Avogadro Colloquia 2019, Rome, December 17, 2019.

Nanostructured oxides as key components for solar energy conversion

Anders Hagfeldt
Laboratory of Photomolecular Sciences (LSPM)

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

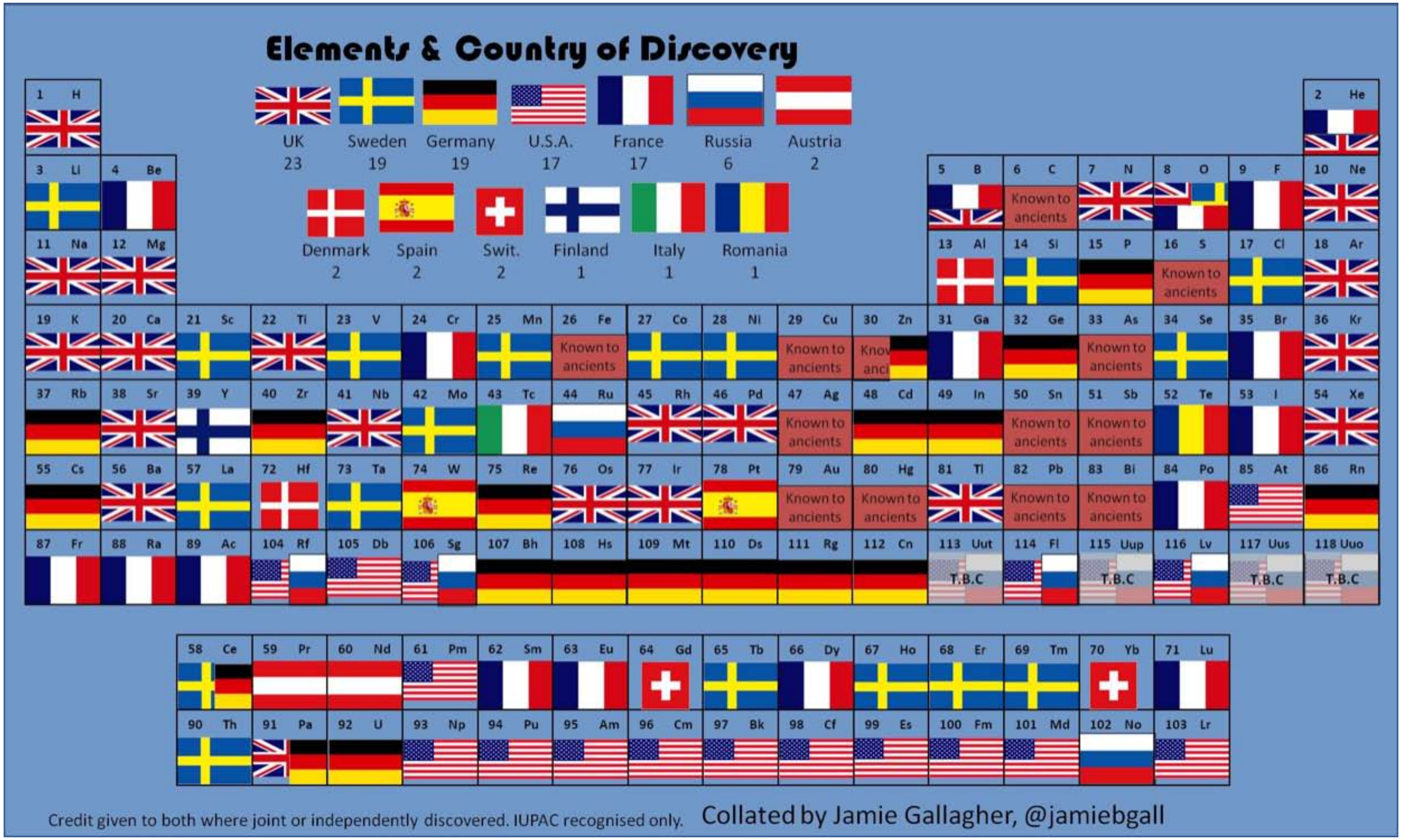
Dyenamo AB
www.dyenamo.se
Materials, research equipment, consultancy, etc, for solar cells and solar fuels.

Journal of Materials Chemistry A

EPFL
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Welcome to Lausanne!

- Element 8: Oxygen
- Dye-sensitized solar cells (DSSC)
- Perovskite solar cells (PSC)
- Photoelectrochemical Water Splitting



The Mine in Ytterby, Stockholm Archipelago

- Yttrium
- Ytterbium
- Terbium
- Erbium
- Holmium
- Skandium
- Tulium
- Gadolinium
- Tantal

Porta Alchemica, Villa Palombara

Esquiline Hill near Piazza Vittorio

Queen Christina of Sweden (abdicated 1654, converted from protestantism to catholicism)

Legend says that Porta Alchemica was raised as a commemoration of a successfull transmutation that took place in Christina’s alchemistry laboratory at Riario Palace, now Palazzo Corsini.

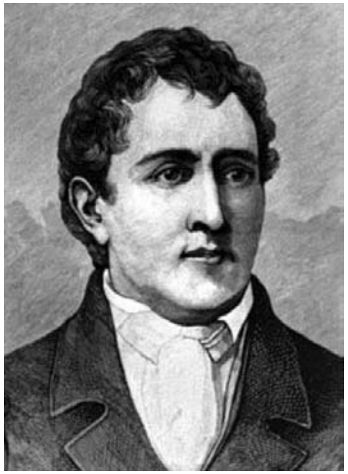
On the Way Towards Modern Chemistry – the *Phlogiston Theory*

Johann Becher, Mainz. 1667. Eliminated fire, water, and air from the classical element model and replaced them with three forms of earth. One form was key for combustion.

Georg Ernst Stahl, Halle. 1703. Named the earth form involved in combustion - *phlogiston*

- A fire-like element called **phlogiston** is contained within combustible bodies and released during combustion
- The theory attempted to explain processes such as combustion and rusting (now known as oxidation)
- When Scheele and Priestley independently discovered oxygen they used phlogiston to explain their results
- A problem: some metals gained mass when they burned, even though they were supposed to have lost phlogiston
- <u>Importance:</u> A theory that could be *experimentally tested*

Who Discovered Oxygen?



Carl Wilhelm Scheele

Joseph Priestley

Marie and Antoine Lavoisier

- In June 1771 Scheele ***discovered*** (in Uppsala) that heated manganese oxide produced a gas that he called fire air and described its properties. This was for various reasons not published until 1776.
- Priestley discovered oxygen using the term dephlogosticated air in 1st of August 1774 and ***published*** in 1775
- Lavoisier ”father of modern chemistry” ***explained*** the role of oxygen in combustion in terms of oxidation, opposing the phlogiston theory. He gave the name oxygen (*Greek:* generate acid) and listed it as an element.

Partington, J. R.; *J. Chem. Educ.* **1962**, *39*, 123.

Cassebaum, H.; Schufle, J. A.; *J. Chem. Educ.* **1975**, *52*, 442.

Oxides for Solar Energy Conversion

Letter | Published: 07 July 1972

Electrochemical Photolysis of Water at a Semiconductor Electrode

AKIRA FUJISHIMA & KENICHI HONDA

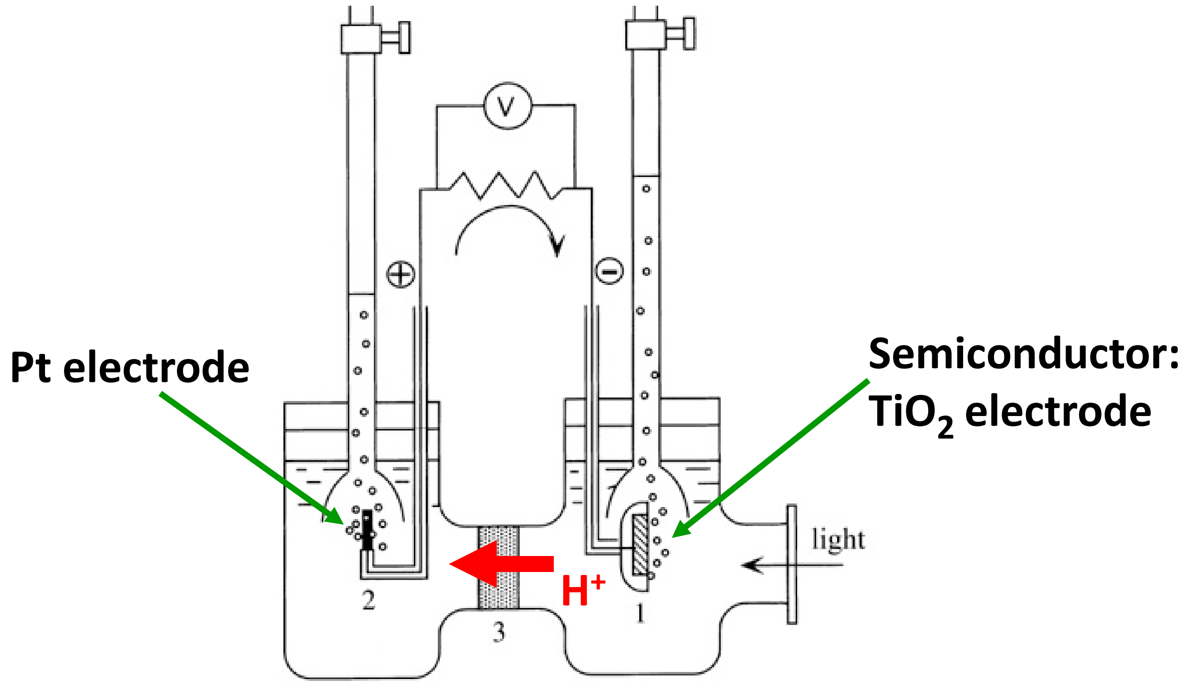
Nature **238**, 37–38(1972) | Cite this article

Water splitting reaction:

$$4H^+ + 4e^- \rightarrow 2H_2\ (gas)$$

$$2H_2O \rightarrow 4H^+ + O_2\ (gas) + 4e^-$$

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2\ (gas)$$



Problem: A stable oxide like TiO_2 only absorbs light in the UV region. How to make a stable photoelectrochemical solar cell absorb visible light?

Dye-Sensitization

Notiz über Verstärkung photoelektrischer Ströme durch optische Sensibilisirung.[1]

Von Dr. James Moser.

(Aus dem physikalisch-chemischen Laboratorium der Wiener Universität).

(Vorgelegt in der Sitzung am 23. Juni 1887.)

Ich erlaube mir mitzutheilen, dass ich die von Herrn E. Becquerel entdeckten photoelektrischen Ströme erheblich dadurch verstärken konnte, dass ich die beiden chlorirten, jodirten oder bromirten Silberplatten in einer Farbstofflösung, z. B. Erythrosin, badete.

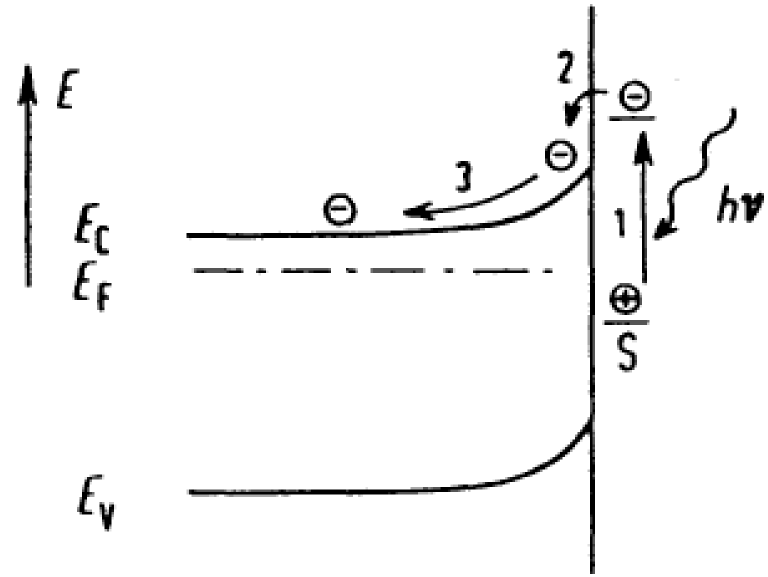
Beispielsweise war zwischen zwei chlorirten Silberplatten die elektromotorische Kraft im Sonnenlicht 0·02, zwischen zwei anderen in gleicher Weise behandelten, aber gebadeten Platten 0·04 Volt.

Bisher sind nur an jodirten Platten von Herrn Egoroff elektromotorische Kräfte beobachtet, und zwar bis $^1/_{15}$ Volt. Ich konnte bei jodirten und bromirten Platten durch Baden in Erythrosin $^1/_4$ Volt erreichen.

Ich halte es für meine Pflicht, schon an dieser Stelle Herrn Max Keiner, der mir bei diesen Versuchen assistirt, meinen verbindlichsten Dank auszusprechen.

[1] Akadem. Anzeiger Nr. XVI.

Colour Photography, Erythrosin dye on Ag-halides. J. Moser, *Monatsh. Chem.* 8 (1887) 373



Mechanism of dye-sensitization. Rose bengal on ZnO. H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem.* 72 (1968) 437.

Gerischer, H.; Michel-Beyerle, M. E.; Rebentrost, F.; Tributsch, H. *Electrochim. Acta* 1968, 13, 1509.

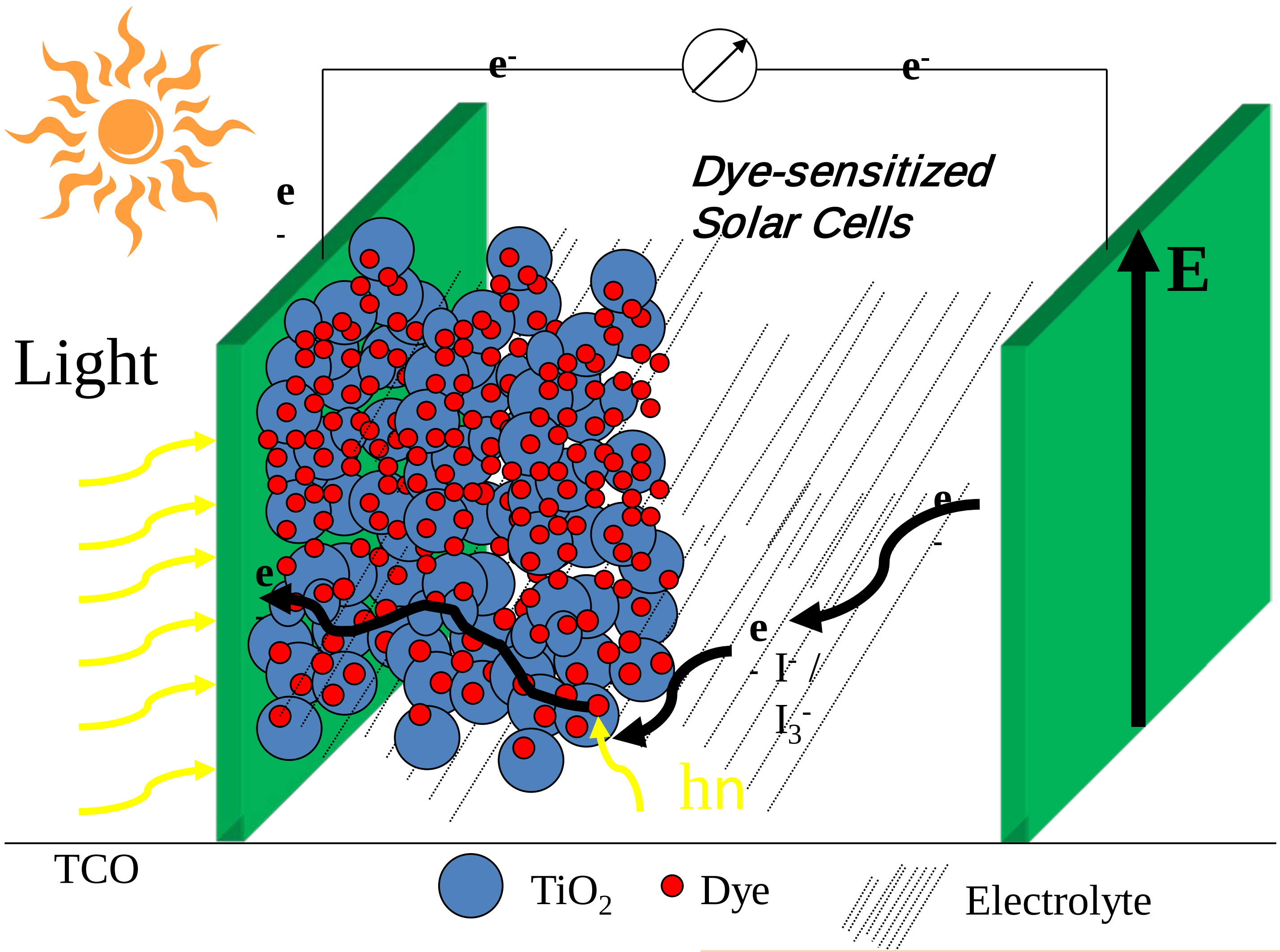
The Quantum Leap of DSSC – a paradigm shift of photovoltaics

Brian O'Regan and Michael Grätzel
HOPV 2012, juanbisquert.

***Nature*, 1991, 353, 7377.**
***J. Phys. Chem*, 1990, 94, 8720.**

From < 1% $\longrightarrow$ 7.1%

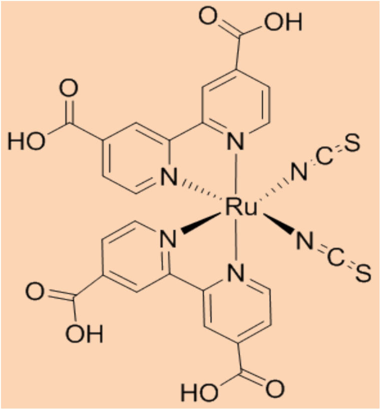
DSSC Operational Principles



Hagfeldt, Boschloo, Kloo, Sun, Pettersson
Chem. Rev. **2010**, *110*, 6595–6663

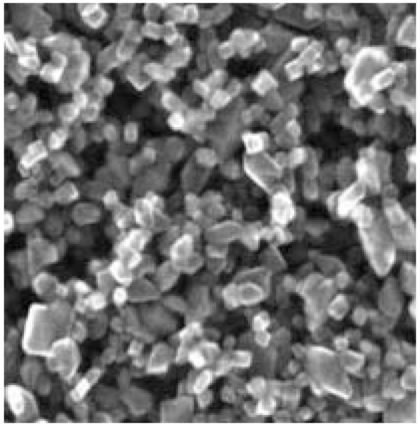
The three key ingredients of dye sensitized solar cells

Sensitizing Dye



Chemical Structure of N3 Dye

Titania Nanoparticles

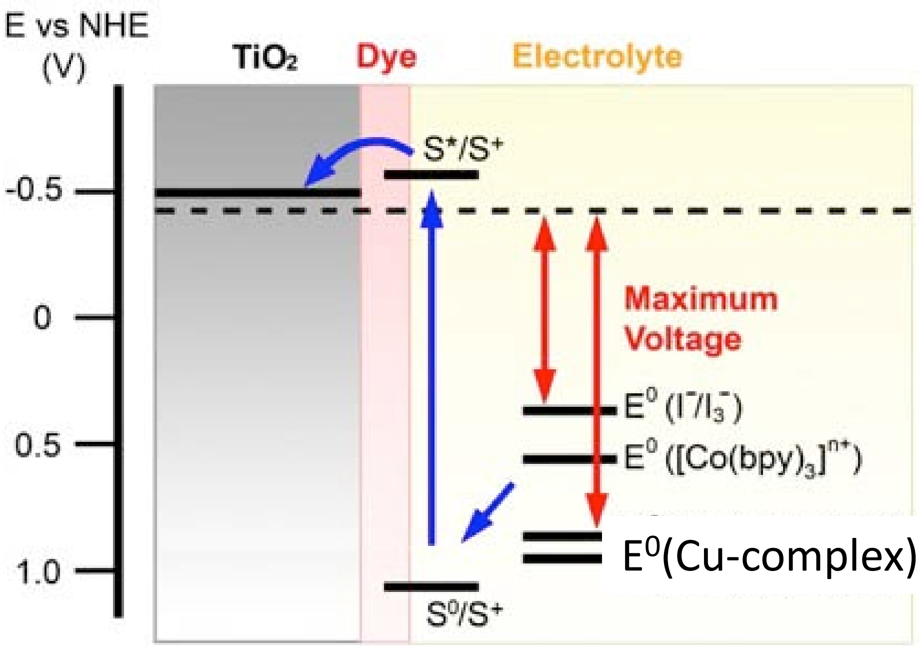


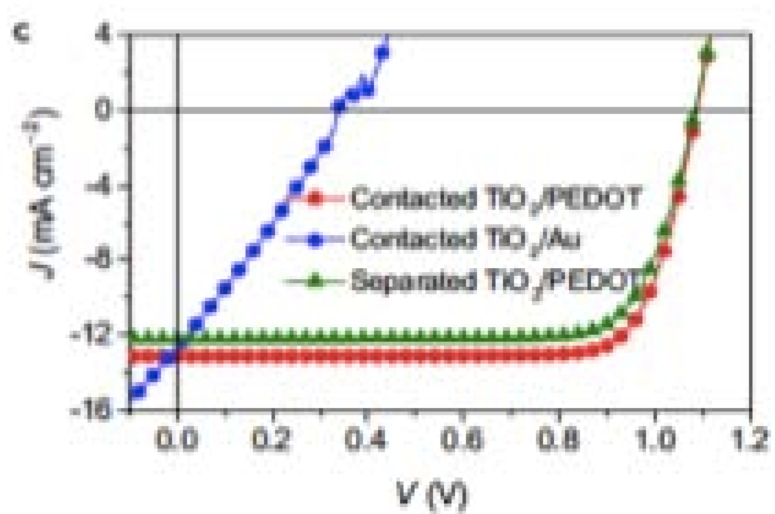
20 nm Titania nanoparticles

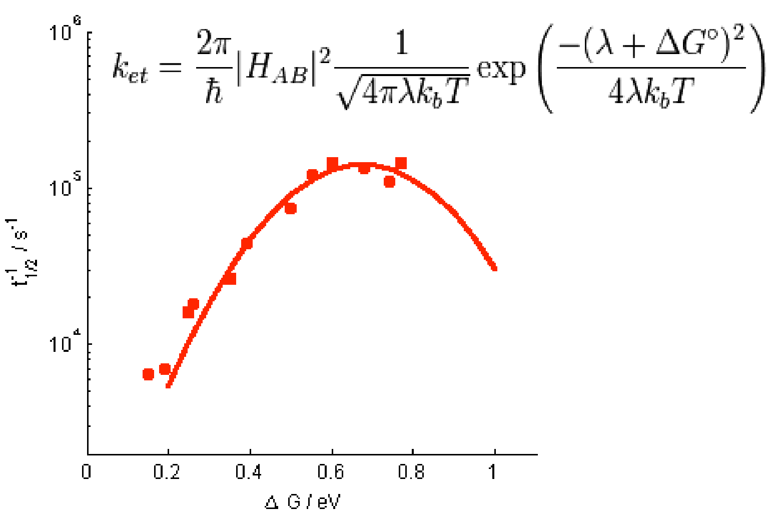
Electrolyte

Ionic liquid
Iodide/tri-iodide
redox couple

DSSC: The Hunt for the Half Volt







New certified record efficiency: 12.25%
Top lab efficiency: 14.5% with V_{oc} > 1.1V

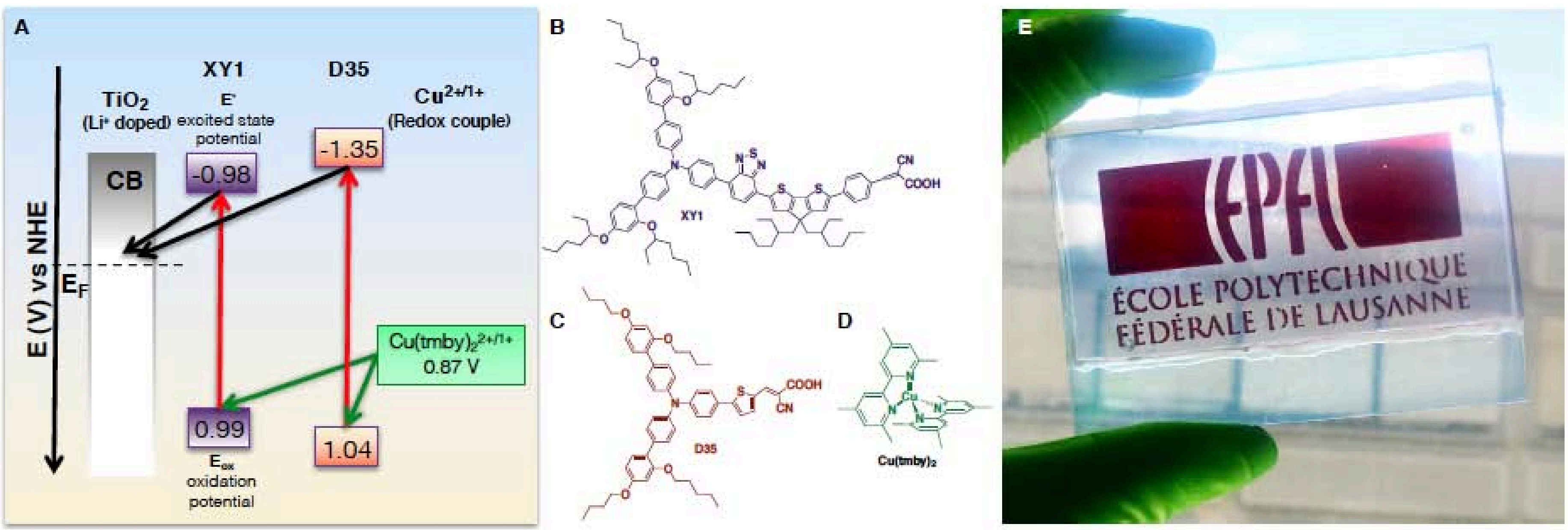
nature photonics

ARTICLES

PUBLISHED ONLINE: 1 MAY 2017 | DOI: 10.1038/NPHOTON.2017.60

Dye-sensitized solar cells for efficient power generation under ambient lighting

Marina Freitag[1†], Joël Teuscher[2], Yasemin Saygili[1], Xiaoyu Zhang[3], Fabrizio Giordano[4], Paul Liska[4], Jianli Hua[3], Shaik M. Zakeeruddin[4], Jacques-E. Moser[2], Michael Grätzel[4*] and Anders Hagfeldt[1*]



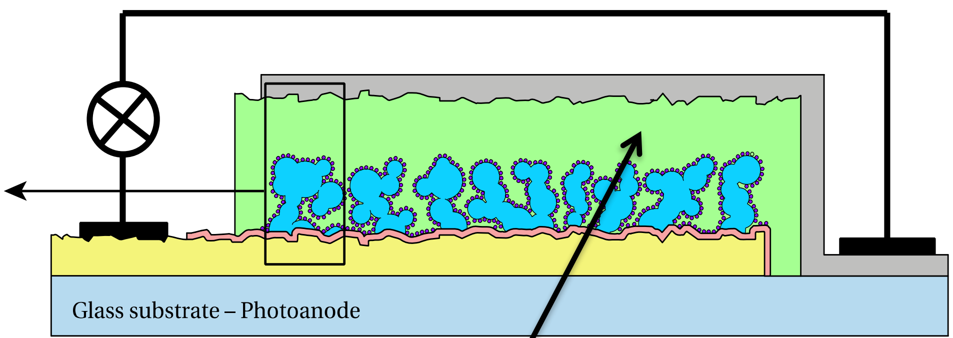
Our best indoor light efficiency is 35%

exeger

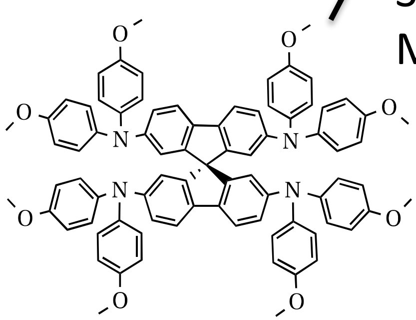
The SoftBank Group Enters Strategic Partnership with Exeger and Invests to Accelerate Deployment of Exeger Solar Technology

Several Concepts Based on DSSC, two examples

Solid-state DSSC



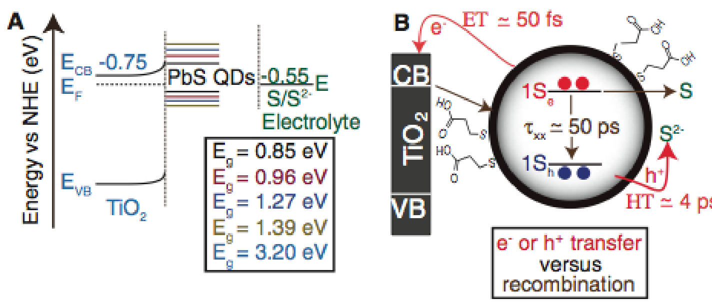
Solid Hole Transporter Material



spiro-MeOTAD

U. Bach, M. Grätzel et al.
Nature 1998, *395*, 583–585.

Quantum Dot Solar Cells



Replace the dye molecule with an inorganic semiconductor, e.g. PbS or $CH_3NH_3PbI_3$

PSCs evolved from the DSSC

The first embodiment of a PSC described by Miyasaka
In his 2009 JACS paper was a mesoscopic dye sensitized
solar cell using ammonium lead halide perovskites
as sensitizer and iodide base liquid electrolyte.

J|A|C|S COMMUNICATIONS

Published on Web 04/14/2009

Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

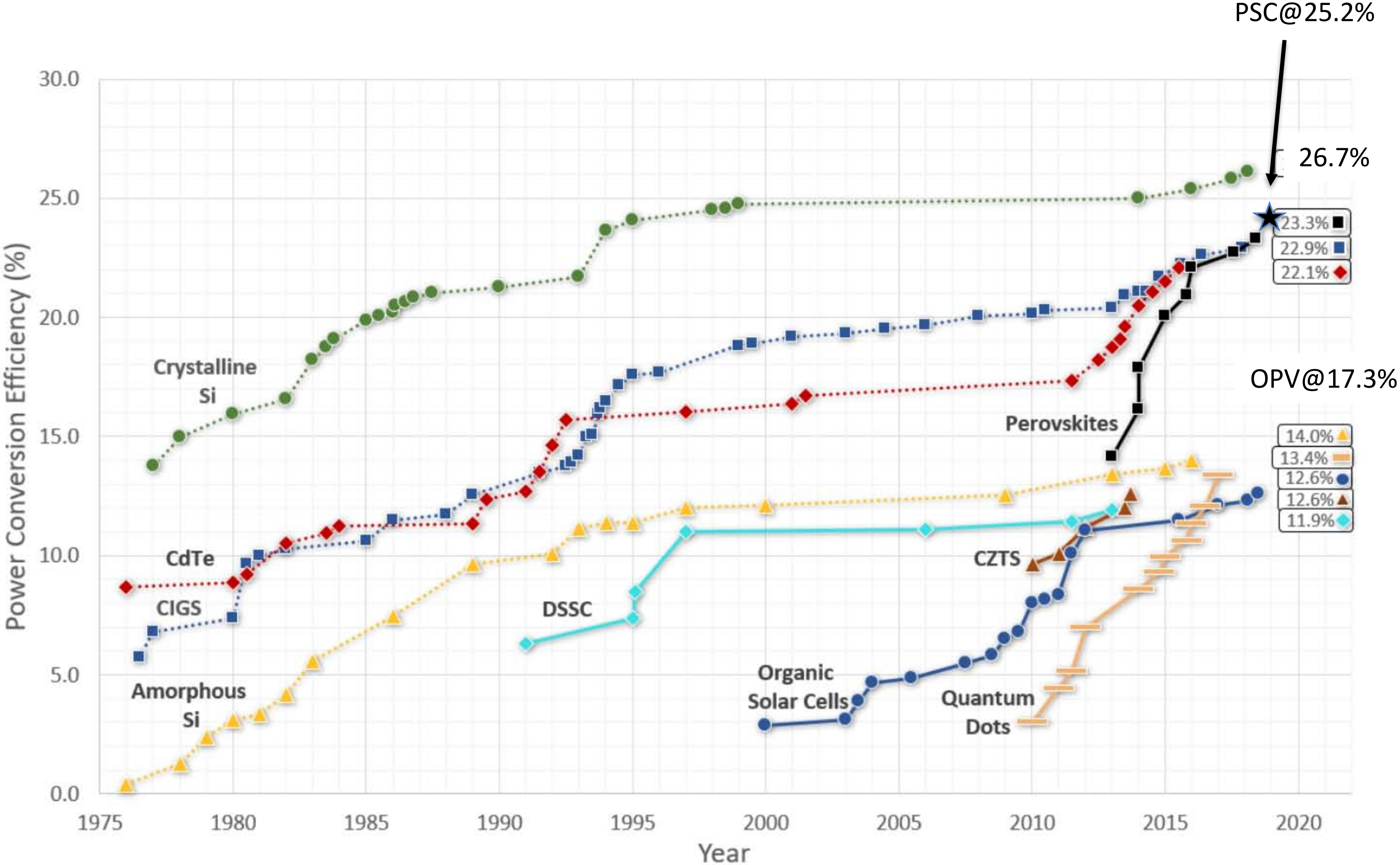
Akihiro Kojima,[†] Kenjiro Teshima,[‡] Yasuo Shirai,[§] and Tsutomu Miyasaka*[,†,‡,∥]

Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan, Graduate School of Engineering, Toin University of Yokohama, and Peccell Technologies, Inc., 1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8502, Japan, and Graduate School of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan

Received December 9, 2008; Revised Manuscript Received April 1, 2009; E-mail: miyasaka@cc.toin.ac.jp

Tsutomu (Tom) Miyasaka playing his violin fabricated in 1835 in Torino Italy during the ICES 2014 conference Dinner in Niseto, Hokkaido, Japan on February 06, 2014.

World Record Solar Cell Efficiencies

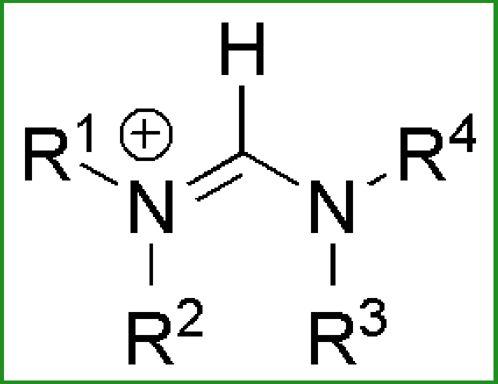


EPFL's most efficient pervoskite solar cells employ mixtures of organic cations and iodide /bromide as anion

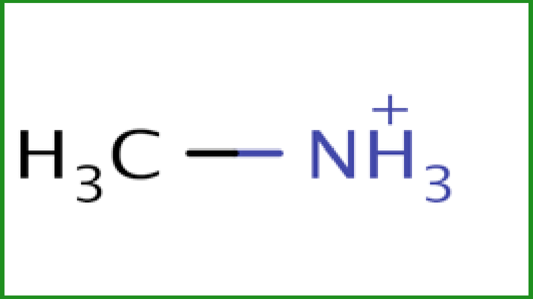
General composition $FA_{1-x}MA_xPb(I_{1-x}Br_x)$

FA =

formamidinium



$R^1 - R^4 = H$



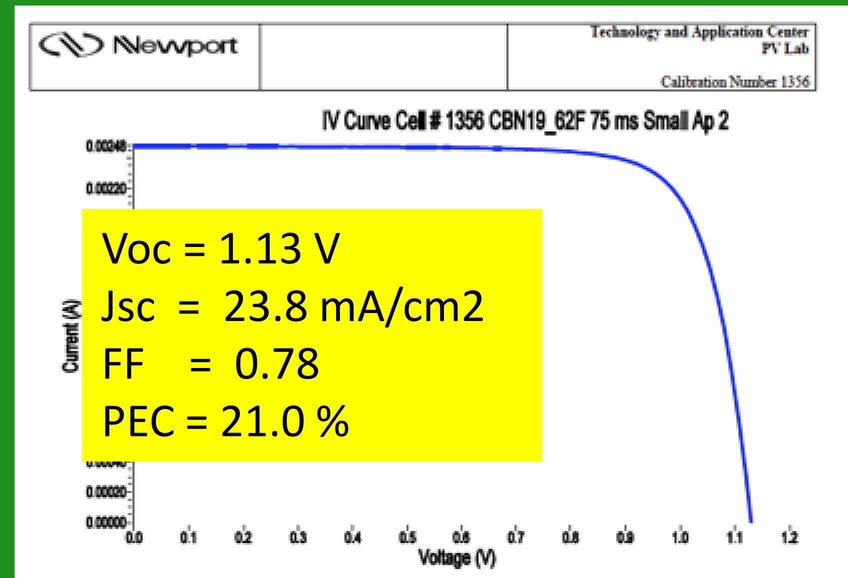
X = 0.15 gives optimal results

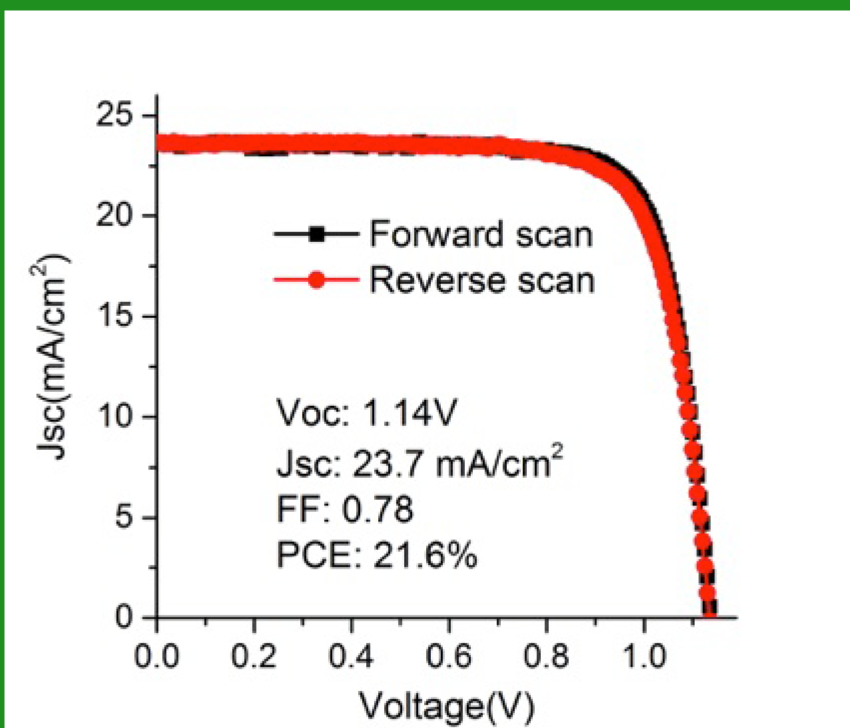
MA = methylammonium

N. Pellet *et al.*, Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar -Light Harvesting. *Angew. Chem. Int. Ed.* **53**, 3151-3157 (2014).
N. J. Jeon *et al.*, Compositional engineering of perovskite materials for high-performance solar cells. *Nat.* **517**, 476-480 (2015).

Our Certified Champion Cell

Dongqin Bi





Certified efficiency at Newport, 21.0%, Dec. 2015 (hysteresis-free)

Nature Energy
DOI: 10.1038/NENERGY.2016.142

Certified world record is 25.2%

Energy & Environmental Science

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c5ee03874j

Received 24th December 2015,
Accepted 14th March 2016

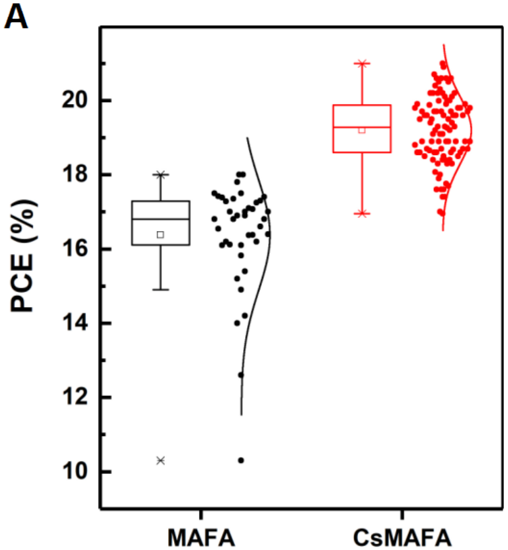
DOI: 10.1039/c5ee03874j

Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency†

Michael Saliba,‡*[ab] Taisuke Matsui,‡[c] Ji-Youn Seo,[a] Konrad Domanski,[a] Juan-Pablo Correa-Baena,[d] Mohammad Khaja Nazeeruddin,[b] Shaik M. Zakeeruddin,[a] Wolfgang Tress,[a] Antonio Abate,[a] Anders Hagfeldt[d] and Michael Grätzel[a]

Michael Saliba

A



B

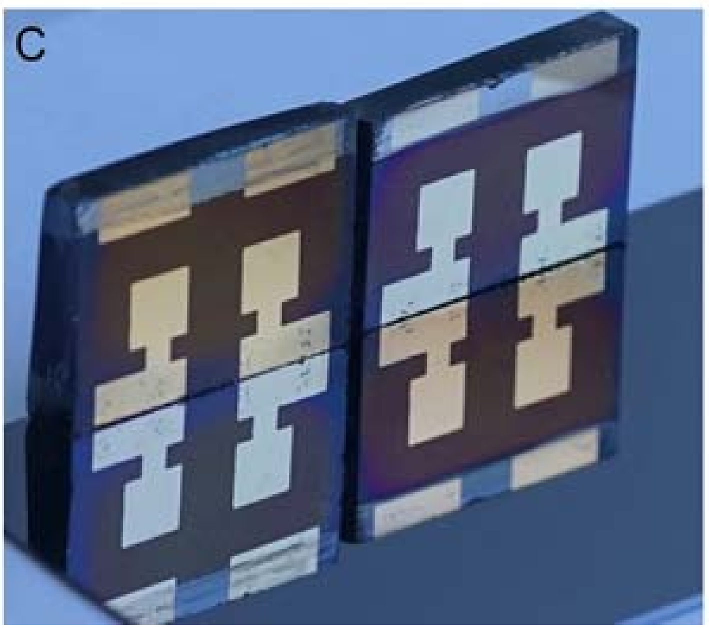
Science

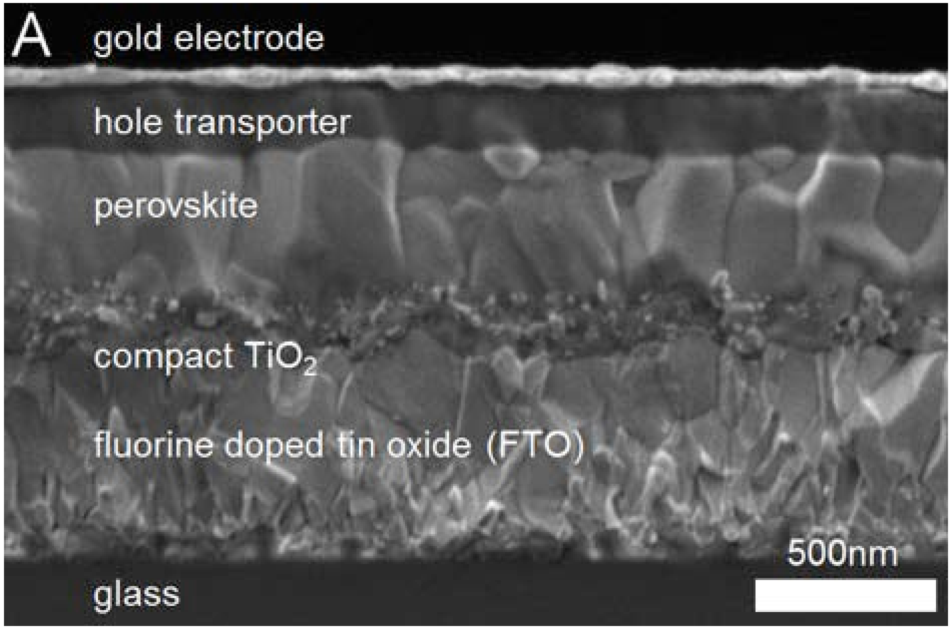
REPORTS

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

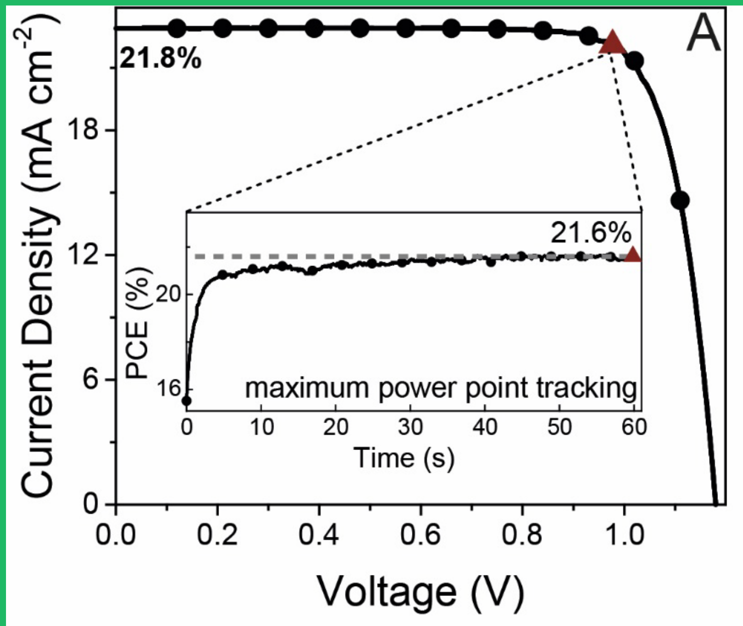
Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance

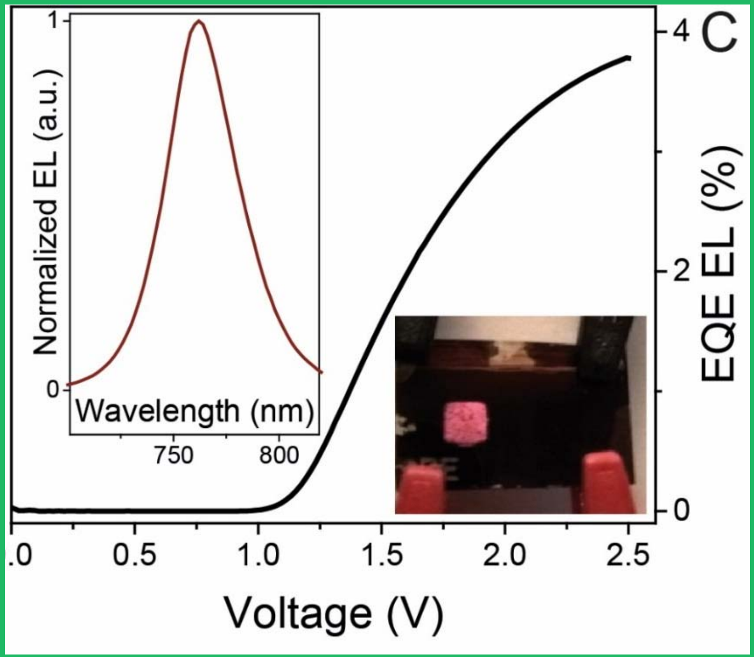
Michael Saliba,[1*†] Taisuke Matsui,[1,2*] Konrad Domanski,[1*] Ji-Youn Seo,[1] Amita Ummadisingu,[1] Shaik M. Zakeeruddin,[1] Juan-Pablo Correa-Baena,[3] Wolfgang R. Tress,[1] Antonio Abate,[1] Anders Hagfeldt,[3] Michael Grätzel[1]†





Device results

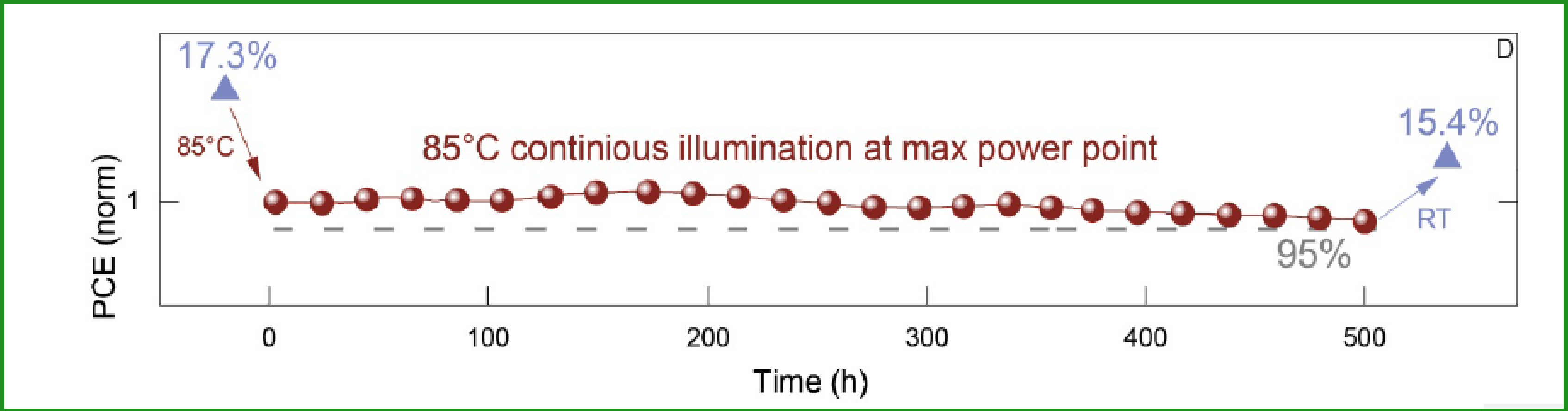




- Highest PCE: 21.6% stabilized
- Highest V_{oc} is 1.24 V (band gap: 1.63 eV)
  Close to theoretical limit (1.33 V).
- Among lowest loss-in-potentials (for any PV material)
- 4% External Radiative Efficiency (ERE, Electroluminescence)
- Towards GaAs!

Stability tests

- Gold/spiro is not a stable contact at high temperatures
  ACS Nano DOI: 10.1021/acs.nano.6b02613
- PTAA Polymer as HTM

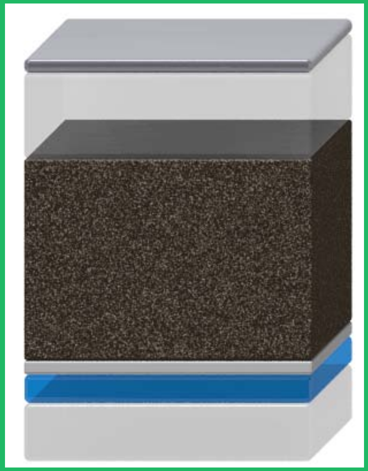


Stress test: 85 ^{o}C, full illumination, MPP
for 500h (in N2 atmosphere)

Stability: 95% is retained after 500h of continous operation (MPP) at 85 ^{o}C and full illumination

Planar PSC Structures

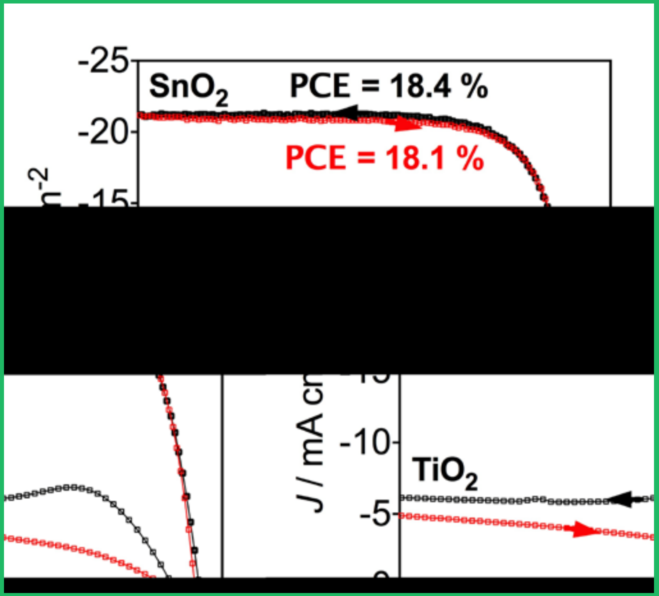
Juan-Pablo
Correa-Baena



hole transporter

Perovskite

electron transporter



Flat amorphous SnO_2 ALD layer works better than flat amorphous TiO_2 ALD Layer - Band Alignment Engineering

J.-P. Correa Baena, L. Steier et al. Energy Environ. Sci. DOI: 10.1039/C5EE02608C

Science

REPORTS

Cite as: S.-H. Turren-Cruz *et al.*, *Science* 10.1126/science.aat3583 (2018).

Methylammonium-free, high-performance and stable perovskite solar cells on a planar architecture

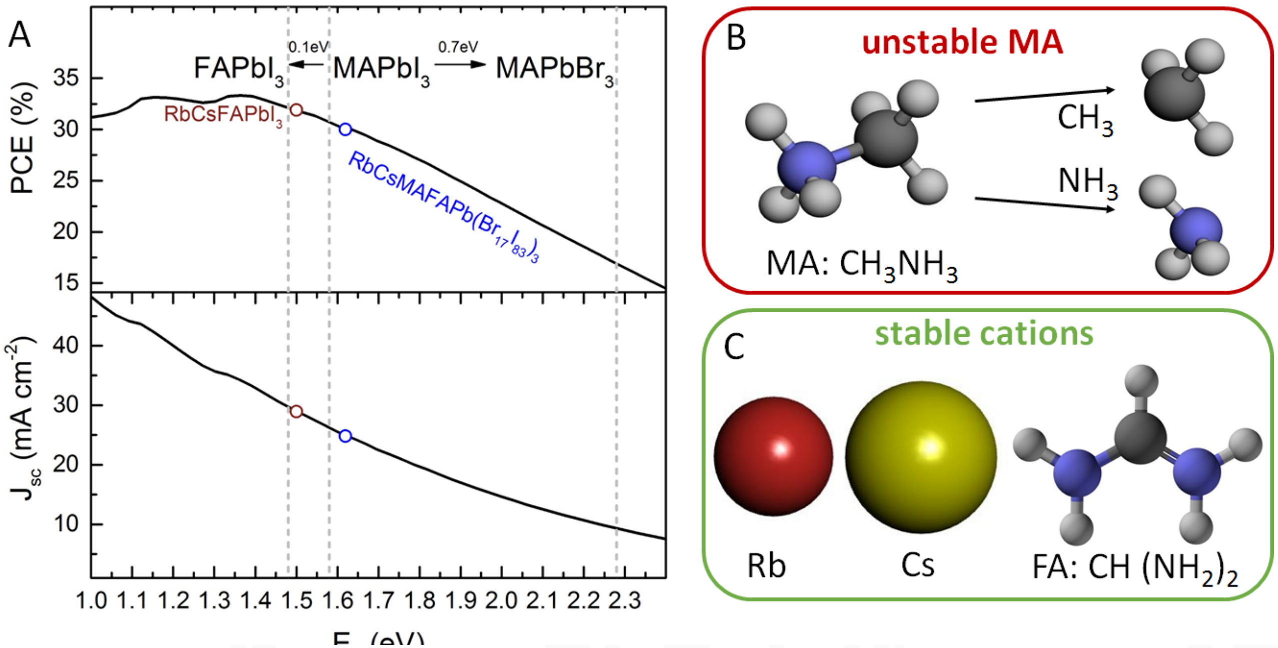
Silver-Hamill Turren-Cruz[1,2,3], Anders Hagfeldt[2]*, Michael Saliba[1]*

[1]Adolphe Merkle Institute, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland. [2]Laboratory of Photomolecular Science, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland. [3]Benemérita Universidad Autónoma de Puebla. CIDS, Av. San Claudio y 18 Sur, Col. San Manuel, Ciudad Universitaria, CP 72570, P.O. Box 1067, Puebla, Pue. 7200, Mexico.

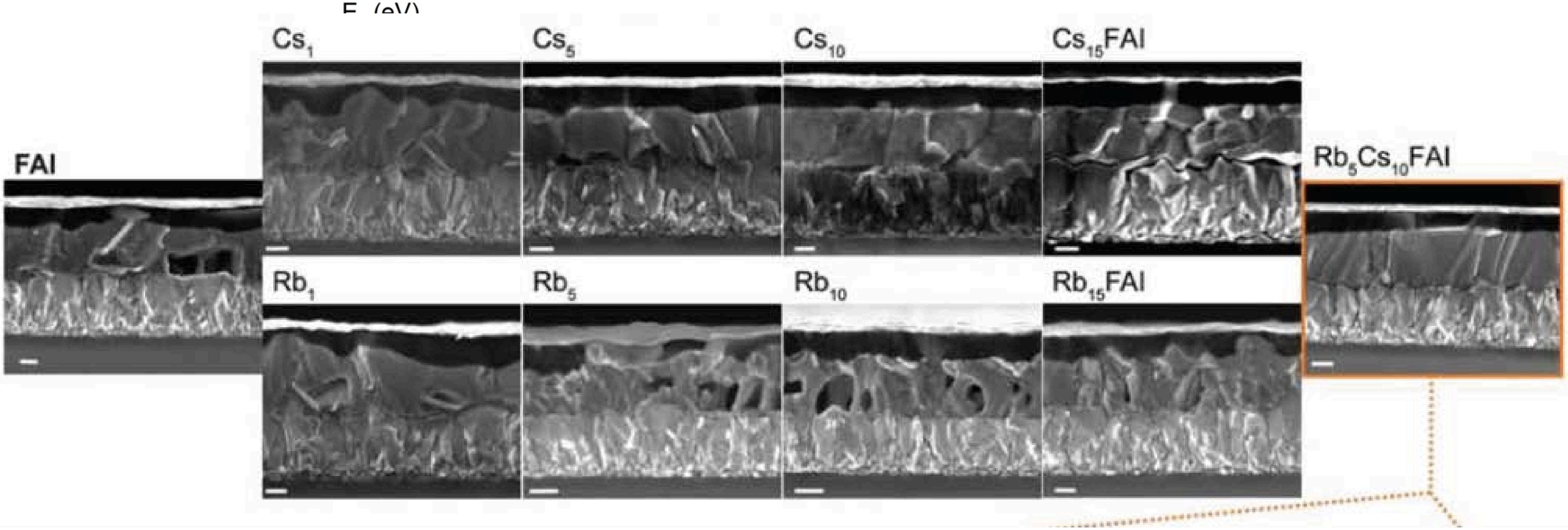
- Implicit goal: **Pure FAPbI3**. (ideally no MA and Br)

- MA volatile in thin-films
- Br blue-shifts the band gap disproportionately (not optimal for single-junction)
- Rb, Cs, FA and I as candidates. (using K is next)

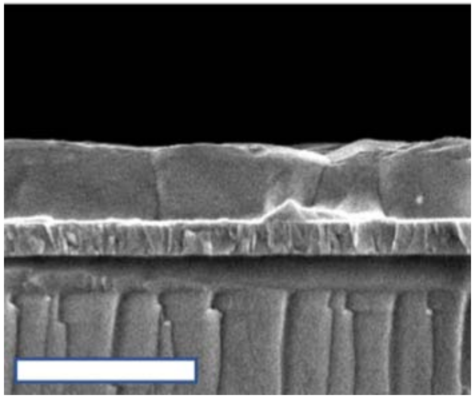
MA-free, Br-free perovskites

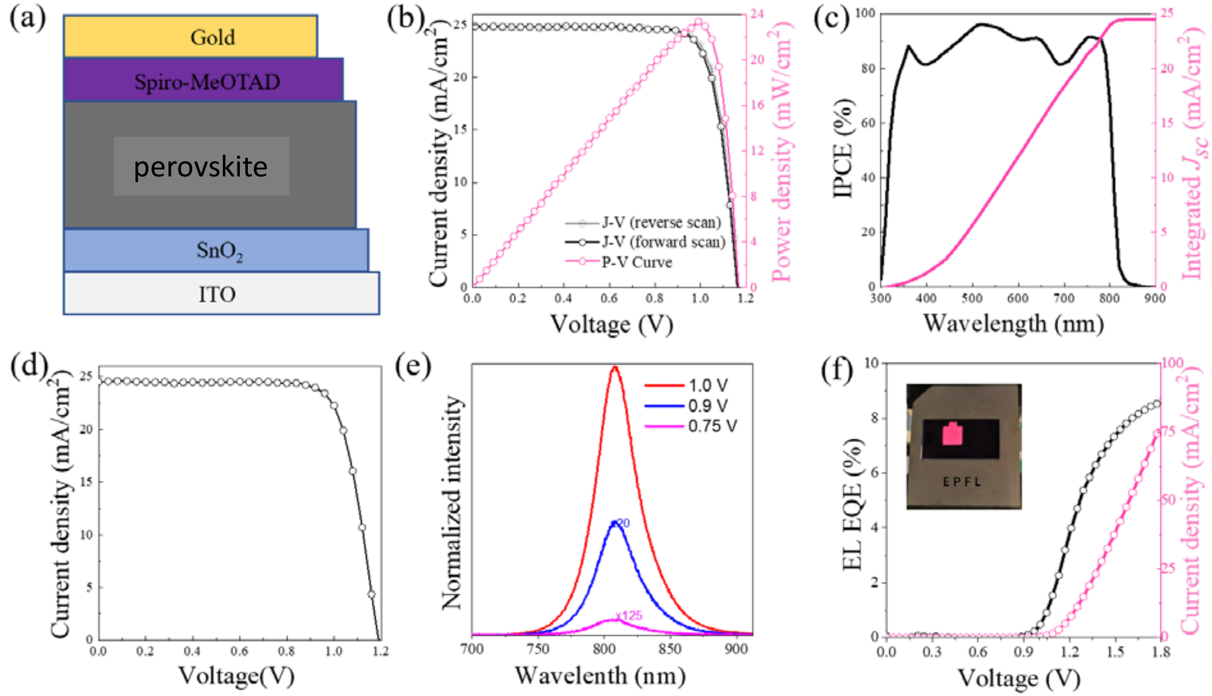


Efficiency of 20.4% with a photocurrent > 25 mA cm^{-2}



Our most recent results - unpublished





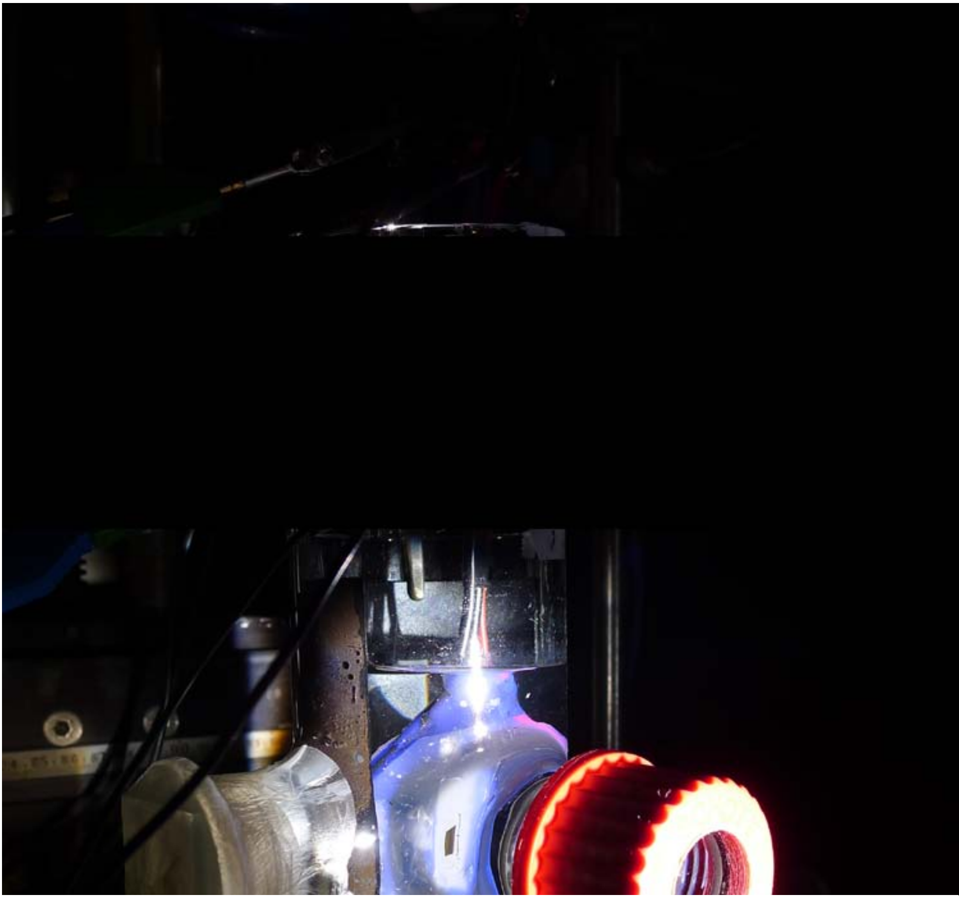
V_{oc} = 1.19V $V_{oc.theoretical}$ = 1.255 V_{oc} loss of *only* 65 mV – new record!

Electroluminescence = 8.6%

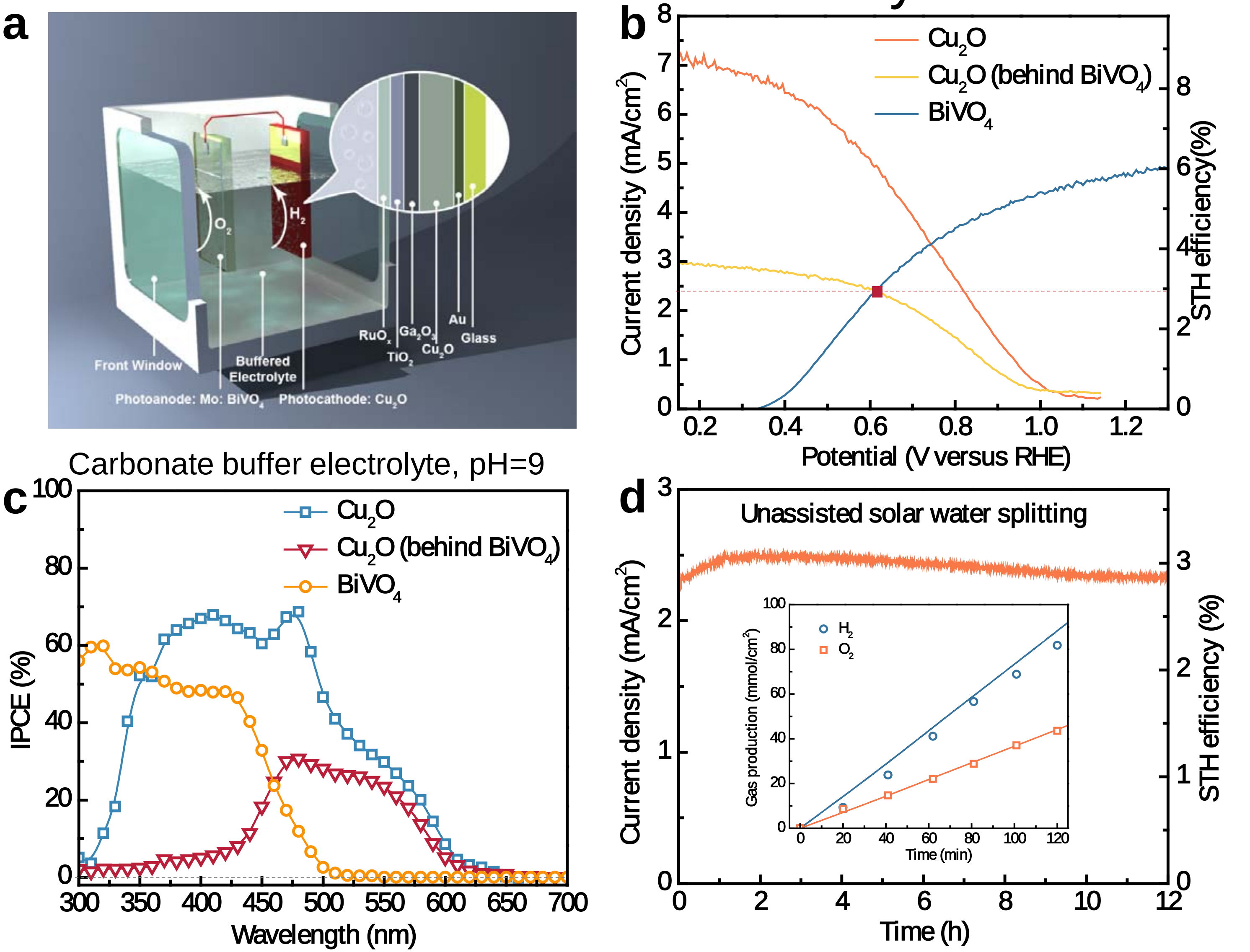
Efficiency = 23.5%.

With J_{sc} > 26 mA/cm^2 and FF = 0.85 we can get efficiencies > 26%

Photoelectrchemical Water Splitting Using Cu_2O and $BiVO_4$




All-oxide unassisted solar water splitting device with a record 3% efficiency



Linfeng Pan et *al*. ***Nature Catalysis,*** (2018), 1, 412–420

Thanks!

LPI Team

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Bitao Dong

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Firouzeh Ebadi Garjan

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Mozhdeh Forouzandeh

Hui-Seon Kim

Kazuteru Nonomura

Haizhou Lu

Linfeng Pan

Faranak Sadegh

Yasemin Saygili

Wolfgang Tress

Nick Vlachopoulos

Zaiwei Wang

Zishuai Wang

Bowen Yang

Shaik Zakeeruddin

Jiahuan Zhang