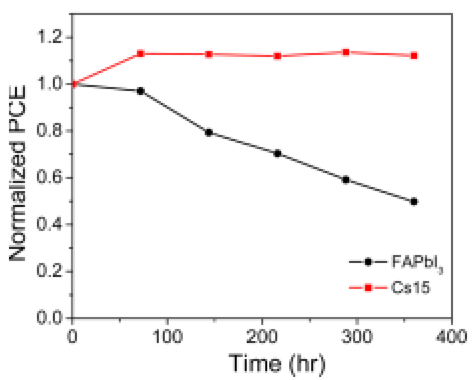
CHEMISTRY OF MATERIALS
Article
pubs.acs.org/cm

Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys

Zhen Li,[†] Mengjin Yang,[†] Ji-Sang Park,[†] Su-Huai Wei,[†,§] Joseph J. Berry,[†] and Kai Zhu*,[†]

[†]National Renewable Energy Laboratory, Golden, Colorado 80401, United States
[§]Beijing Computational Science Research Center, Beijing 100094, China





3D metal halide perovskites used in photovoltaics
Mixed cations [FAMA], [FACs]

	t	Faza, kolor	Faza po wygrzaniu	Eg	PCE	Przejście fazowe
$MAPbI_3$	0,89	Tetragonal, black	Tetragonal	1,5	20,3	Regular, 60° C
$FAPbI_3$	1,02	Hexagonal, yellow	regular	1,49	17	Regular, 150° C
$CsPbI_3$	0,79	Rhombic, yellow	Rhombic, yellow	1,72	10,77	Regular, 300° C
$FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$		Regular, black	Regular black	1,62	22,1	
$FA_{0.85}Cs_{0.15}PbI_3$	0,99	Tetragonal, black	tetragonal	1,52	17,3	
$FA_{0.85}Cs_{0.15}Pb(I_{0.83}Br_{0.17})_3$	1,01	Tetragonal, blacka	tetragonal	1,74	20,0	

Tomas Leijtens, Kevin Bush, Rongrong Cheacharoen, Rachel Beal,
Andrea Bowring and Michael D. McGehee,
Towards enabling stable lead halide perovskite solar cells; interplay between structural, environmental, and thermal stability, J. Mater. Chem. A, 2017, 5,11483
Department of Materials Science, Stanford University, Lomita Mall, Stanford, CA, USA.

3D metal halide perovskites used in photovoltaics
Mixed cations [FAMA], [FACs]

	Eg [eV]	PCE [%]	cell	ref
$FA_{0.83}Cs_{0.17}Pb(I_{0.83}Br_{0.17})_3$	1,74	23,6 PSC/Si	Tandem monolit PSC/Si	[2]
$FA_{0.75}Cs_{0.25}Pb_{0.5}Sn_{0.5}I_3$ $FA_{0.83}Cs_{0.17}Pb(I_{0.5}Br_{0.5})_3$	1,2 1,8	17,0 PSC/PSC	Tandem PSC/PSC	[3]

[1] **High-performance photovoltaic perovskite layers fabricated through intramolecular exchange**

Woon Seok Yang,[1*] Jun Hong Noh,[1*] Nam Joong Jeon,[1] Young Chan Kim,[1] Seungchan Ryu,[1] Jangwon Seo,[1] Sang Il Seok[1,2]†

[1]Division of Advanced Materials, Korea Research Institute of Chemical Technology, 141 Gajeong-Ro, Yuseong-Gu, Daejeon 305-600, Korea. [2]Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea.

Science, 2015, 348(6240),1234

[2] NREL, *Best Research-Cell Efficiencies*, 2017

nature energy

ARTICLES

PUBLISHED: 17 FEBRUARY 2017 | VOLUME: 2 | ARTICLE NUMBER: 17009

[2]

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 OX1 3PU, UK. [5]D2 Solar LLC, San Jose 95131, USA. [6]Sunpreme, Sunnyvale 94085, USA. †These authors contributed equally to this work. *e-mail: Zachary.holman@asu.edu; Mmcgehee@stanford.edu

[3]

Science

REPORTS

Cite as: G. E. Eperon *et al.*, *Science* 10.1126/science.aaf9717 (2016).

Perovskite-perovskite tandem photovoltaics with optimized bandgaps

Giles E. Eperon,[1,3]* Tomas Leijtens,[2]* Kevin A. Bush,[2] Rohit Prasanna,[2] Thomas Green,[1] Jacob Tse-Wei Wang,[1] David P. McMeekin,[1] George Volonakis,[4] Rebecca L. Milot,[1] Richard May,[2] Axel Palmstrom,[2] Daniel J. Slotcavage,[2] Rebecca A. Belisle,[2] Jay B. Patel,[1] Elizabeth S. Parrott,[1] Rebecca J. Sutton,[1] Wen Ma,[5] Farhad Moghadam,[5] Bert Conings,[1,6] Aslihan Babayigit,[1,6] Hans-Gerd Boyen,[6] Stacey Bent,[2] Feliciano Giustino,[4] Laura M. Herz,[1] Michael B. Johnston,[1] Michael D. McGehee,[2†] Henry J. Snaith[1†]

[1]Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK. [2]Department of Materials Science, Stanford University, Lomita Mall, Stanford, CA, USA. [3]Department of Chemistry, University of Washington, Seattle, WA, USA. [4]Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK. [5]SunPreme, Palomar Avenue, Sunnyvale, CA, USA. [6]Institute for Materials Research, Hasselt University, Diepenbeek, Belgium.

Mixed cations [RbCsMAFA]

Science

REPORTS

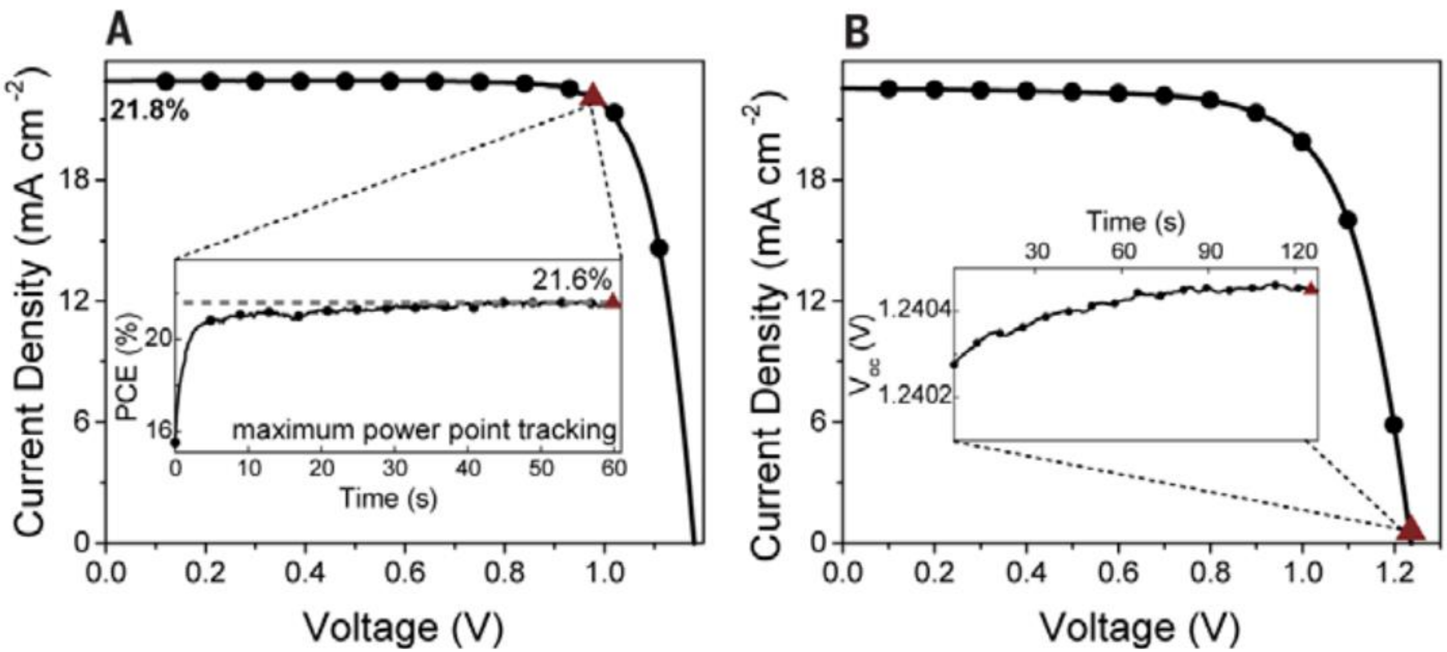
Cite as: M. Saliba *et al*., *Science* 10.1126/science.aah5557 (2016).

Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance

Michael Saliba,[1*†] Taisuke Matsui,[1,2*] Konrad Domanski,[1*] Ji-Youn Seo,[1] Amita Ummadisingu,[1] Shaik M. Zakeeruddin,[1] Juan-Pablo Correa-Baena,[3] Wolfgang R. Tress,[1] Antonio Abate,[1] Anders Hagfeldt,[3] Michael Grätzel[1]†

[1]Laboratory of Photonics and Interfaces, École Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland. [2]Advanced Research Division, Materials Research Laboratory, Panasonic Corporation, 1006 Kadoma, Kadoma City, Osaka 571-8501, Japan. [3]Laboratory of Photomolecular Science, École Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland.

Mixed cations [RbCsMAFA]



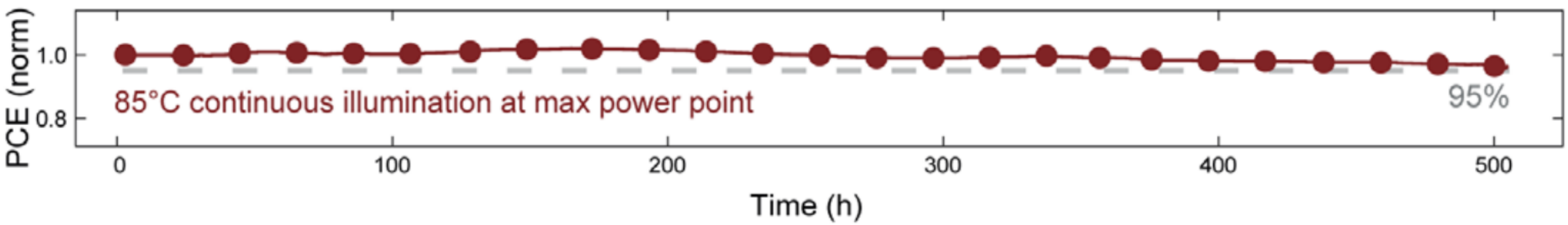
A) J-V characteristic for 10 mVs^{-1} cell with 21.8% efficiency (Voc = 1180 mV, J_{sc} = 22.8 mA cm^{-2}, FF 81%).

B) cell with the highest Voc. 19% PCE stabilized for 0.5 cm^2 cell.

Saliba et al. *Science*, 2016, 354(6309), 206

Mixed cations [RbCsMAFA]

Kationy mieszane [RbCsMAFA]



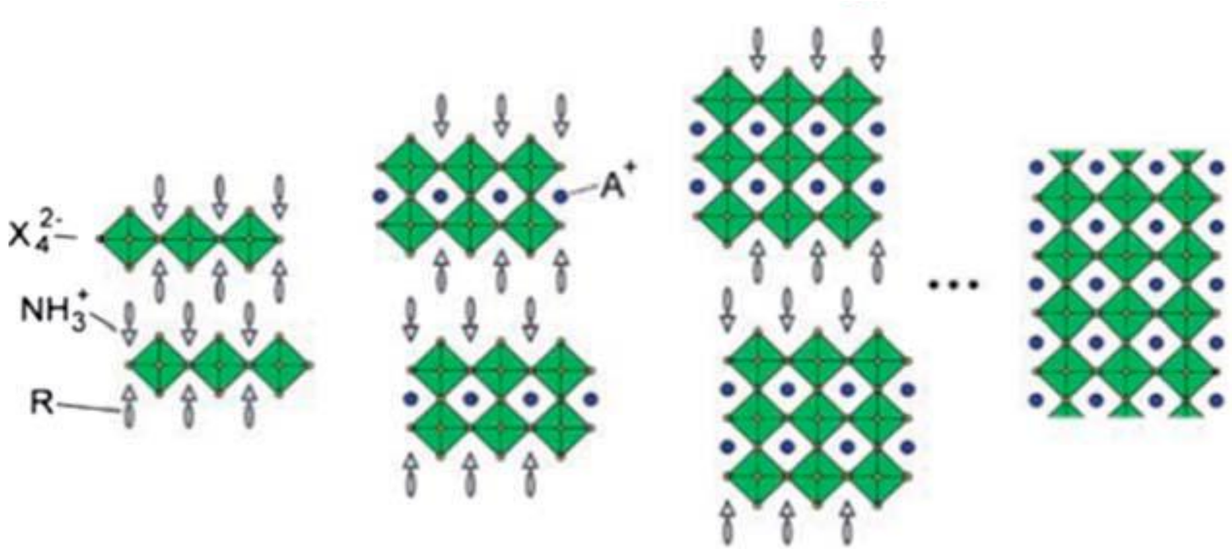
Thermal stability test. Aging 500 hours at 85°C, full solar lighting at the point of maximum power in the atmosphere N2. Aging procedure more stringent than for industrial standards.

Saliba et al. *Science*, 2016, 354(6309), 206

Layered perovskites

$R_2(A)_{n-1}B_nX_{3n+1}$ (n=1, 2, 3, 4, …) n the numer of layer (Ruddlesden-Popper structure).

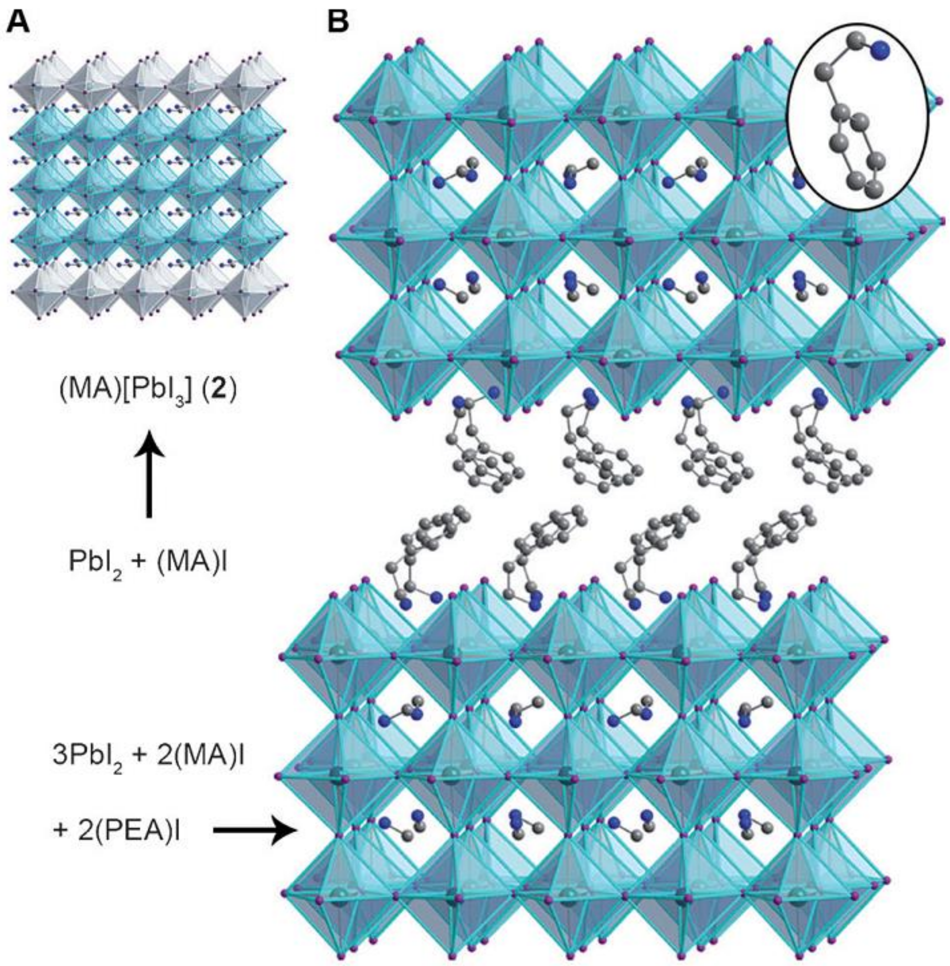
Dla R= kation butyloamoniowy (n butylammonium)
R – large alkylammonium cations:
PEA = $C_8H_9NH_3$ phenylethylammonium cation
BA = $C_4H_9NH_3$ butylammonium cation



n = 1   n = 2   n = 3   n = ∞

Layered perovskites

$(PEA)_2(MA)_2Pb_3I_{10}$



$PEA = C_6H_5(CH_2)_2NH_3^+$

V_{oc} = 1.18 V
PCE = 4.73%

E_g =2,1 eV

2D-3D structures - the ways of icreasing stability

nature energy
ARTICLES
PUBLISHED: 14 AUGUST 2017 | VOLUME: 2 | ARTICLE NUMBER: 17135

Efficient ambient-air-stable solar cells with 2D–3D heterostructured butylammonium-caesium-formamidinium lead halide perovskites

Zhiping Wang, Qianqian Lin, Francis P. Chmiel, Nobuya Sakai, Laura M. Herz and Henry J. Snaith*

Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, UK.

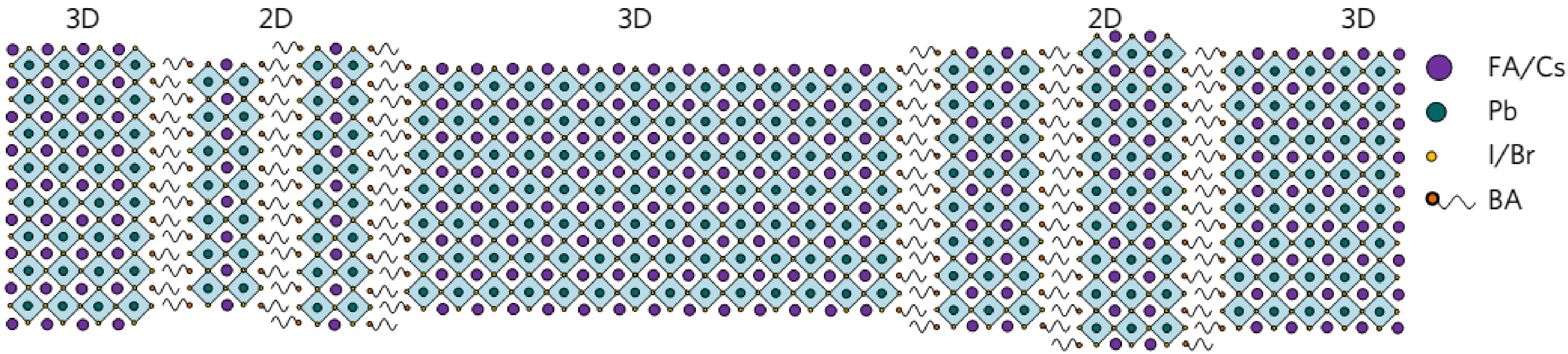
3D perovkite $FA_{0.83}Cs_{0.17}Pb(I_yBr_{1-y})_3$

2D perovskite $(BA)_2(MA)_3Pb_4I_{13}$

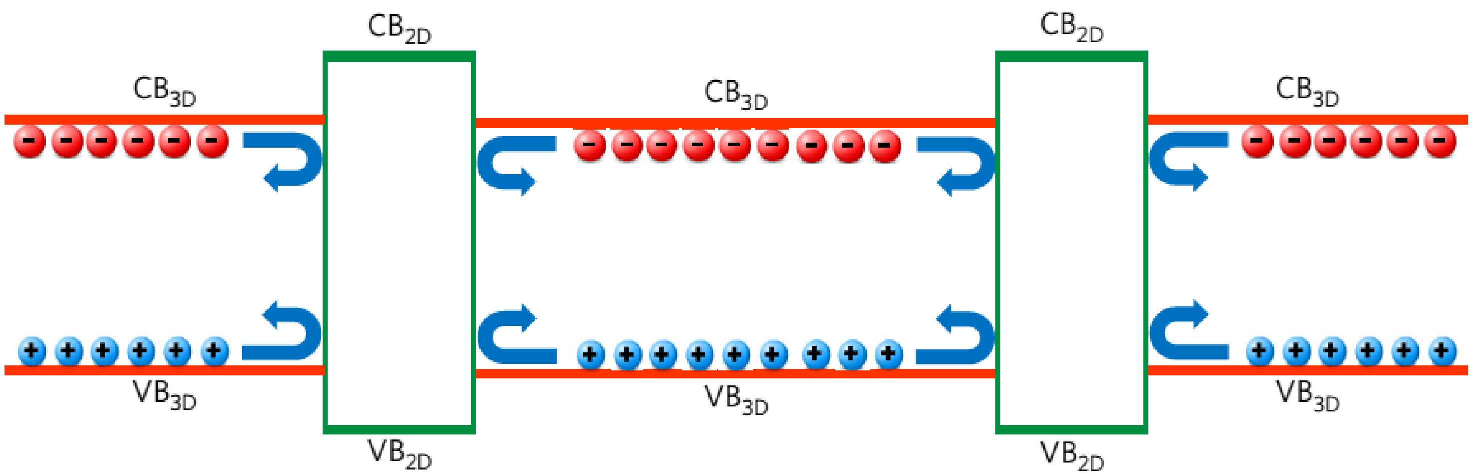
2D-3D structure:

$BA_{0.09}(FA_{0.83}Cs_{0.17})_{0.91}Pb(I_{0.6}Br_{0.4})_3$ ($x = 0.09$)

2D-3D structures



Model struktury 2D-3D



Model of energetic bands of 2D-3D structure, CB- conductivity band, VB valence band.

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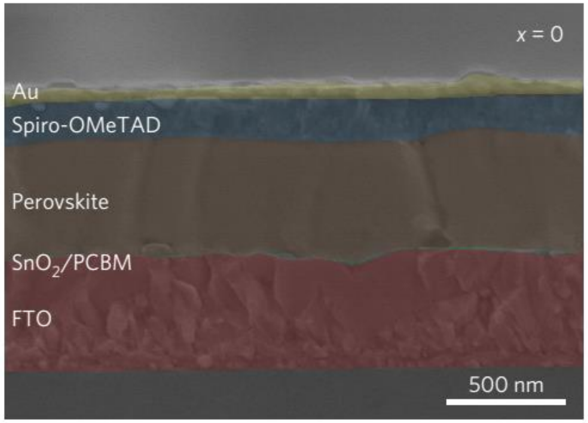
2D-3D structures

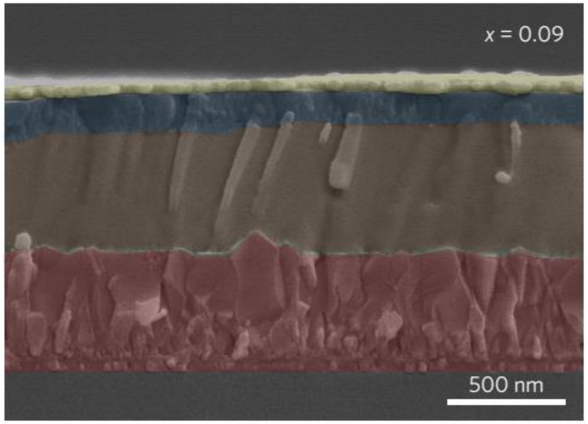
3D



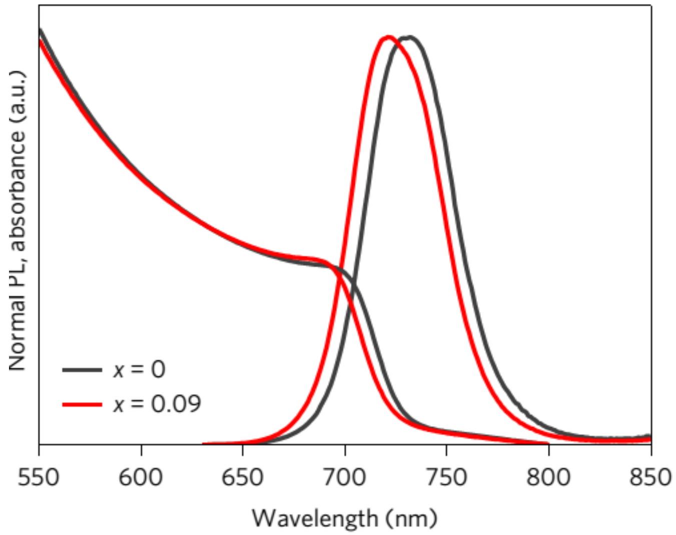
$FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ ($x = 0$)

3D-2D

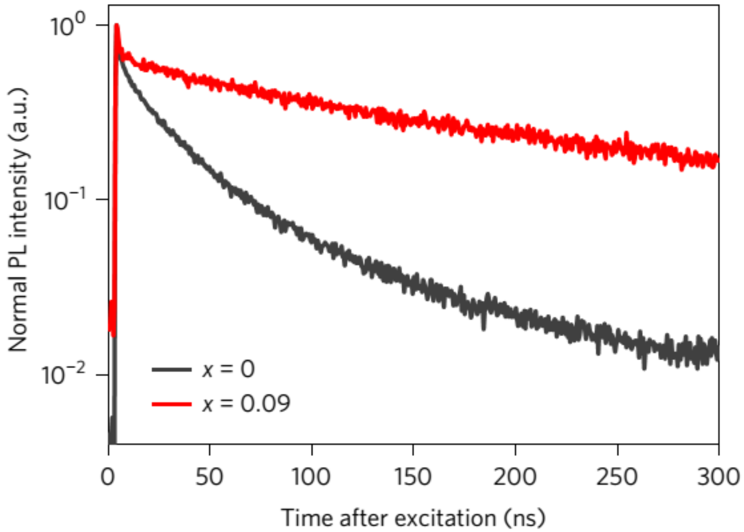
b



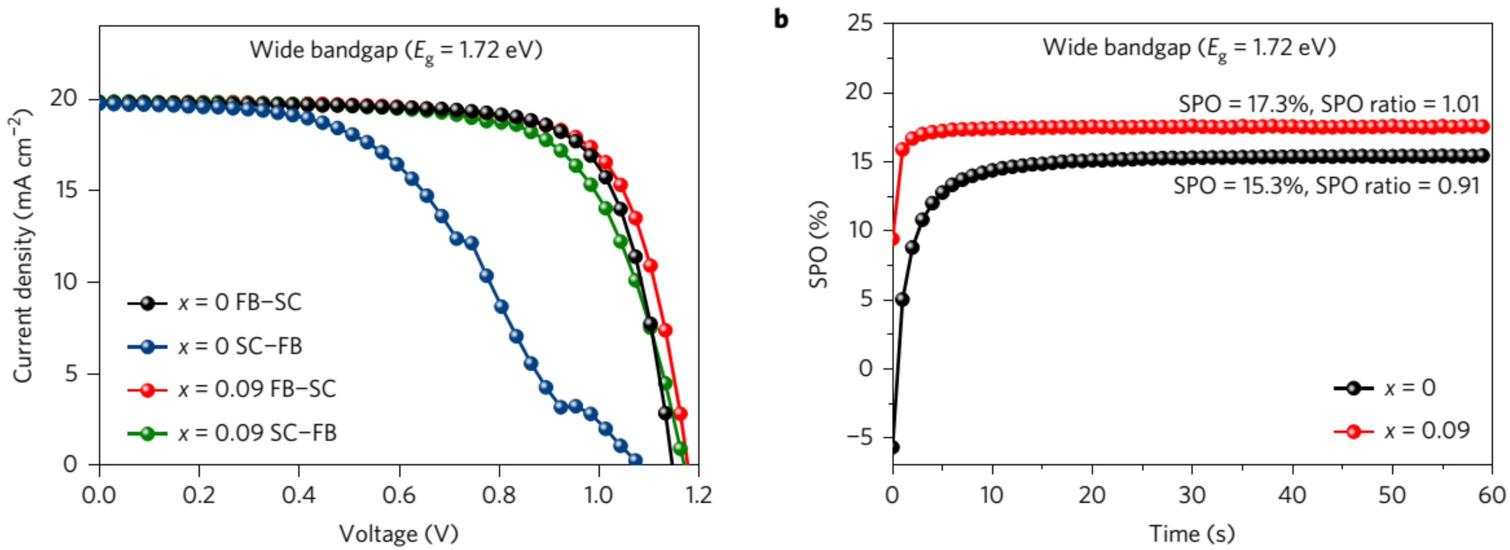
$BA_{0.09}(FA_{0.83}Cs_{0.17})_{0.91}Pb(I_{0.6}Br_{0.4})_3$ ($x = 0.09$)



e



2D-3D structures



(a) J-V characteristics: 3D perovskite $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ (x=0) (E_g = 1.72 eV) and for 3D-2D $BA_{0.09}(FA_{0.83}Cs_{0.17})_{0.91}Pb(I_{0.6}Br_{0.4})_3$ (x= 0,09)

(a) Stabilized cell efficiency (SPO) of the best cell (SPO ratio - ratio of SPO to PCE.

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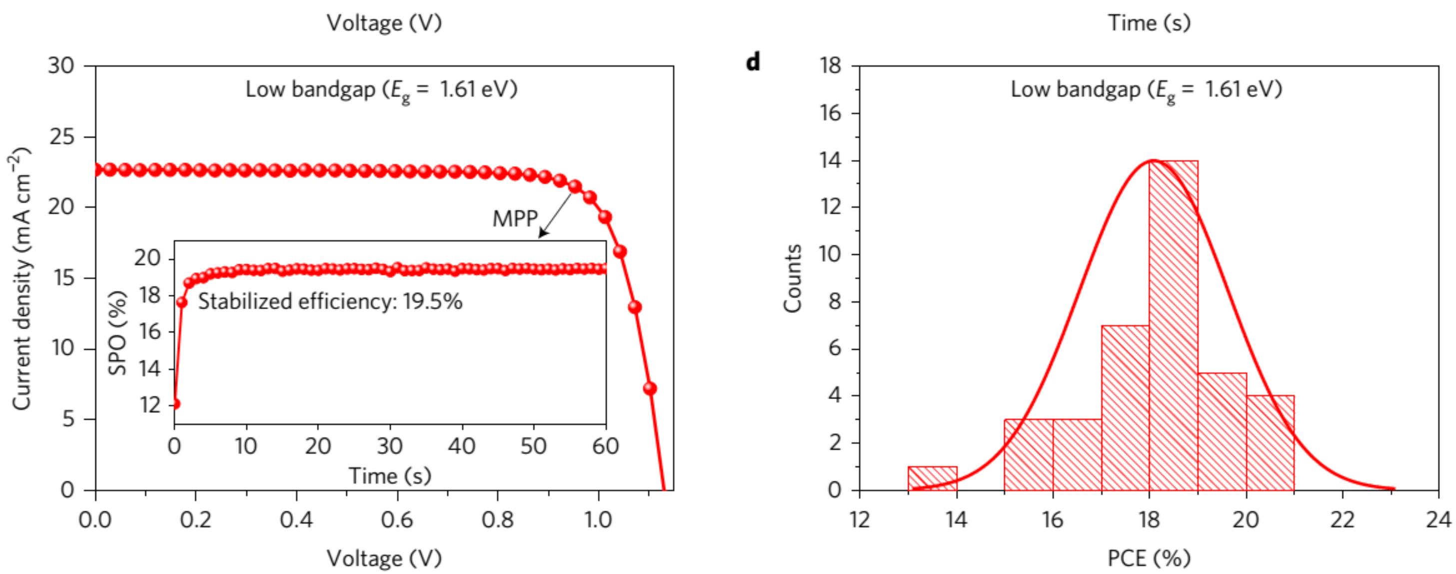
2D-3D structures



J-V characteristics: 3D perovskite for $BA_{0.05}(FA_{0.83}Cs_{0.17})_{0.95}Pb(I_{0.8}Br_{0.2})_3$ (E_g = 1.61 eV). Statistical distribution

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2D-3D structures

Table 1 | Solar cell performance parameters determined from *J–V* curves and stabilized power output measurements.

Device	PCE (%)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	SPO (%)
Wide-bandgap $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ (x = 0)					
Average	15.1 ± 1.0	18.8 ± 0.9	1.15 ± 0.02	0.70 ± 0.03	14.1 ± 0.9
Champion	16.9	19.8	1.14	0.75	15.3
Wide-bandgap $BA_{0.09}(FA_{0.83}Cs_{0.17})_{0.91}Pb(I_{0.6}Br_{0.4})_3$ (x = 0.09)					
Average	15.5 ± 1.1	18.9 ± 0.7	1.17 ± 0.02	0.70 ± 0.04	15.8 ± 0.8
Champion	17.2	19.8	1.18	0.73	17.3
Low-bandgap $BA_{0.05}(FA_{0.83}Cs_{0.17})_{0.91}Pb(I_{0.8}Br_{0.2})_3$					
Average	18.1 ± 1.5	22.1 ± 0.7	1.09 ± 0.04	0.75 ± 0.05	17.5 ± 1.3
Champion	20.6	22.7	1.14	0.80	19.5

Average device characteristics with standard deviation were obtained on the basis of 32 cells for each set. The champion cell data are taken from the *J–V* curves shown in Fig. 4.

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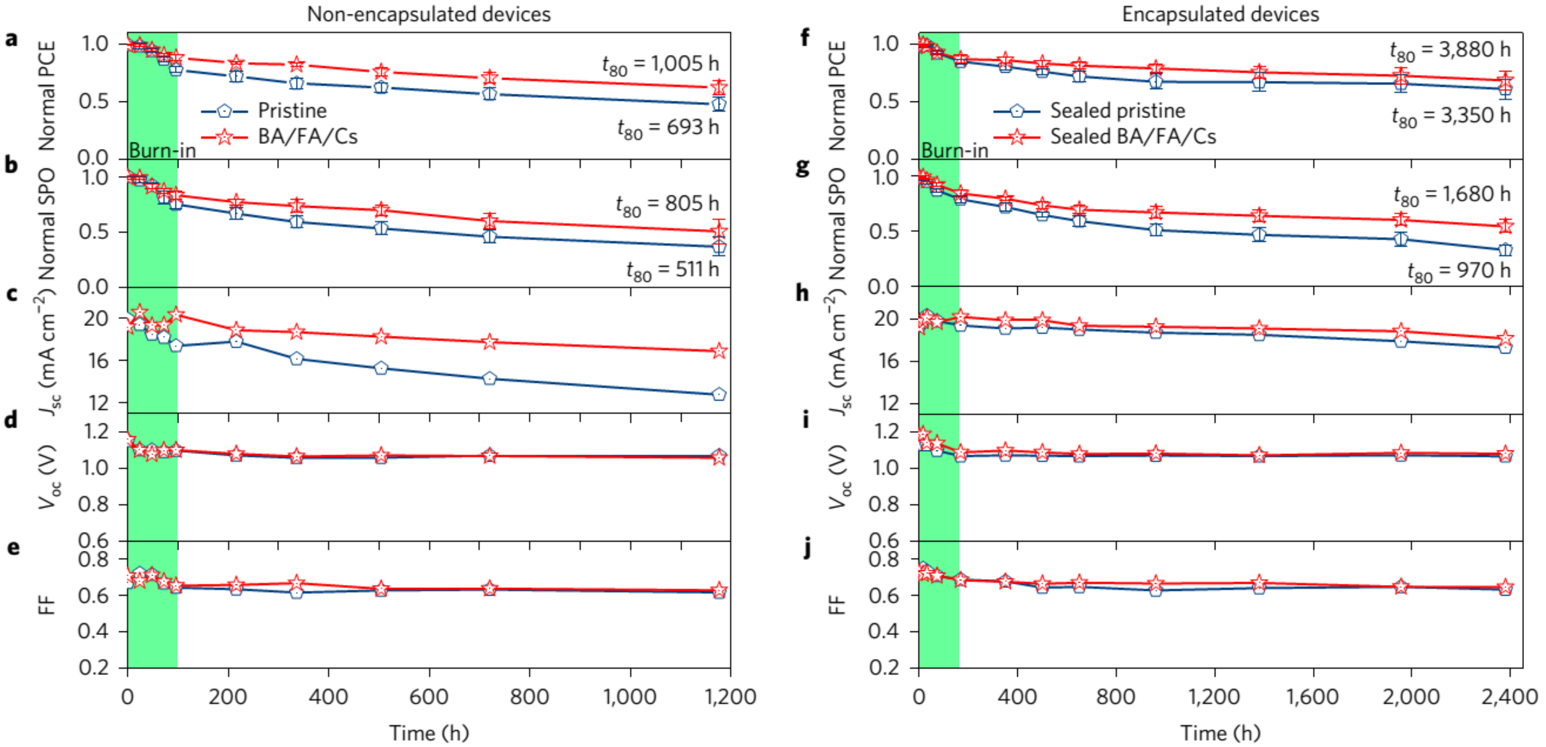
2D-3D structures



Aging - AM1.5 xenon lamp with a power of 76 mW/cm^2 in the air (approx. 45 RH%) without UV filter, in V_{oc} conditions, tested for different time intervals by a separate AM1.5 simulator with a power of $100 mWcm^{-2}$. Light pulse aging with Suntest XLS +. The structure of the cell glass/FTO/SnO2/ C60 /perovskit/spiro-OMeTAD (with Li-TFSI and tBP) / Au.

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Energy & Environmental Science

Selective growth of layered perovskite for stable and efficient photovoltaics.

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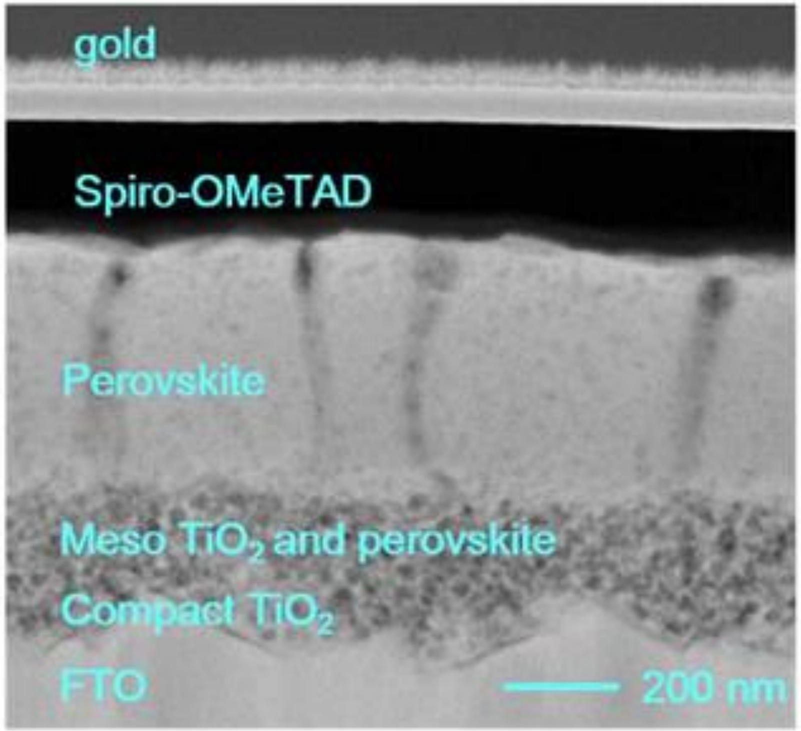
2D-3D structures

PEA_2PbI_4 - $Cs_{0,1}FA_{0,74}MA_{0,13}PbI_{2,48}Br_{0,39}$



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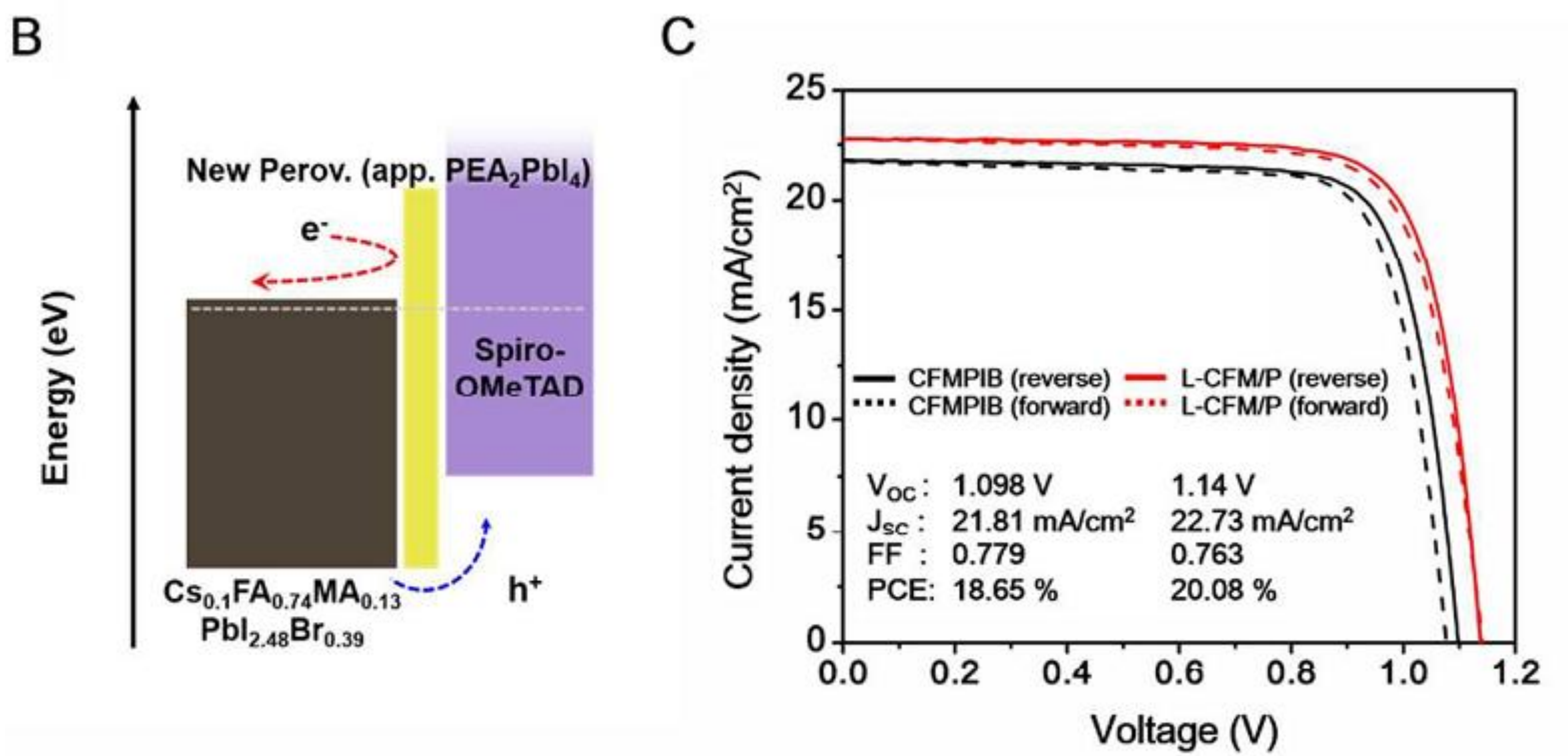
2D-3D structures



CFMPIB - $Cs_{0.1}FA_{0.74}MA_{0.13}PbI_{2.48}Br_{0.39}$

L-CFM/P (CFMPIB i PEA_2PbI_4)

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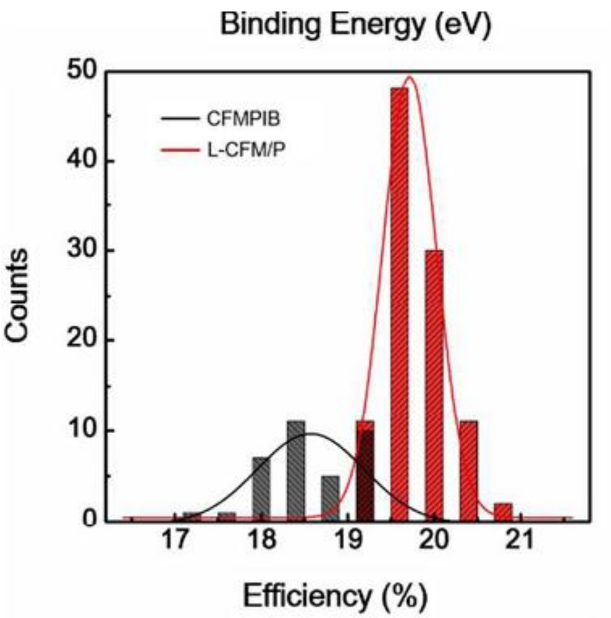

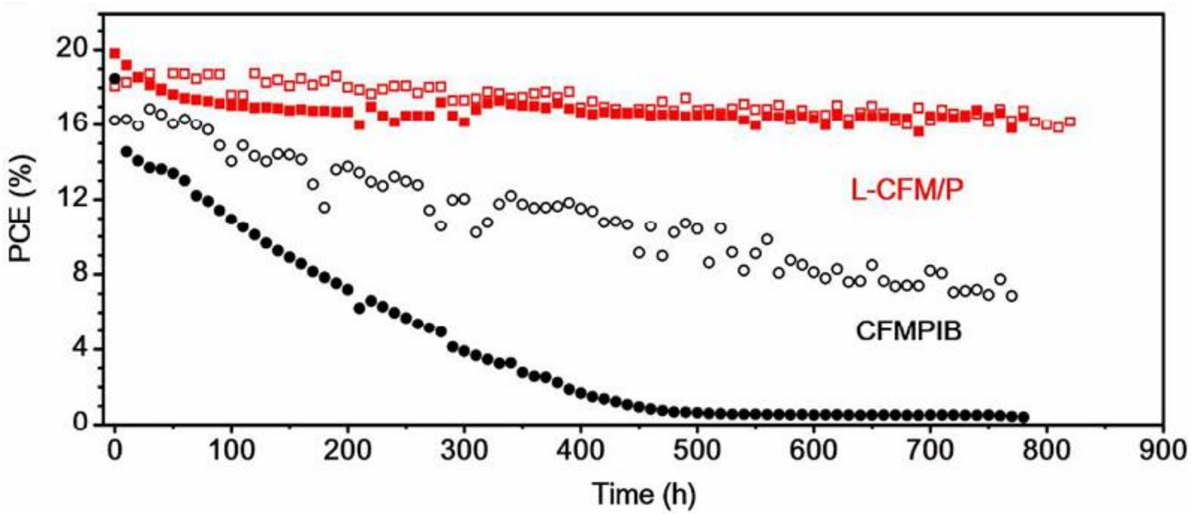

Photo-stability test for continuous (full) lighting in an inert atmosphere (blank stamps) and in the air (full) encapsulated under glass

$Cs_{0.1}FA_{0.74}MA_{0.13}PbI_{2.48}Br_{0.39}$ (CFMPIB)

L-CFM/P (perowskit CFMPIB i PEA_2PbI_4).

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Vol. 38, No. 1 Journal of Semiconductors January 2017

Recent progress in stability of perovskite solar cells*

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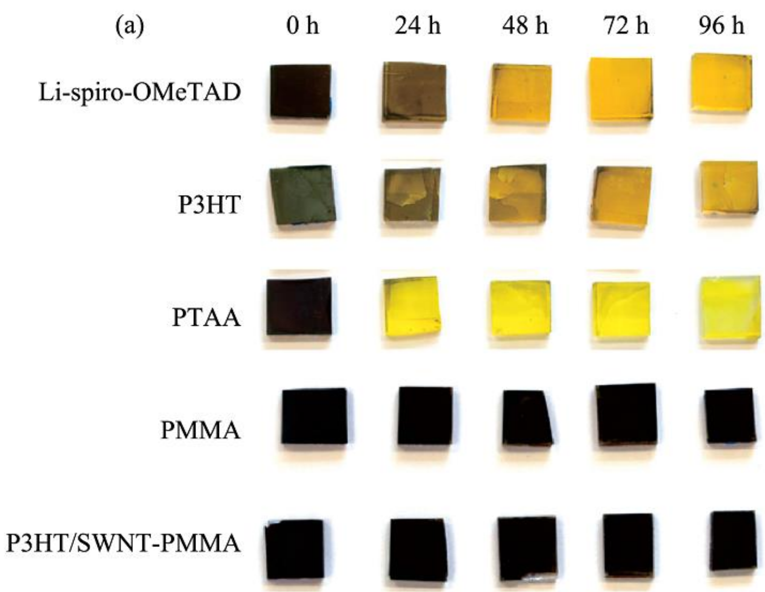
[3]Key Lab of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China
[4]College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China



PMMA- Poly(methyl 2-methylpropenoate)
P3HT- Poly(3-hexylthiophene)
PTAA –poly(triarylamine)
SWNT - carbon nanotube, single-walled

ARTICLES
https://doi.org/10.1038/s41560-017-0067-y
nature energy

Tailored interfaces of unencapsulated perovskite solar cells for >1,000 hour operational stability

Jeffrey A. Christians[1], Philip Schulz[1], Jonathan S. Tinkham[2], Tracy H. Schloemer[2], Steven P. Harvey[1], Bertrand J. Tremolet de Villers[1], Alan Sellinger[1,2], Joseph J. Berry[1*] and Joseph M. Luther[1*]

[1]National Renewable Energy Laboratory, Golden, CO, USA. [2]Department of Chemistry, Colorado School of Mines, Golden, CO, USA.

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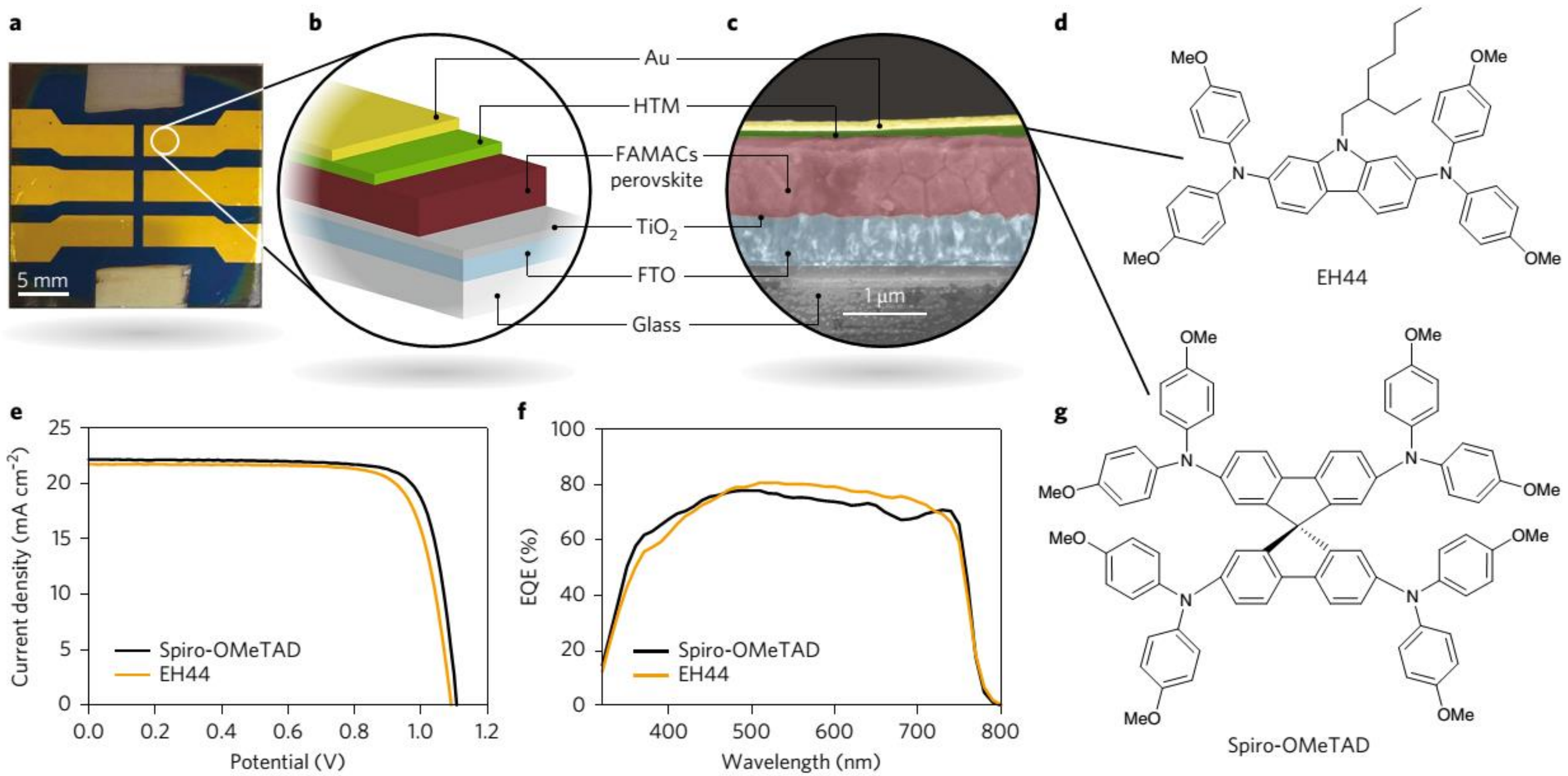
NREL Scientists Demonstrate Remarkable Stability in Perovskite Solar Cells

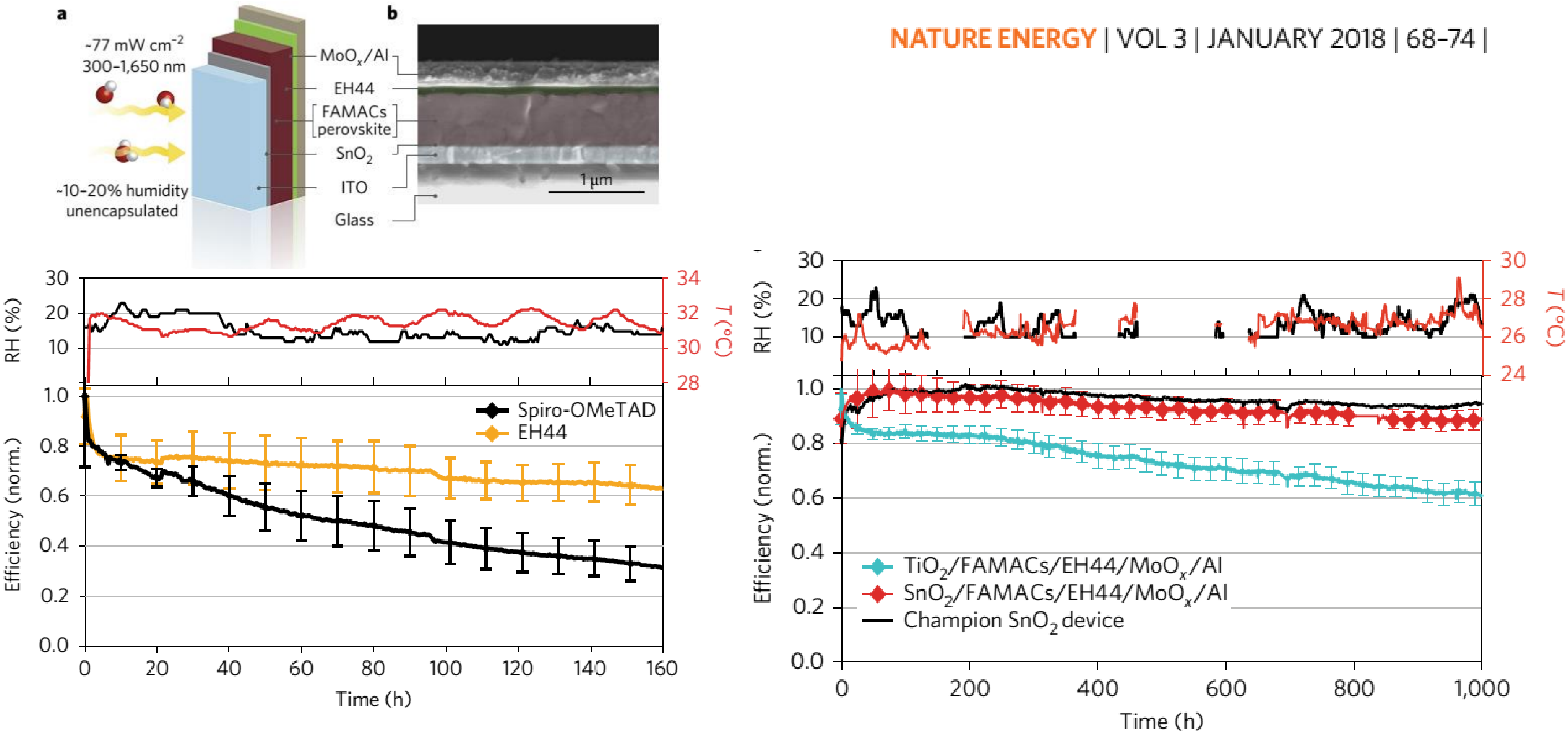
January 30, 2018

https://www.nrel.gov/news/press/2018/nrel_scientists_demonstrate_remarkable_stability_in_perovskite.html

New HTL and electrodes

NATURE ENERGY | VOL 3 | JANUARY 2018 | 68-74 |





NATURE ENERGY | VOL 3 | JANUARY 2018 | 68–74 |

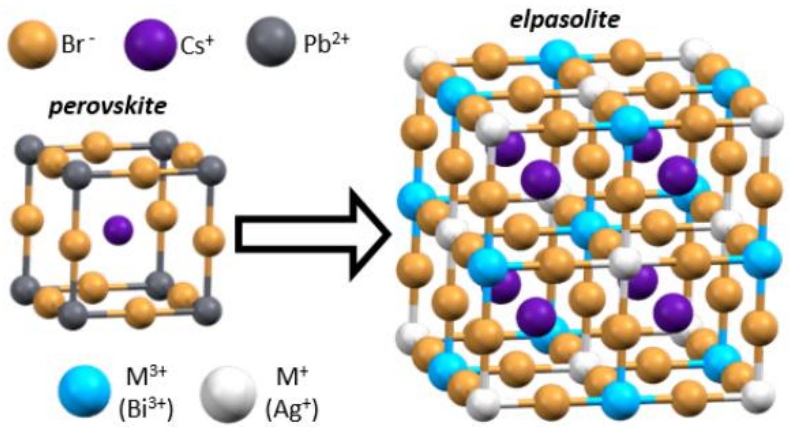
Stability during operation of the TiO2 / FAMACs / EH44 / Au (a) and ETL / FAMACs / EH44 / Mox / Al cells (ETL = TiO_2 (4 cells) or SnO_2 - 15 cells) (b) in air under certain conditions of humidity and temperature .

Double halide perovskites

Colloidal nanocrystals of lead-free double-perovskite (elpasolite) semiconductors: synthesis and anion exchange to access new materials

Sidney E. Creutz, Evan N. Crites, Michael C. De Siena, Daniel R. Gamelin*

Department of Chemistry, University of Washington, Seattle, WA 98195-1700, United States



$Cs_2AgBiBr_6$ – doubling of the unit cell size and replacement of Pb^2 by M^+ i M^{3+} cations

$Cs_2AgInCl_6$, MA_2AgSbI_6, $MA_2TlBiBr_6$, MA_2KBiCl_6, …..

Double halide perovskites

ACS Energy Letters

ACS Editors' Choice

Cite This: ACS Energy Lett. 2018, 3, 297–304

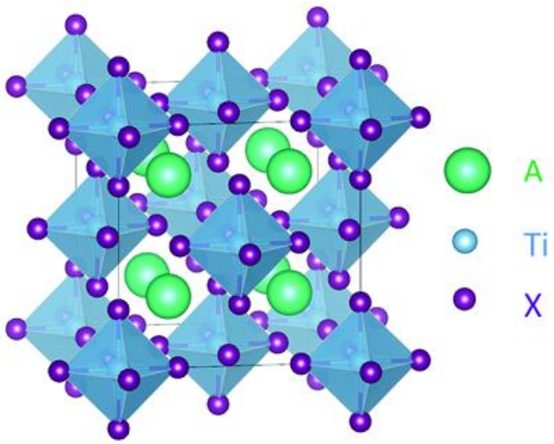
Earth-Abundant Nontoxic Titanium(IV)-based Vacancy-Ordered Double Perovskite Halides with Tunable 1.0 to 1.8 eV Bandgaps for Photovoltaic Applications

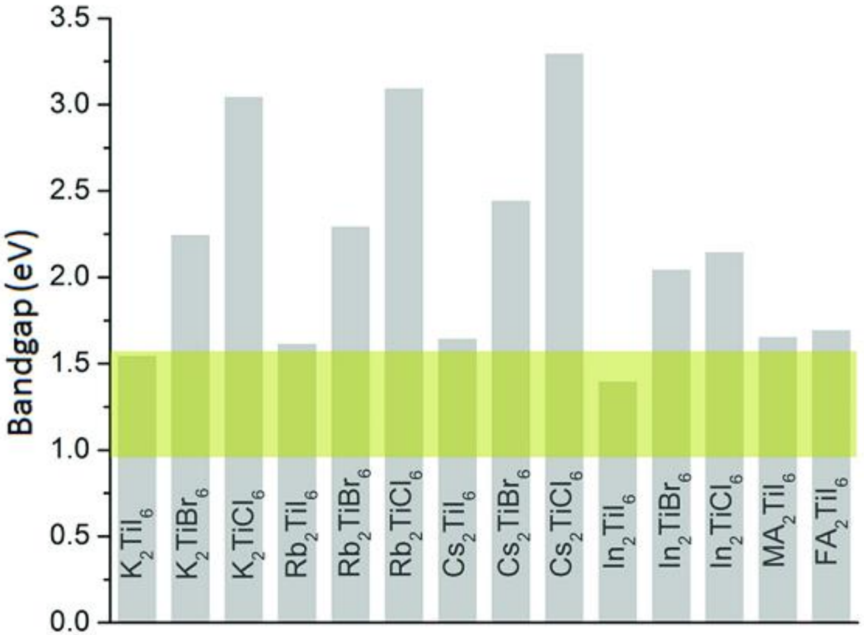
Ming-Gang Ju,[†,§] Min Chen,[‡,§] Yuanyuan Zhou,[*,‡] Hector F. Garces,[‡] Jun Dai,[†] Liang Ma,[†] Nitin P. Padture,[*,‡] and Xiao Cheng Zeng[*,†]

[†]Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, United States

[‡]School of Engineering, Brown University, Providence, Rhode Island 02912, United States

Double halide perovskites





ACS Energy Lett. 2018, 3, 297−304

Double halide perovskites

Journal of Materials Chemistry A

Please do not adjust margins

Published on 05 September 2017

Highly stable, phase pure $Cs_2AgBiBr_6$ double perovskite thin films for optoelectronic applications

Enrico Greul,[a] Michiel L. Petrus,[a] Andreas Binek[a], Pablo Docampo[b] and Thomas Bein[a]*

[a] *Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU) Butenandtstr. 5-13, 81377 Munich, Germany. *E-mail: tbein@cup.uni-muenchen.de*

[b] *School of Electrical and Electronic Engineering, Newcastle University, Merz Court, Newcastle upon Tyne, NE1 7RU, UK*

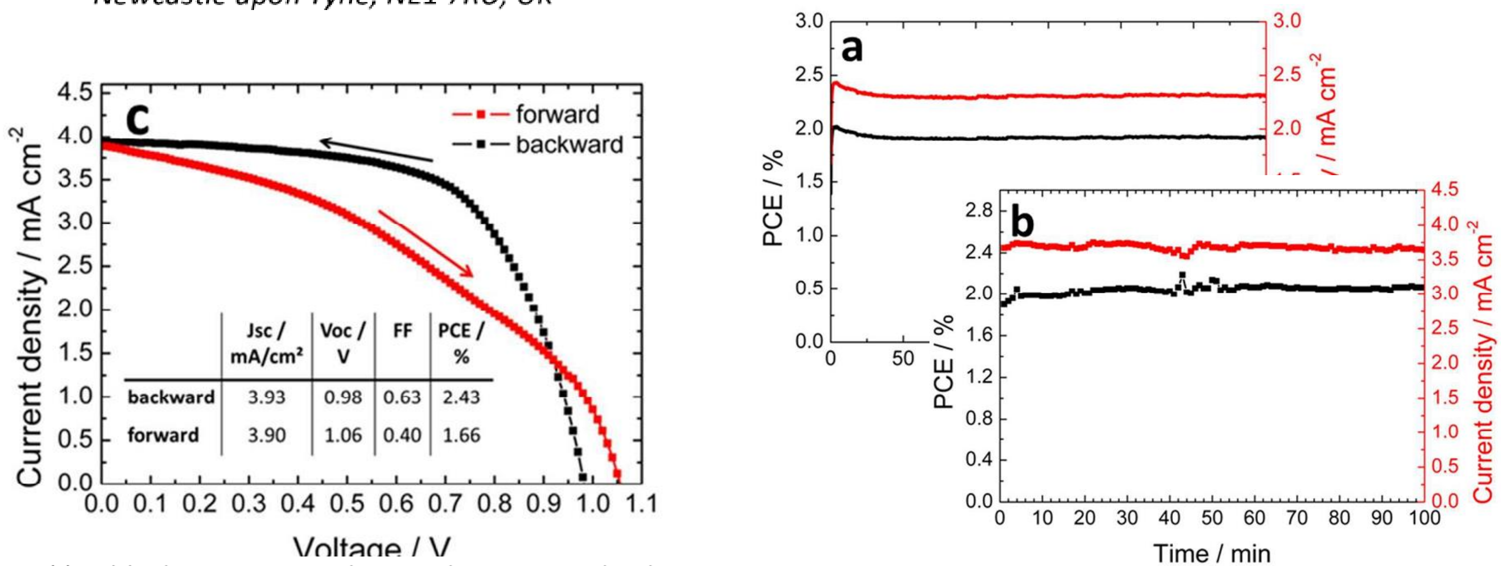


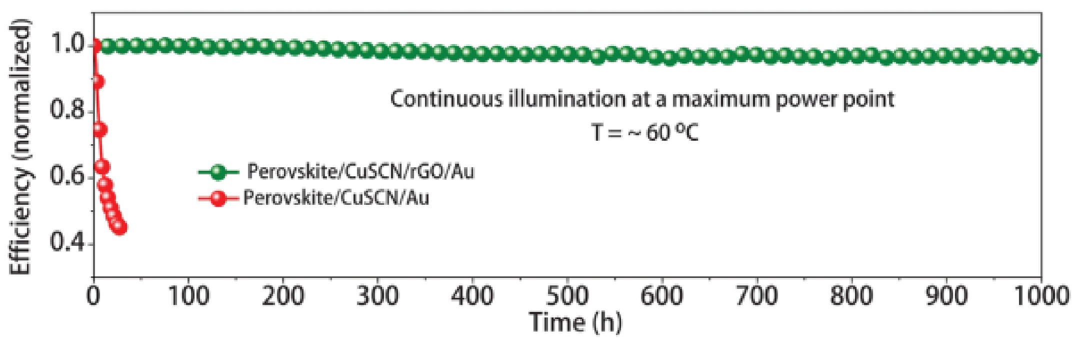
Fig. 6 (a) Stabilized power output and current density measured under ambient conditions without encapsulation. (b) Photovoltaic performance as a function of time under continuous illumination under ambient conditions. All devices were manufactured according the procedure described in Fig. 1 with a 285 °C annealing step.

SOLAR CELLS

Science **358**, 768–771 (2017) 10 November 2017

Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%

Neha Arora,[1*] M. Ibrahim Dar,[1*†] Alexander Hinderhofer,[2] Norman Pellet,[1] Frank Schreiber,[2] Shaik Mohammed Zakeeruddin,[1] Michael Grätzel[1†]



The ways of icreasing stability

CuSCN copper(I) thiocyanate

Commercialization

More than a 12 firms are involved in commercializing perovskite solar cells:

- Energy Materials Corp.(US),
- Frontier Energy Solution (South Korea),
- Microquanta Semiconductor (China),
- Oxford PV (UK),
- Saule Technologies (Poland),
- Sekisui/Panasonic/Toshiba (Japan),
- Solaronix SA (Switzerland),
- Solliance (Netherlands), Swift Solar (US),
- Tandem PV (US),
- WonderSolar (China).

(2 7 J U N E 2 0 1 9 | V O L 5 7 0 | N A T U R E | 4 2 9)

Commercialization

OXFORD PV

Oxford PV's industrial site in Brandenburg an der Havel, Germany, where the complete 250 MW production line will commence perovskite-on-silicon tandem solar cell production at the end of 2020.

Oxford PV tandem perovskite on the silicon pass the IEC 61646 test stability:
200 thermal cycles (-40° C to +85° C) with <5 % drop, full sun light soaking 1000 hours (85%RH/85° C) with <4% drop, damp heat 1000 hours <4% drop)

The future of perovskite photovoltaic is bright. Perovskite solar cell technology is close to commercialization.

In the last few years there has been huge progress in the efficiency and in improving the stability of perovskite cells.

The perovskit /Si tandem cells has the greatest prospects for large-scale electricity production in near future.

Thank you for your attention