Can We Fabricate High Efficiency Colloidal Quantum Dot (CQD) Solar Cells?

UNSW AUSTRALIA

Never Stand Still | Faculty of Engineering | School of Photovoltaic and Renewable Energy Engineering

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02/11/2017

Supervisors:

Shujuan Huang

Robert Patterson

Gavin Conibeer

The CQD Group

- Officially started in 2013
- ARC Discovery Project

- Supervisors:

Shujuan Huang, Robert Patterson, Gavin Conibeer

- Students and postdocs:

Current: Zihan Chen, Zhi Li Teh, Yijun Gao, Yicong Hu

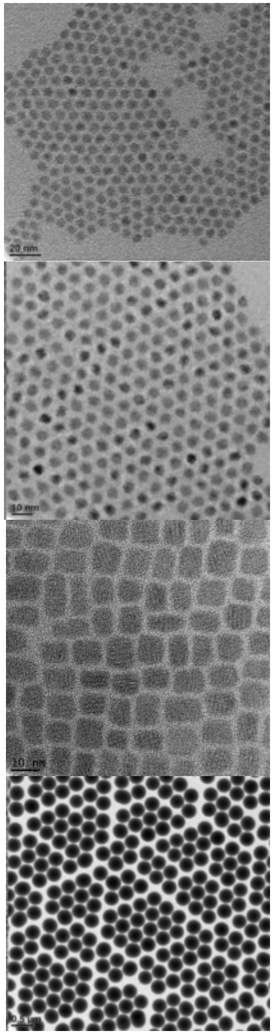
Thesis submitted: Lin Yuan, Zhilong Zhang

Graduated: Naoya Kobamoto

Postdoc: Long Hu

The CQD Group

Content

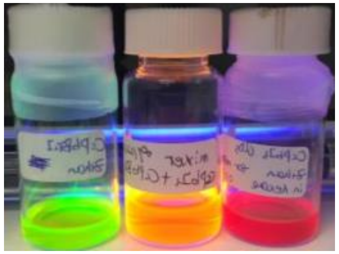


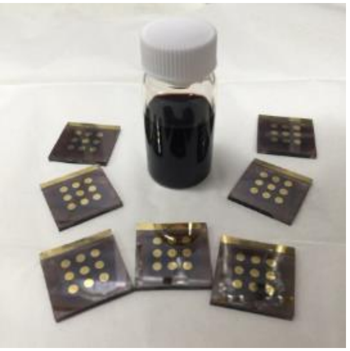
Part I: Introduction & (PbSe) CQDs

- General introduction to CQDs
- Why PbSe CQDs?
- My PhD work, including the most efficient PbSe cell fabricated >8%

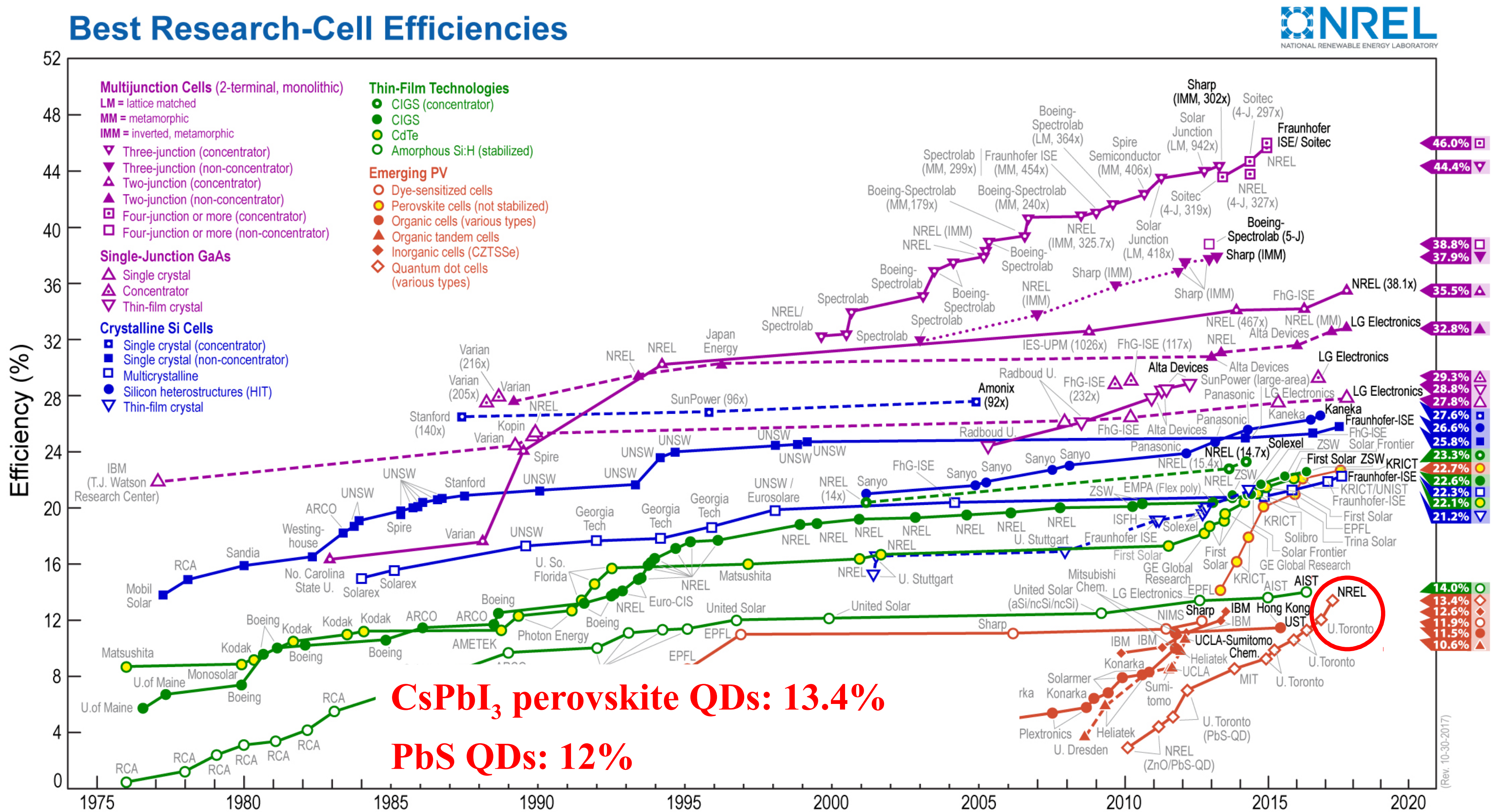
Part II: Other works from the CQD group

- Lead sulphide QD solar cells >10%
- Non-toxic materials: copper indium sulphide (CIS), silver bismuth sulphide ($AgBiS_2$) nanoparticle solar cells
- Other materials we can provide





NREL chart



CsPbI$_3$ perovskite QDs: 13.4%

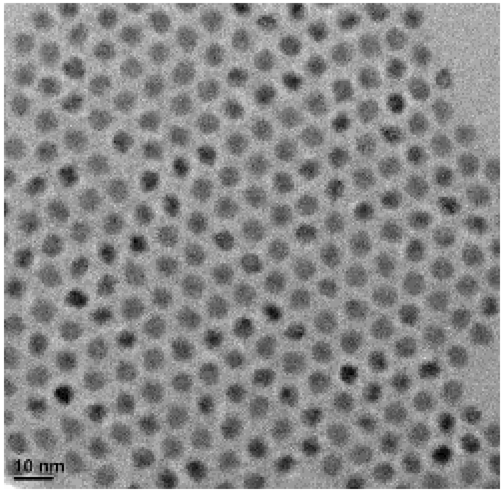
PbS QDs: 12%

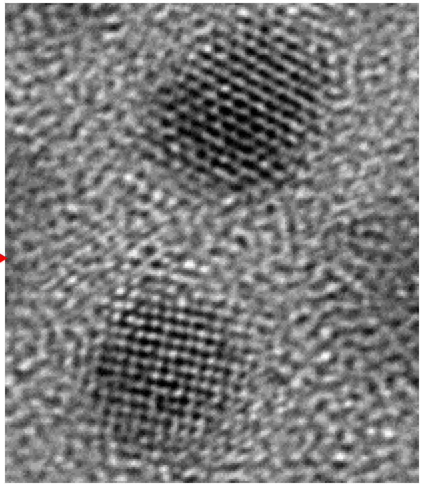
What Are Colloidal Quantum Dots?

"**Colloids**"- Dispersed particles in a solution

***CQDs are extremely small**

QD colloids

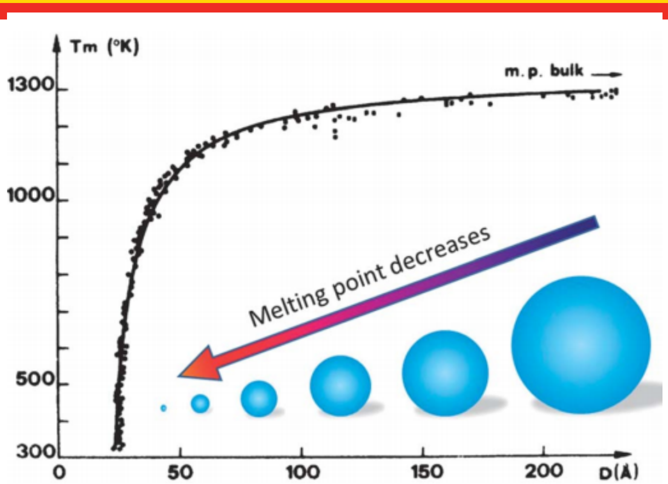




5 nm PbSe QDs

1 nm = one billionth of a metre

Scaling law of materials

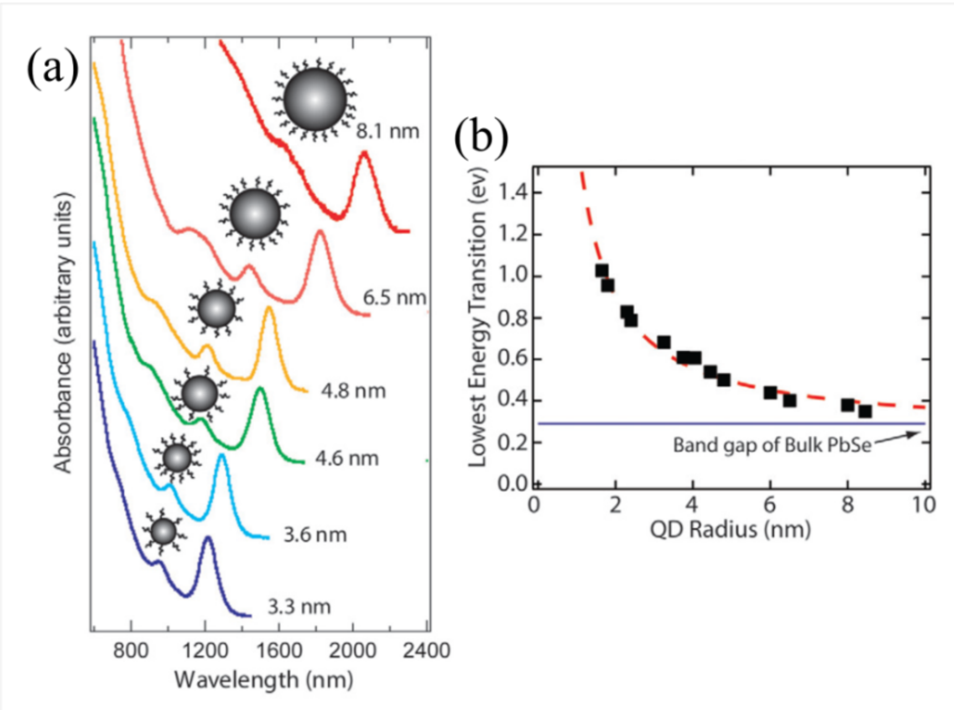


→ **Low temperature → High Quality Materials**

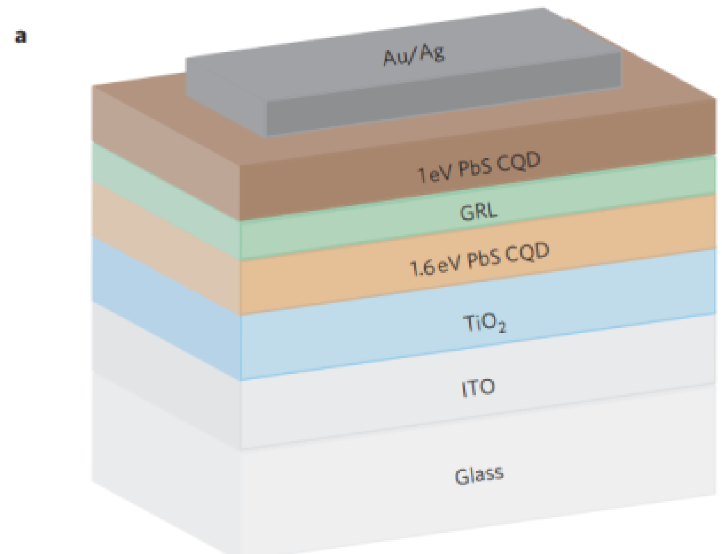
Weidman et.al. ACS Nano, 2014, 8 (6), pp 6363–6371

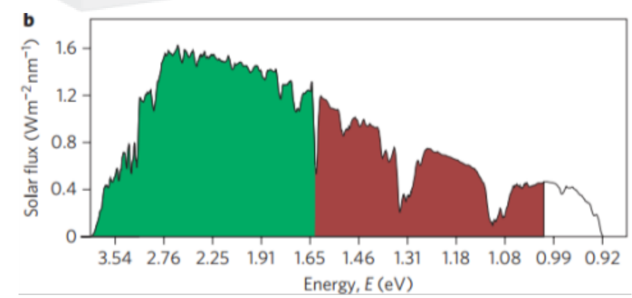
http://www.sigmaaldrich.com/technical-documents/articles/materials-science/nanomaterials/quantum-dots.html

Quantum Confinement Effect



Brus equation:

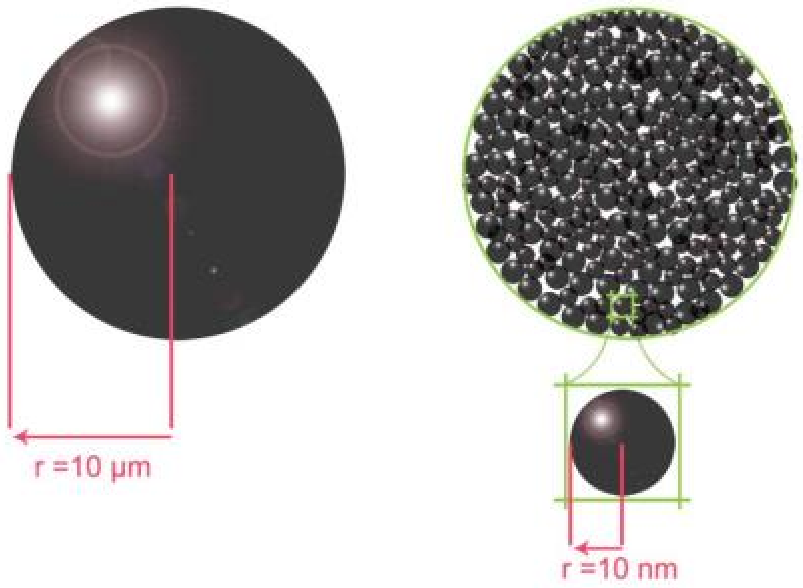


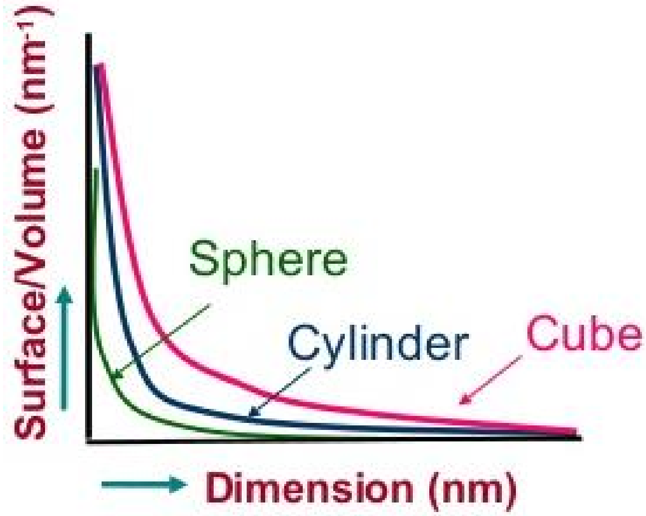


***Band gap of QD is highly tunable**

Semonin et.al., Mater. Today 2012, 15, 508
Wang et.al., Nature Photonics 5, 480–484 (2011)

Surface to Volume Ratio

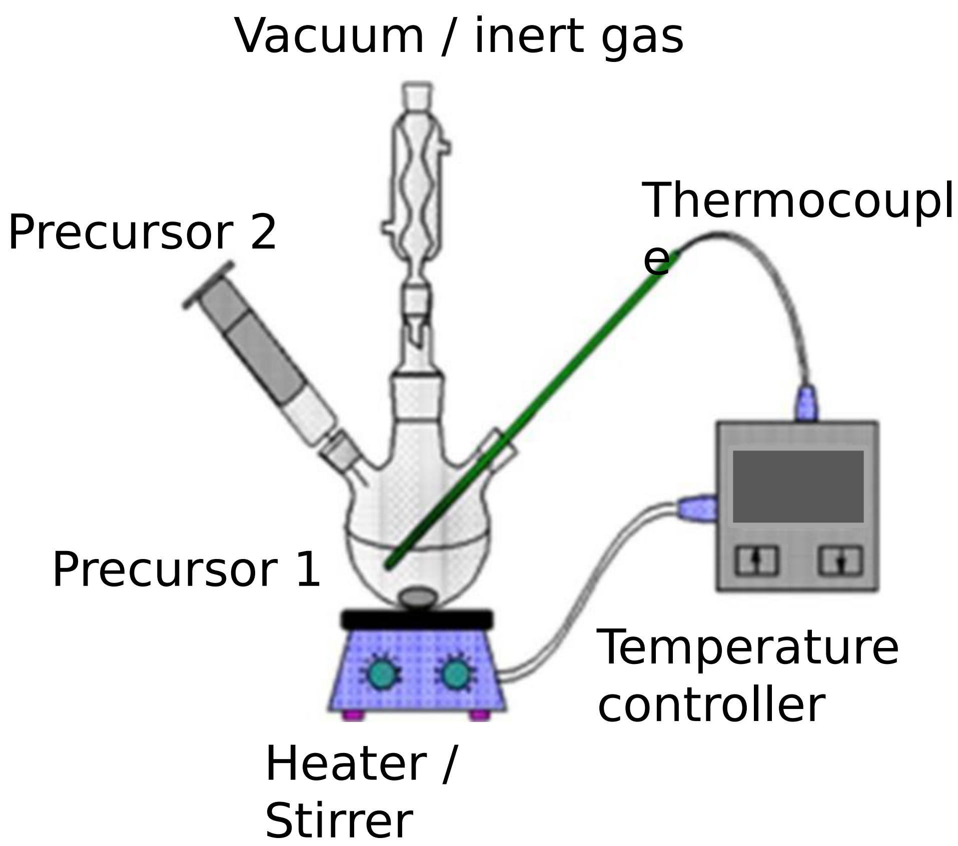




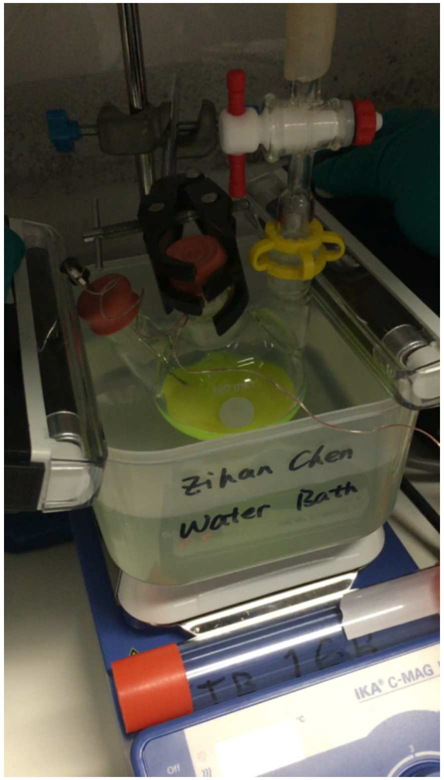
Weidman et.al. ACS Nano, 2014, 8 (6), pp 6363–6371
Yang et.al. J. Mater. Chem. C, 2013,1, 4052-4069

***The properties of QDs can be dominated by the surface conditions**

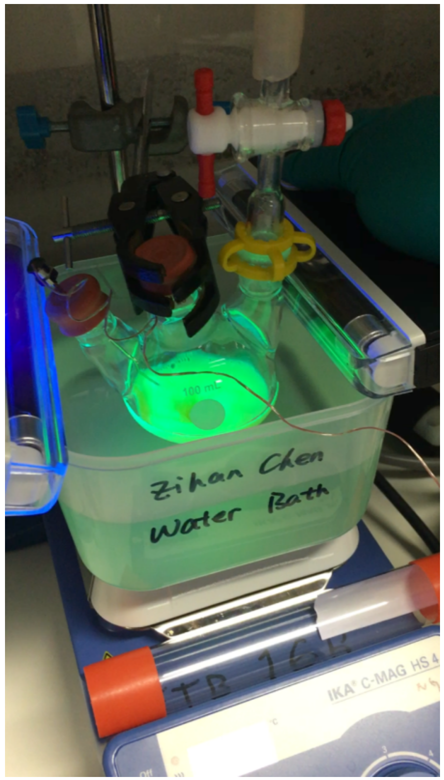
How do we synthesise QDs here?



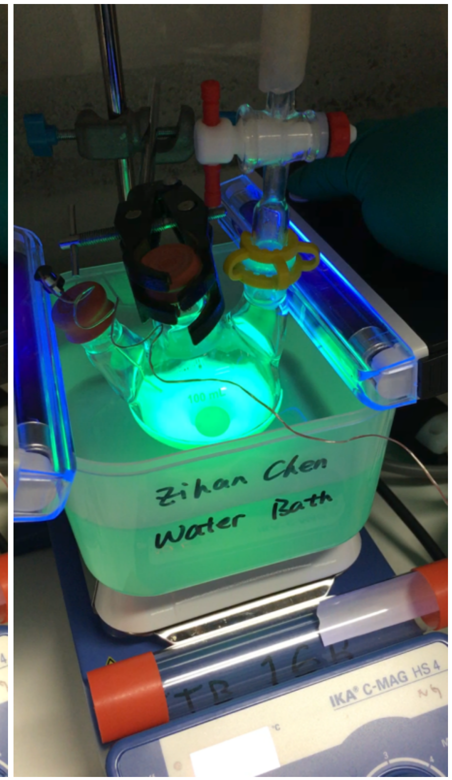
How do we know?



Dark

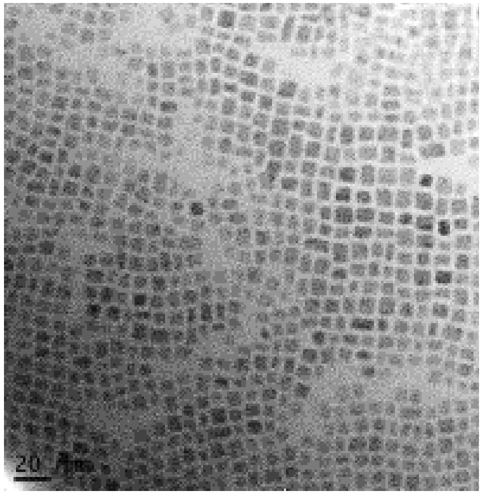


One UV torch

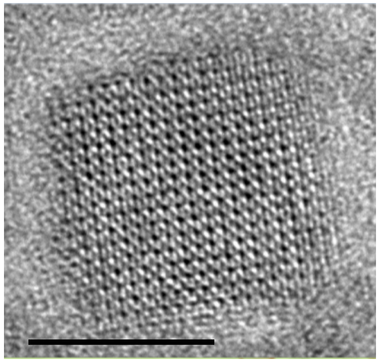


Two UV torches

$CsPbBr_3$ QDs



TEM image



HR TEM

Materials we make here

- Metal chalcogenide QDs
  - PbS, **PbSe**, PbTe
  - CdS, CdSe, CdTe
  - ZnS etc……

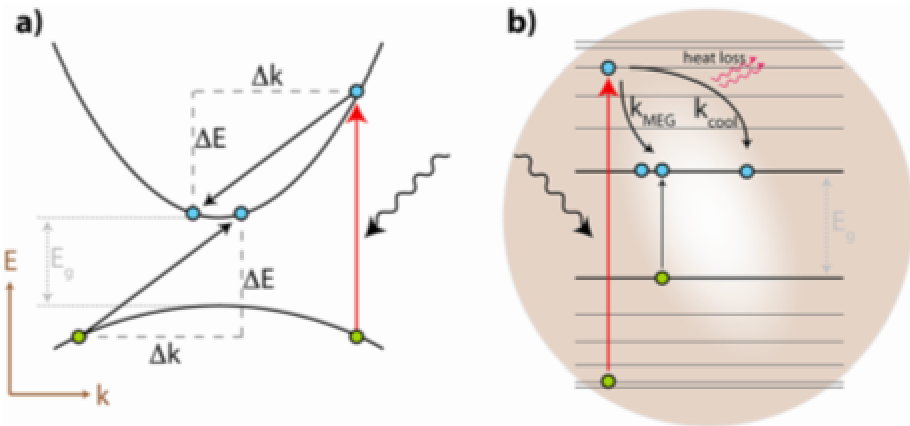
- Perovskite QDs
  - Cesium lead halides: $CsPbX_3$ (X = Cl, Br, I or mixed)

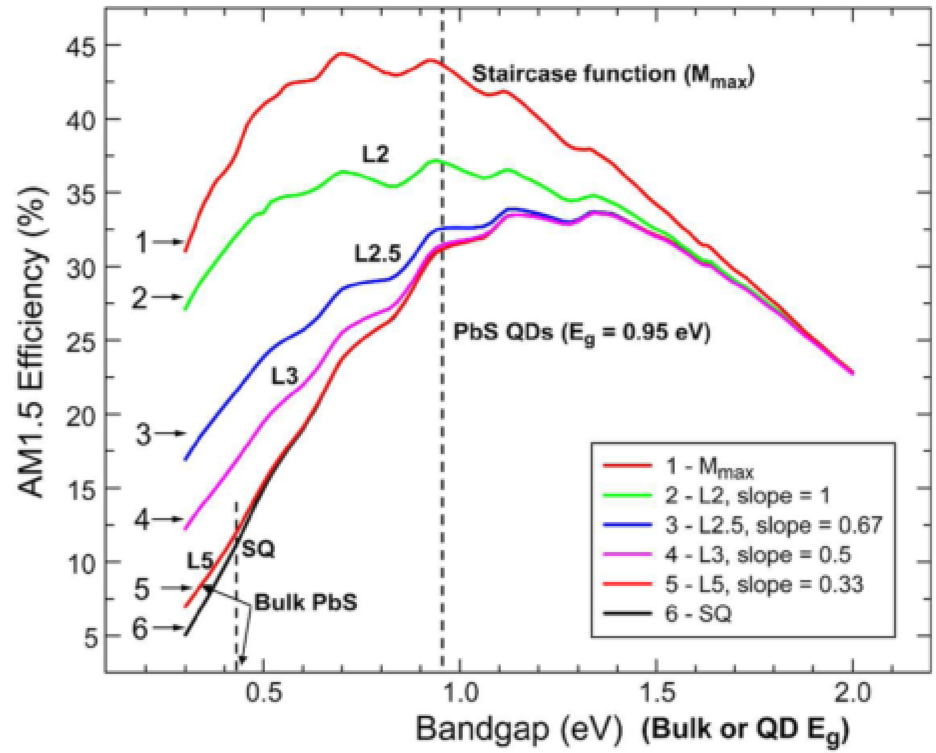
- Low-toxicity NPs:
  - Silver bismuth sulfide ($AgBiS_2$)
  - Copper indium sulfide ($CuInS_2$)

- Oxide NPs:
  - ZnO, TiO_2, SiO_2 etc.

Why Lead Selenide (PbSe) QDs?

Multiple Exciton Generation

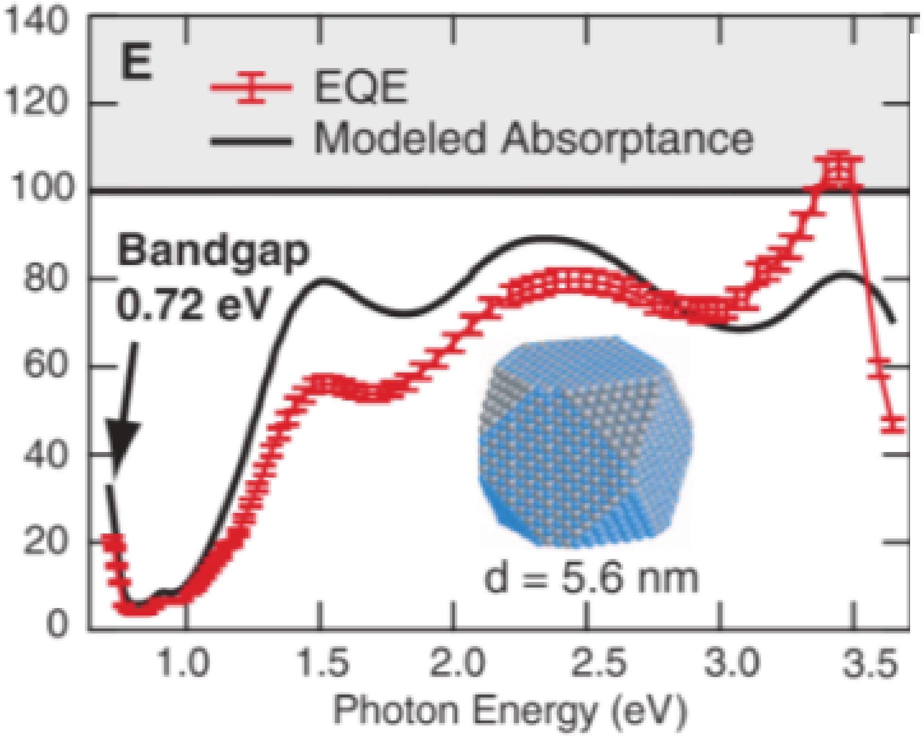


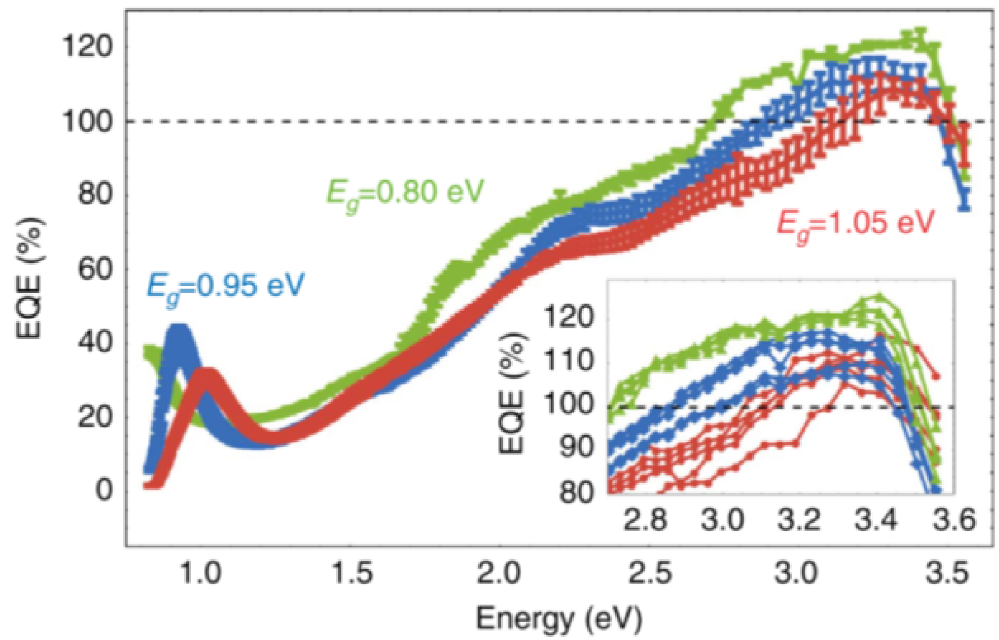


Beard et.al., Nano Lett., 2010

Why Lead Selenide (PbSe) QDs?

*MEG is more efficient in PbSe nanoparticles





Beard et.al., Acc. Chem. Res., 2013
Semonin et.al., Science, 2011
Davis et.al., Nat Comm., 2015

PbSe solar cells with EQE > 100%

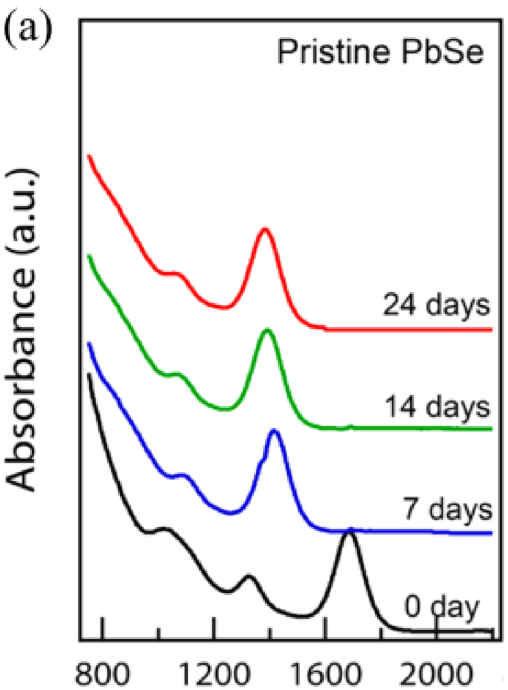
Works on PbSe QDs

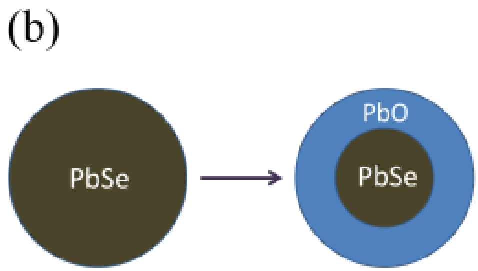
- **Problems with air-stability of thin films**
  - Air-stability
  - Hot carrier lifetime
  - ***The Journal of Physical Chemistry C 119, 24149 (2015)***

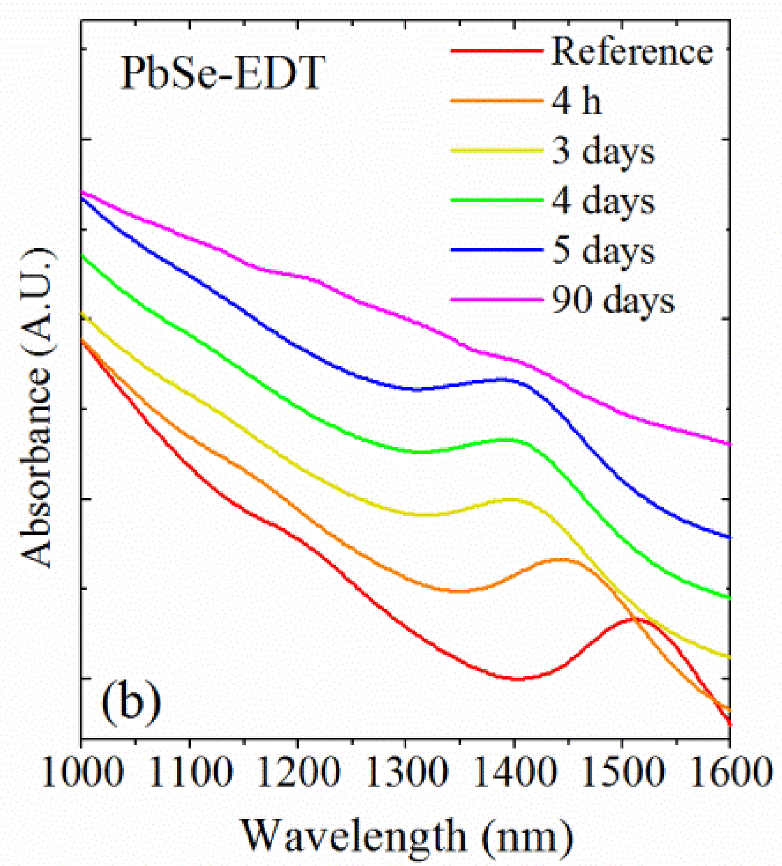
- **Problems with PbSe QD cell surface recombination**
  - With perovskite nanoparticles
  - Devices suppressed previous highest PCE, to **7.2%**
  - ***Advanced Energy Materials. 2016, 1601773***

- **Problems with PbSe QD surface**
  - More robust QD surface passivation
  - Updated highest PCE for PbSe cell again, to **8.2%**
  - ***Advanced Materials. 2017, 1703214***

Oxidation problem of PbSe QDs



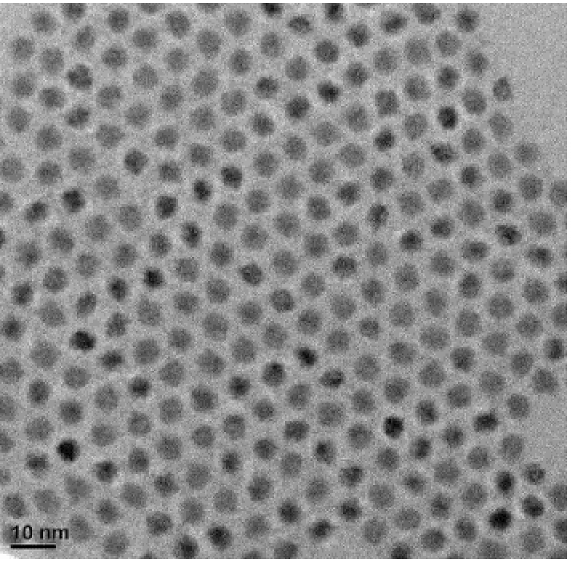


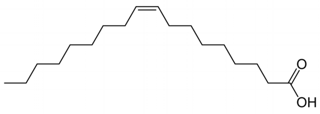


Bae et.al., J. Am. Chem. Soc., 2012

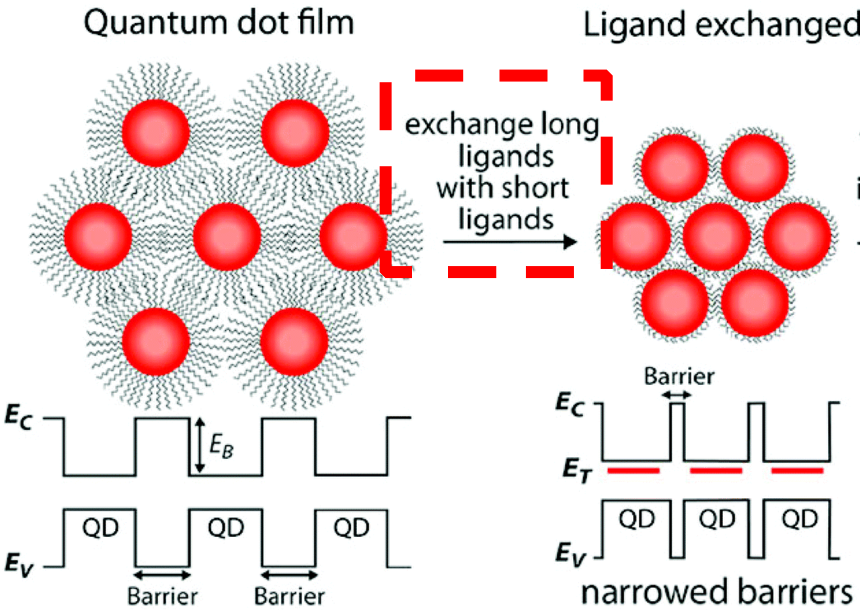
Zhang et.al., J. Phys. Chem. C., 2015

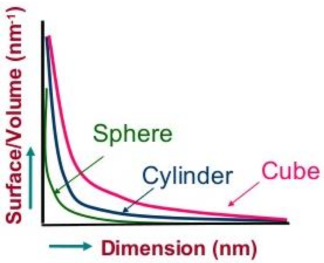
Ligands exchange of PbSe QDs





Oleate ligands

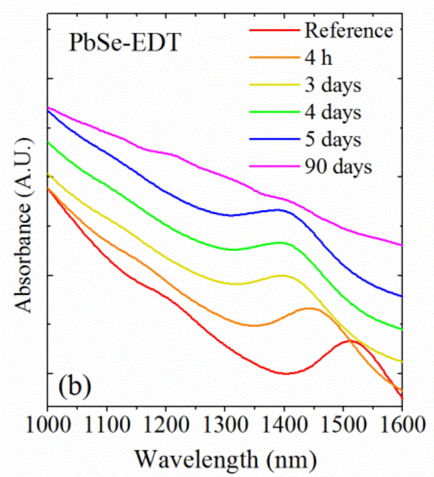


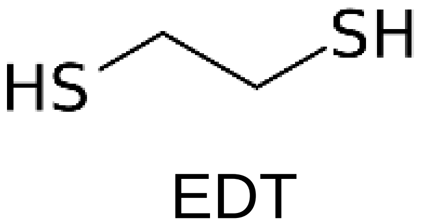


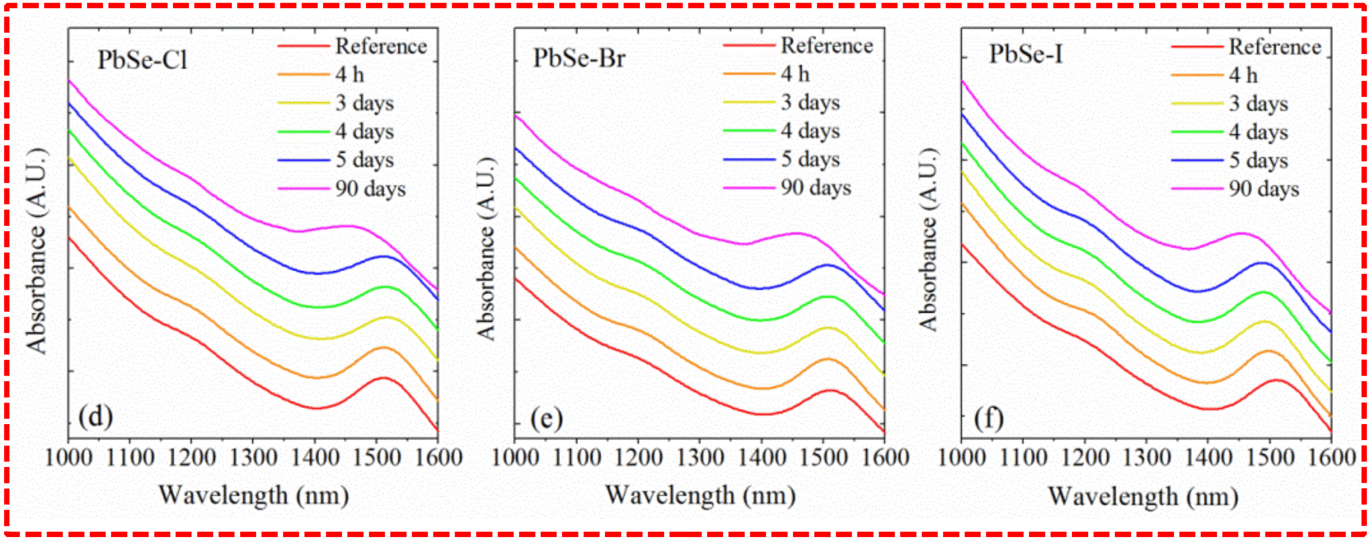
***Carrier transfer improves**

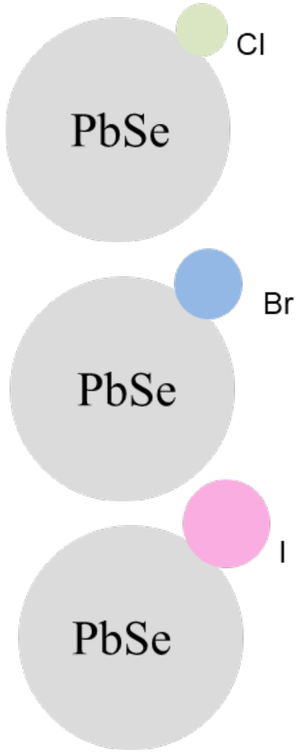
Palmstrom et.al., Nanosclae, 2015
Tang et.al., Adv. Mat., 2012

PbSe QDs: Air-stability and ligands



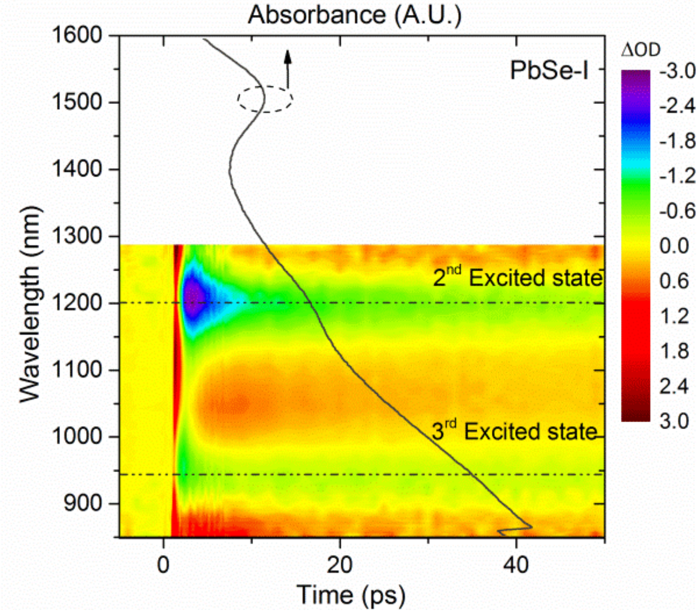


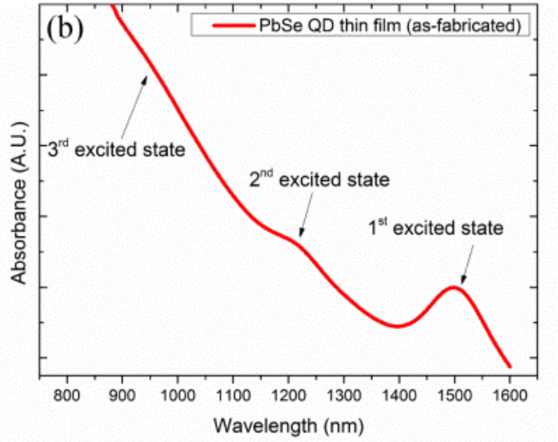


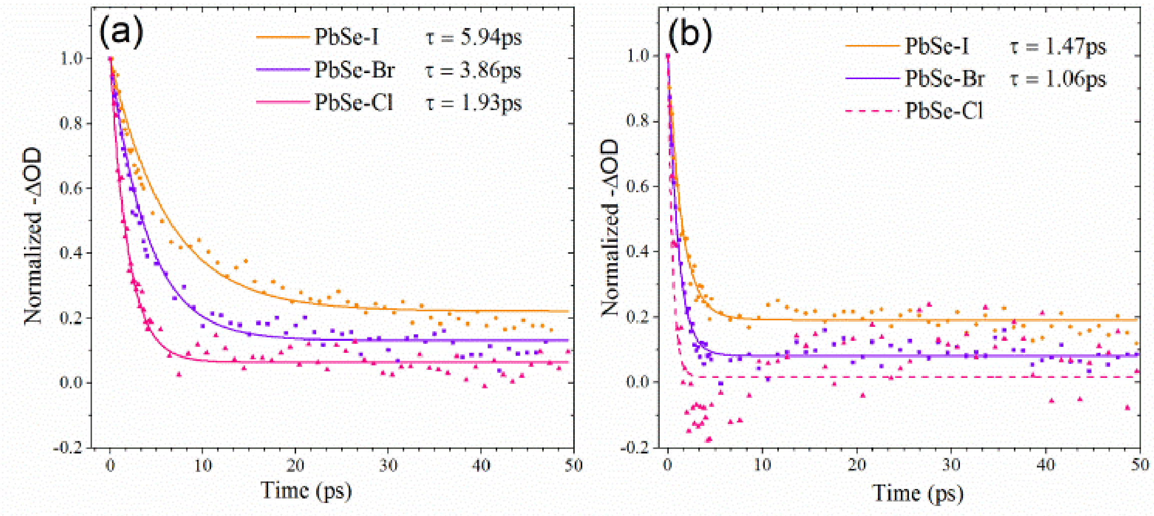


Zhang et.al., J. Phys. Chem. C., 2015

PbSe QDs: Hot carrier effect and ligands

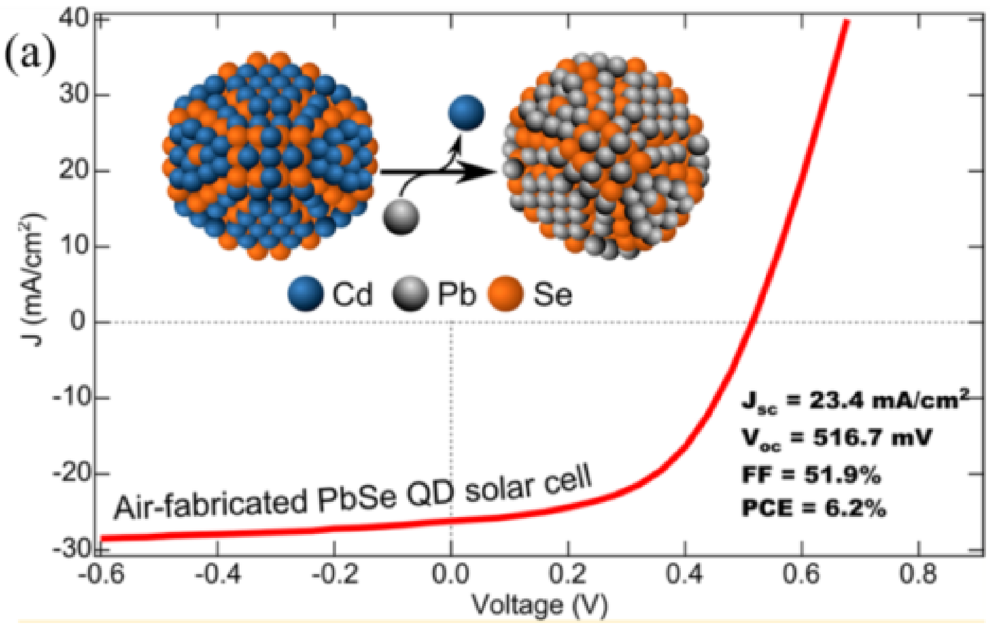


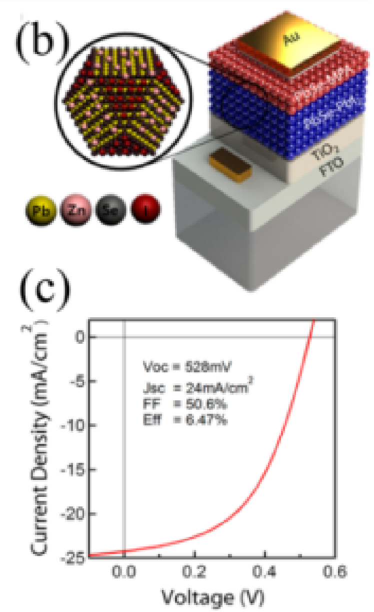




Zhilong Zhang, Jianfeng Yang, Xiaoming Wen, Lin Yuan, Santosh Shrestha, John A. Stride, Gavin J. Conibeer, Robert J. Patterson and Shujuan Huang. Effect of Halide Treatments on PbSe Quantum Dot Thin Films: Stability, Hot Carrier Lifetime and Application to Photovoltaics. ***The Journal of Physical Chemistry C*** 119, 24149 (2015).

PbSe QD solar cells





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6.2% in 2014

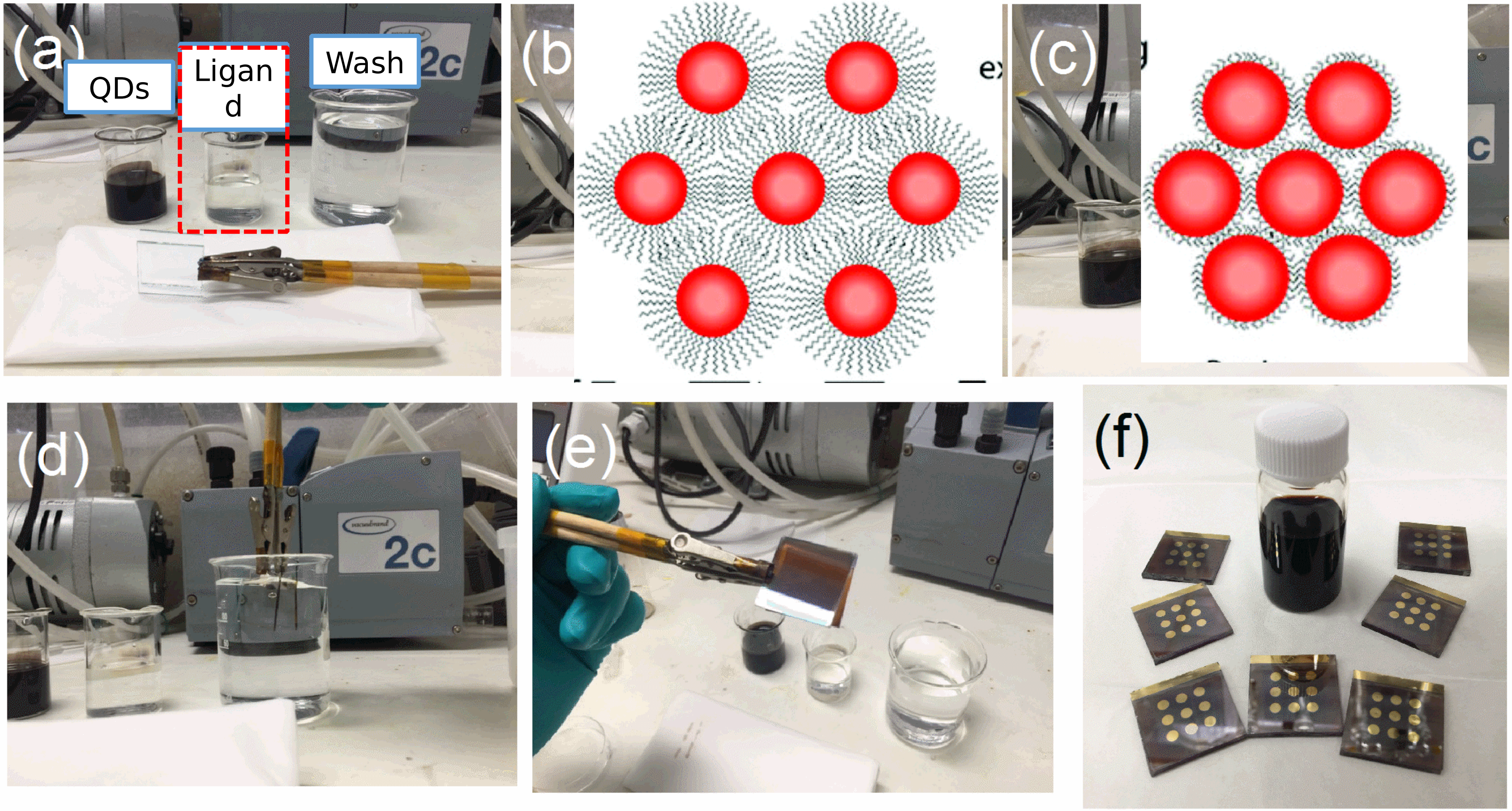
6.5% in 2015

CdSe QDs + $PbCl_2$ → Air-stable PbSe QDs (Cd, Cl passivated)

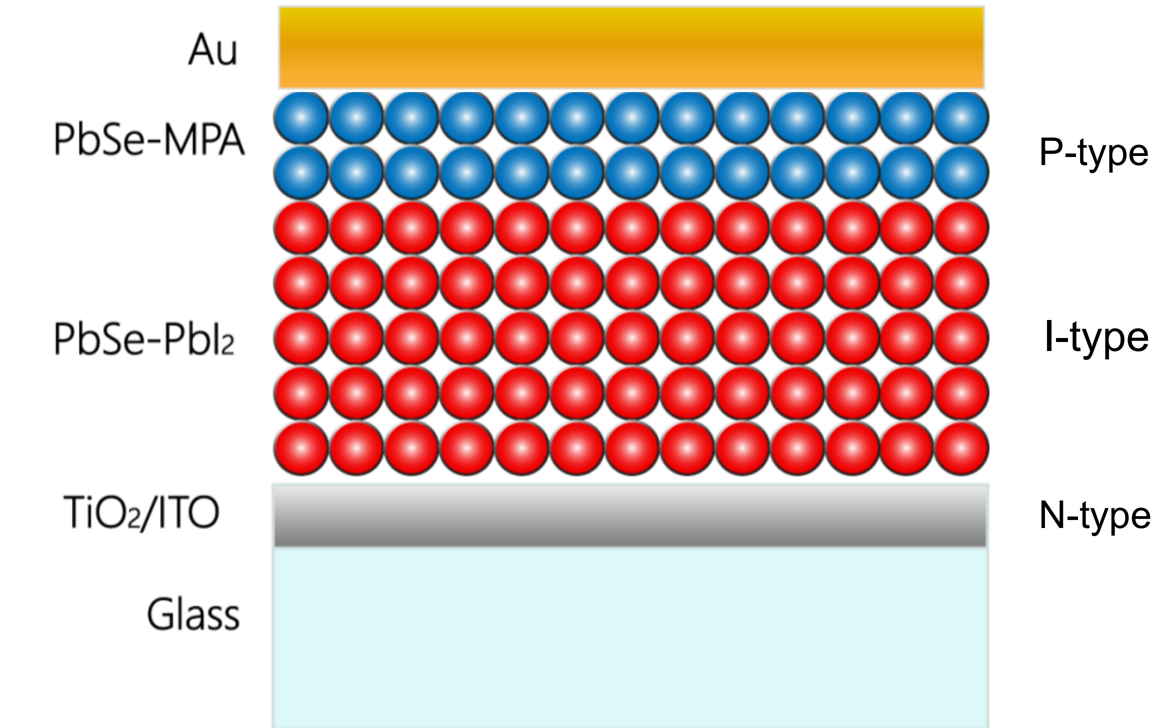
Zhang et.al., Nano Lett., 2014

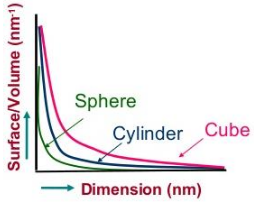
Kim et.al., ACS Nano, 2015

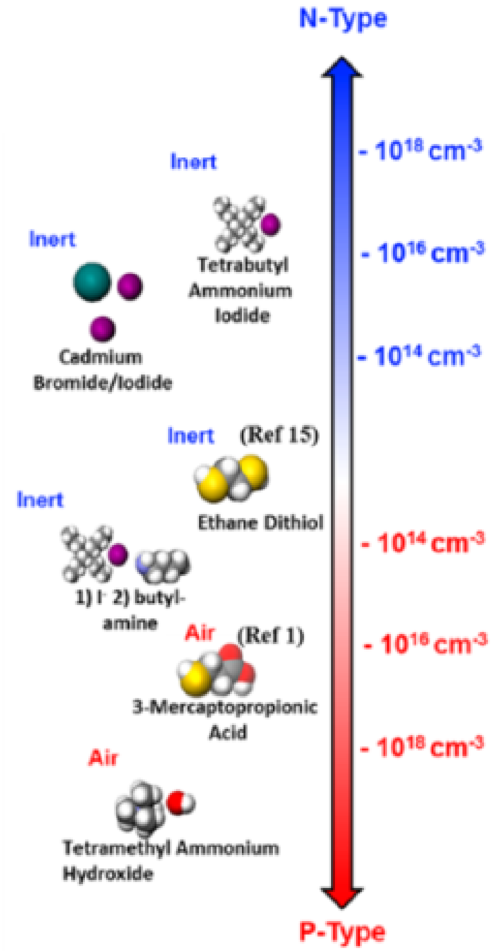
PbSe QD solar cells – Dip coating



PbSe QD solar cells

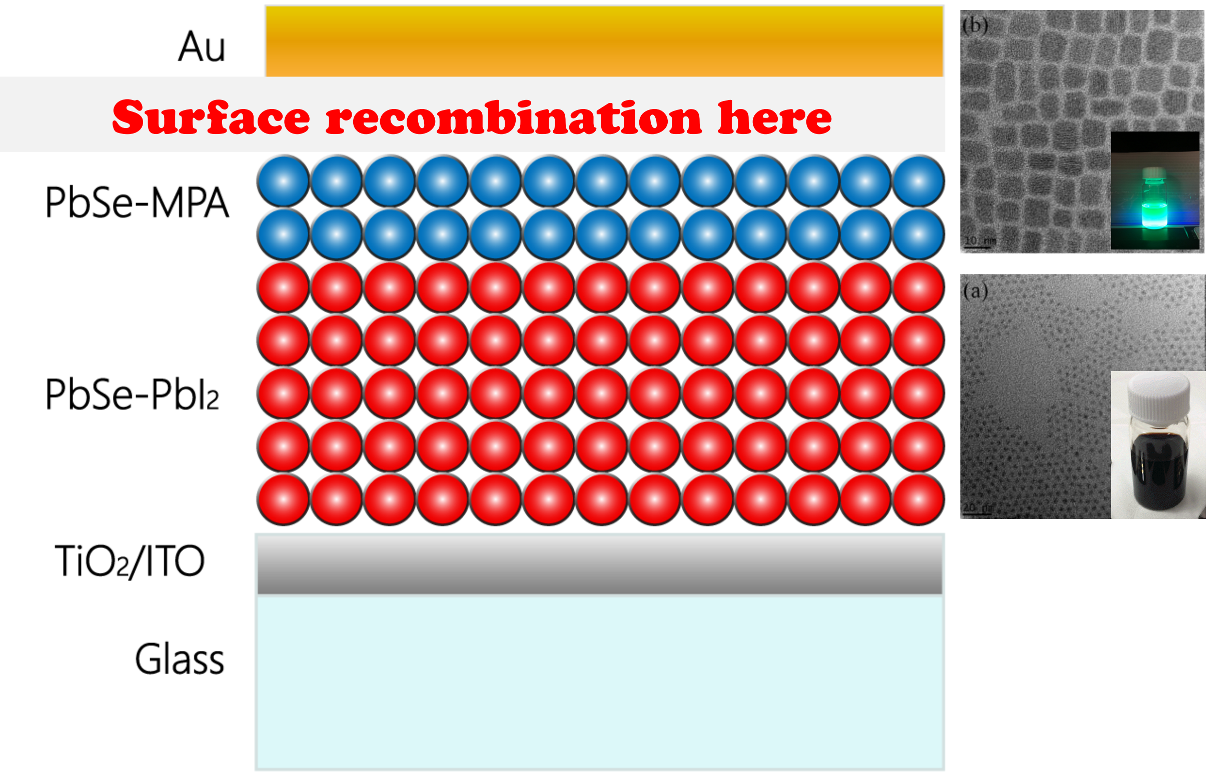






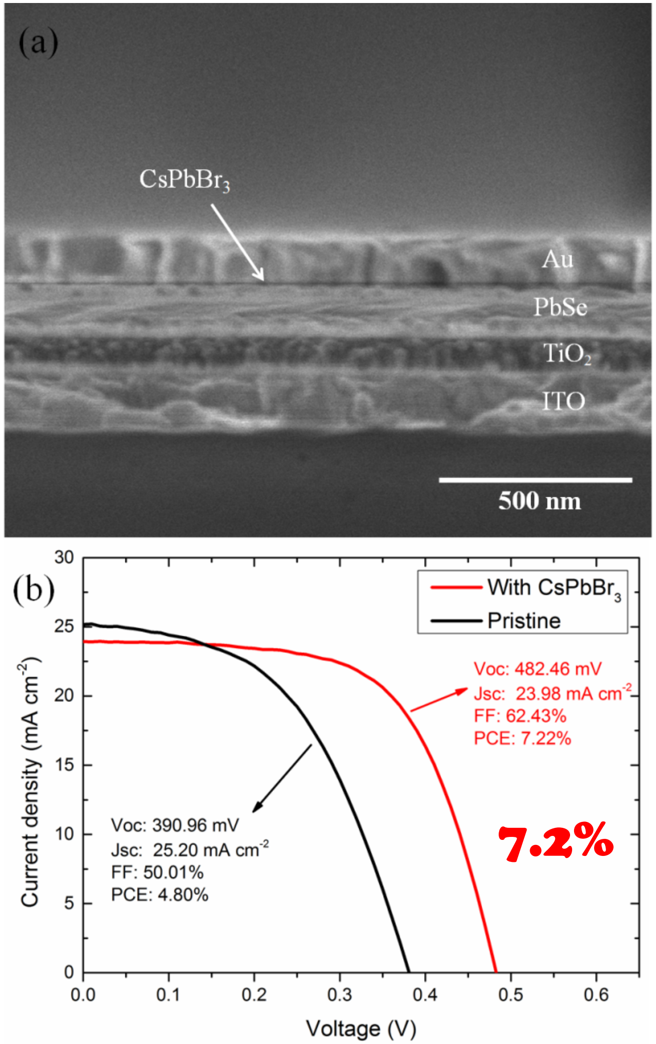
Voznyy et.al., ACS Nano, 2012

PbSe QD solar cells: $CsPbBr_3$

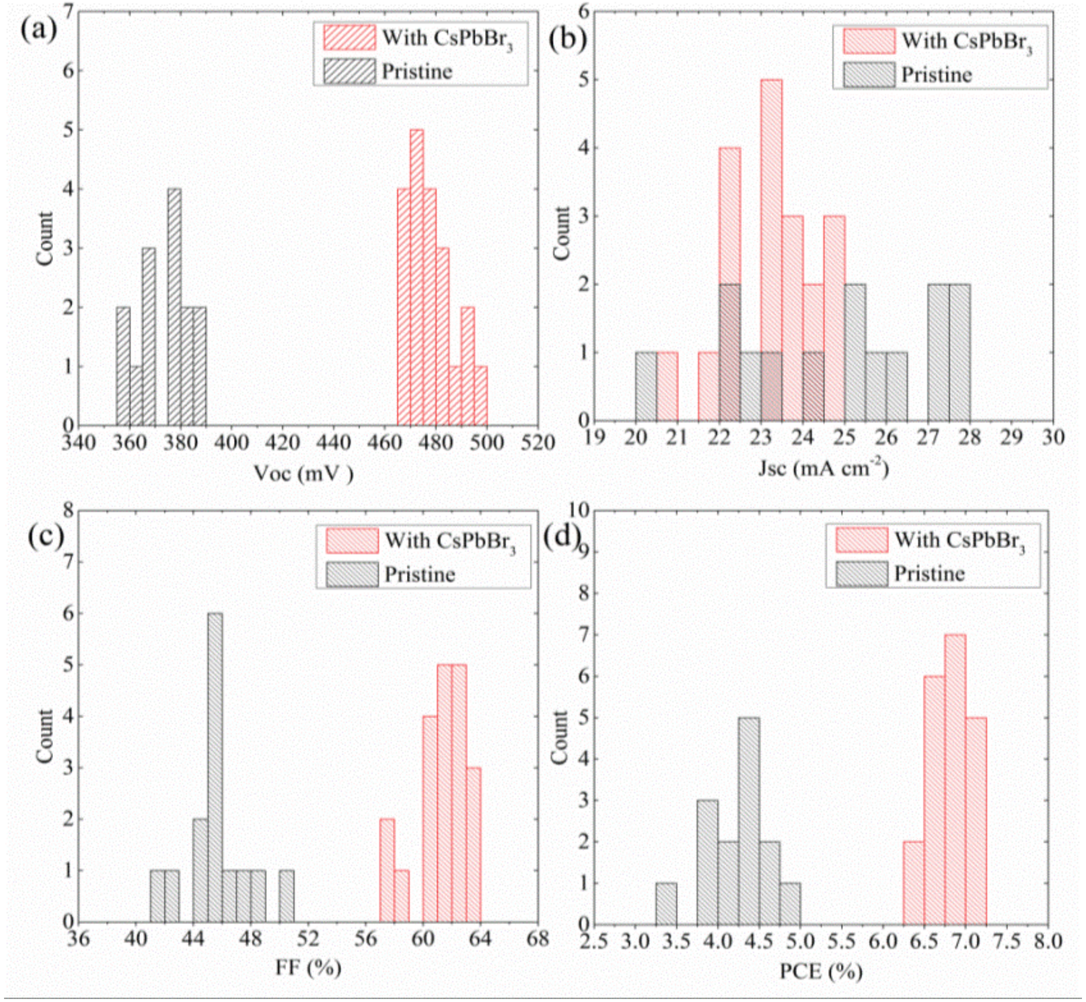


*Previous highest PCE reported: 6.5%

Zhang et al., Adv. Energy Mat., 2016

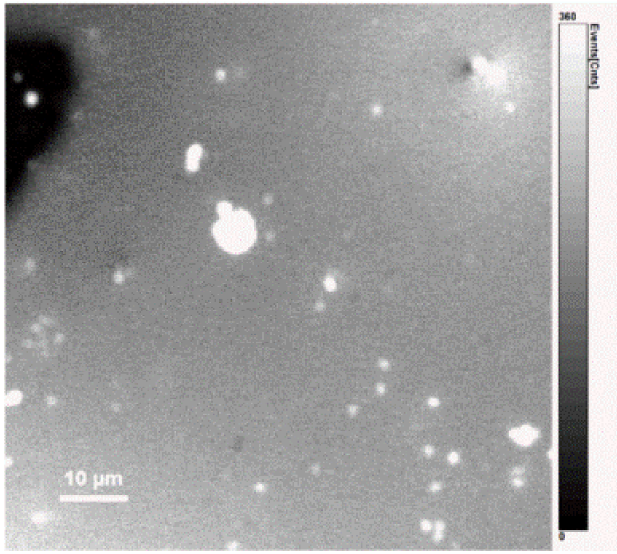


PbSe QD solar cells: $CsPbBr_3$



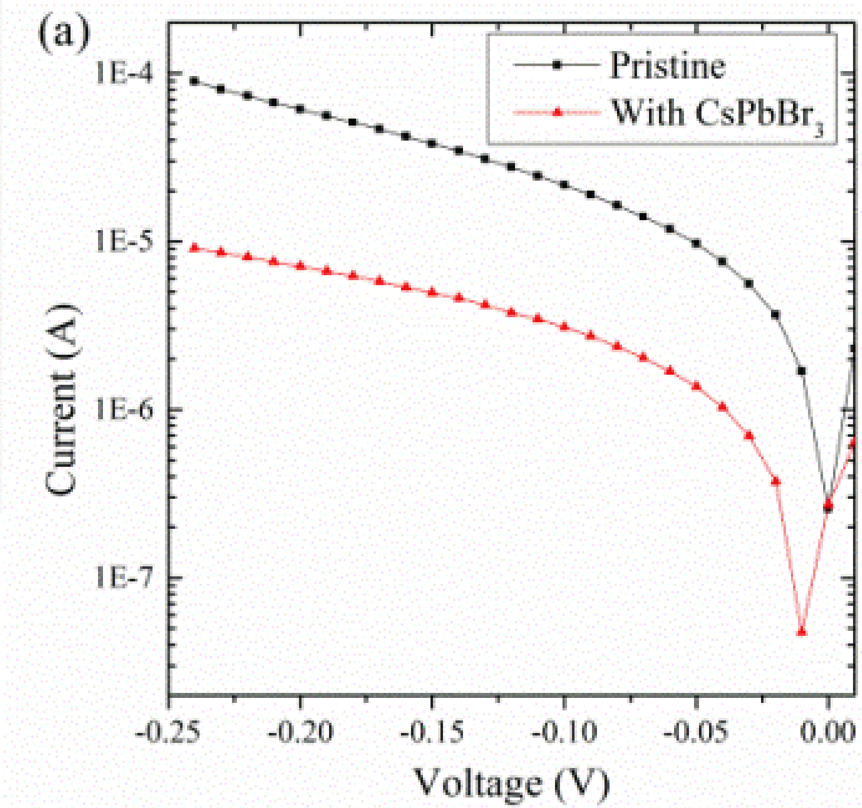
Zhang et al., Adv. Energy Mat., 2016

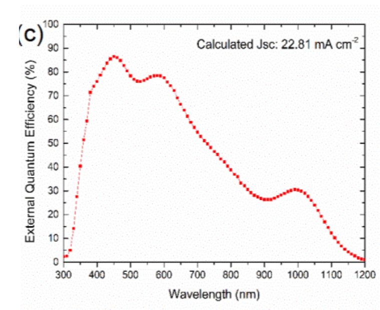
PbSe QD solar cells: $CsPbBr_3$



Fluorescence image of $CsPbBr_3$ QDs

*Red photons have longer penetration length

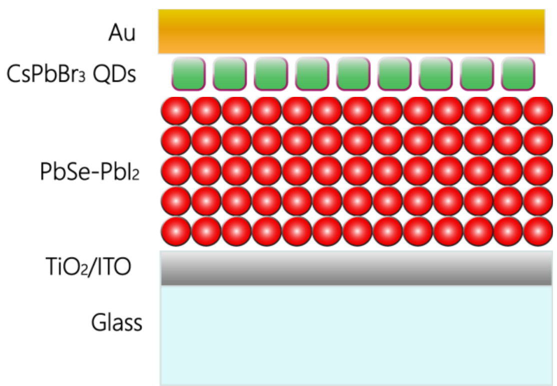


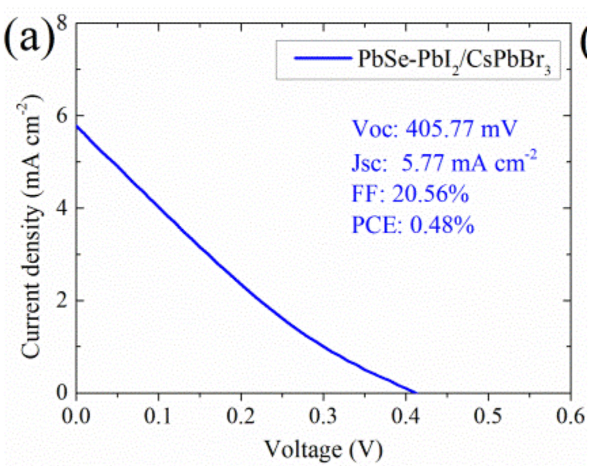


Zhang et al., Adv. Energy Mat., 2016

PbSe QD solar cells: $CsPbBr_3$

Electron-blocking effect?





Conclusion:

- With CsPbBr3 back layer PCE improved
- Highest PCE **7.2%**, best reported at the time
- Some kind of surface passivation?

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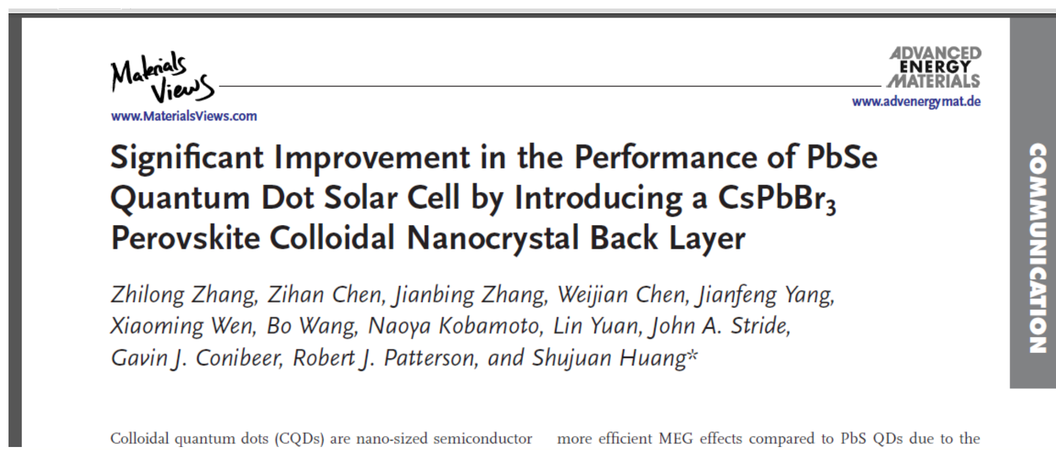
6.5% in 2015 → **7.2% in 2016**



Materials Views www.MaterialsViews.com

ADVANCED ENERGY MATERIALS www.advenergymat.de

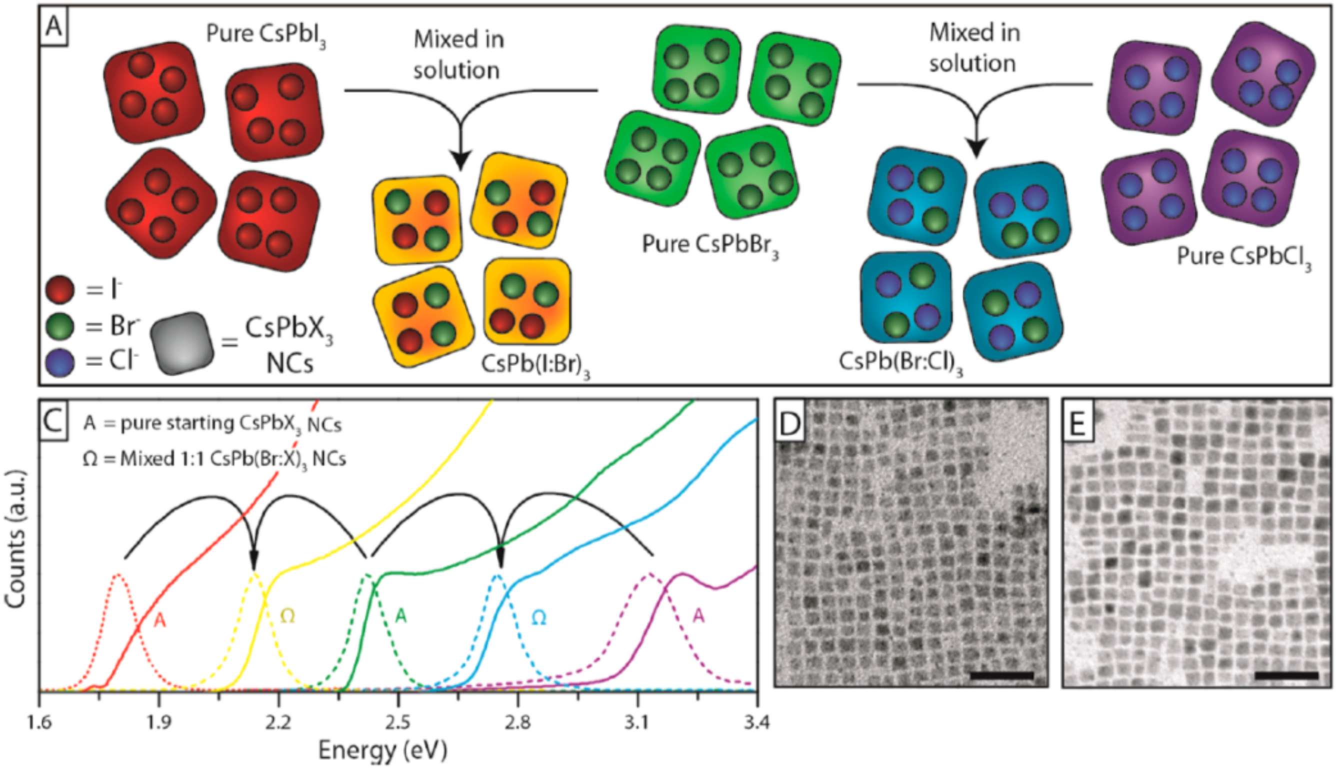
COMMUNICATION

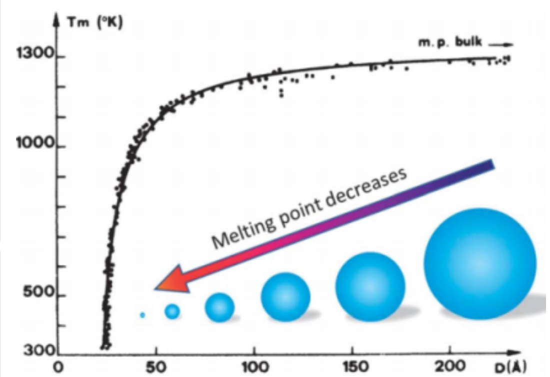
Significant Improvement in the Performance of PbSe Quantum Dot Solar Cell by Introducing a $CsPbBr_3$ Perovskite Colloidal Nanocrystal Back Layer

*Zhilong Zhang, Zihan Chen, Jianbing Zhang, Weijian Chen, Jianfeng Yang, Xiaoming Wen, Bo Wang, Naoya Kobamoto, Lin Yuan, John A. Stride, Gavin J. Conibeer, Robert J. Patterson, and Shujuan Huang**

Colloidal quantum dots (CQDs) are nano-sized semiconductor more efficient MEG effects compared to PbS QDs due to the

Ion Exchange between Perovskite NPs



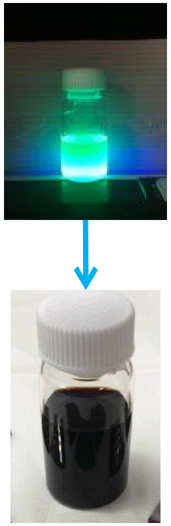


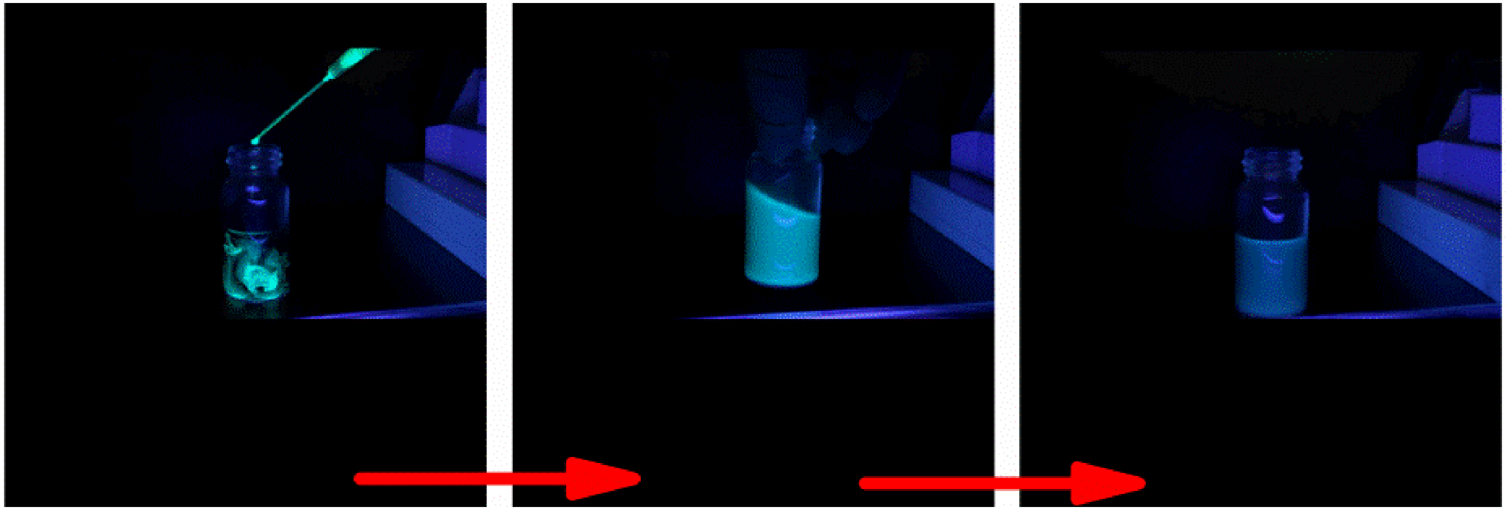
Scaling law of NPs

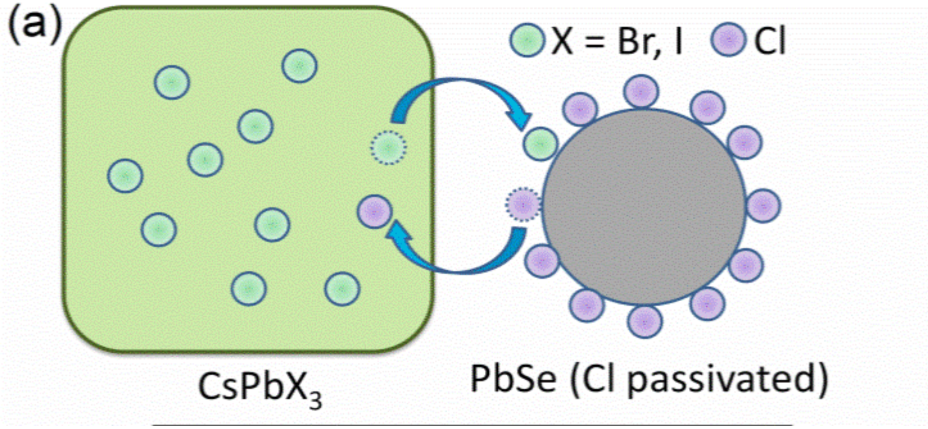
- Halogens are flexible in perovskite NCs
- Hybrid halide perovskite NCs formed upon mixing (room temperature)

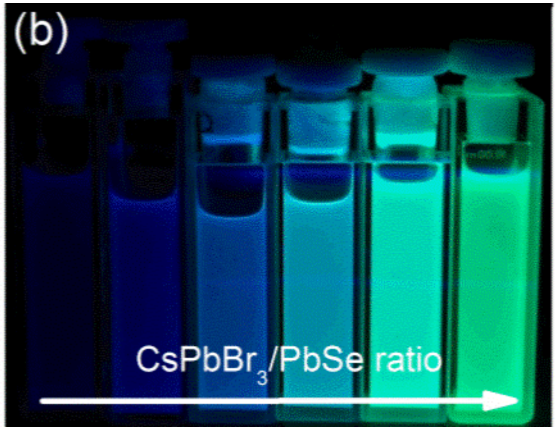
Akkerman et.al., J. Am. Chem. Soc., 2015

Does this happen between PbSe and perovskite QDs?



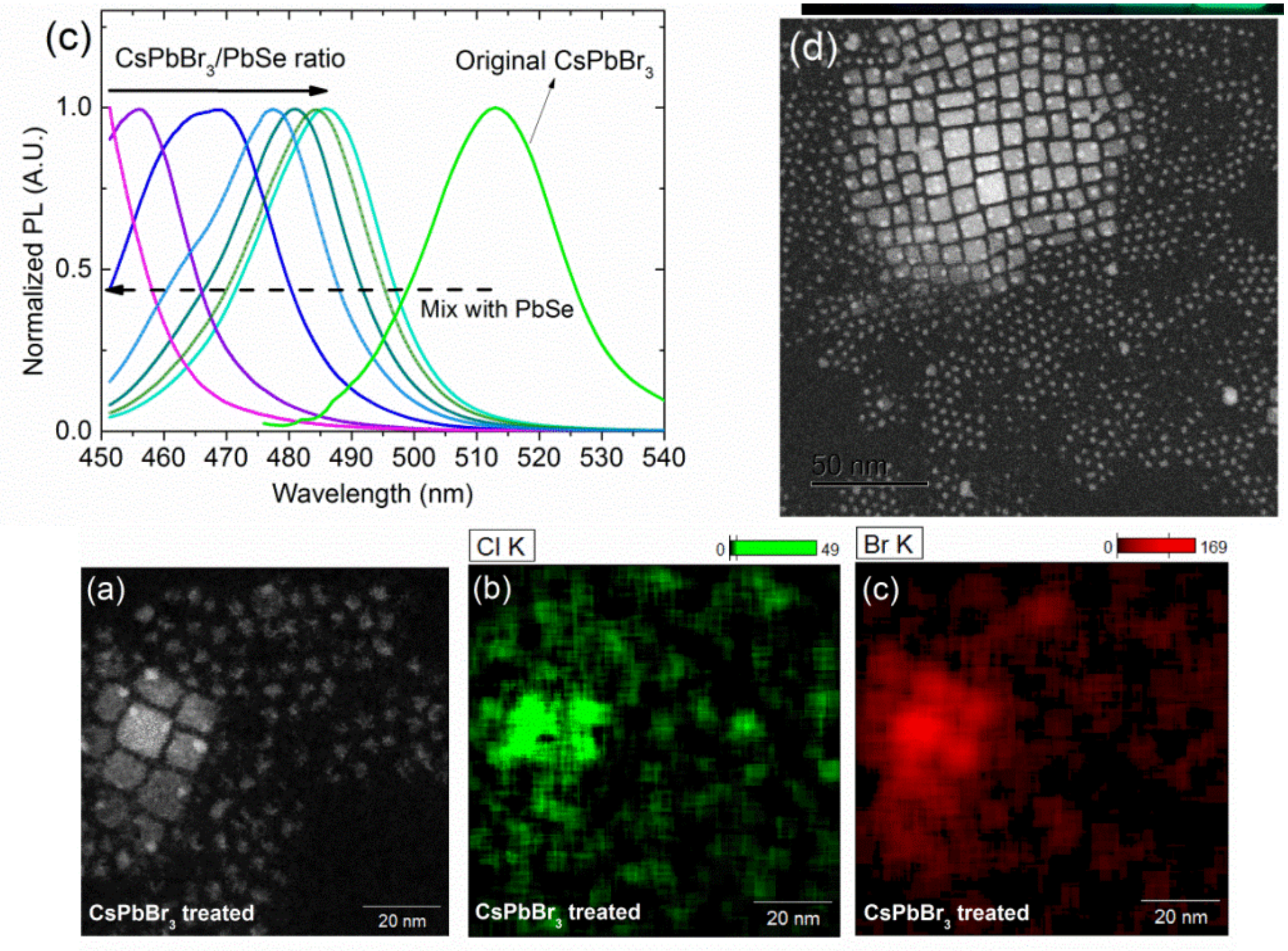






Zhang et.al., Adv. Mat., 2017

Ion Exchange between PbSe QDs and Perovskite NPs

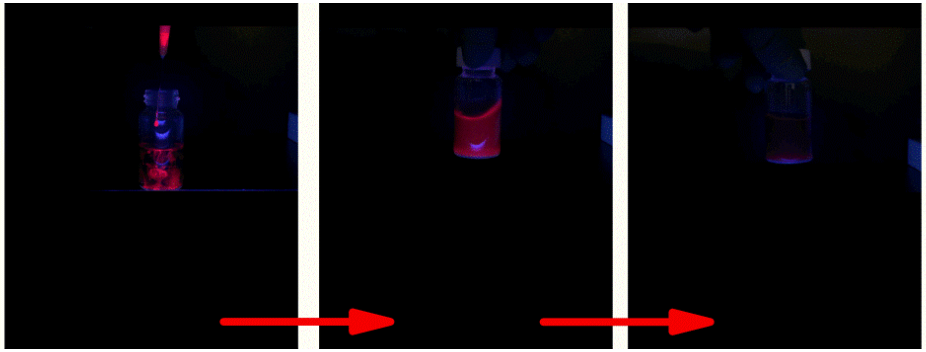


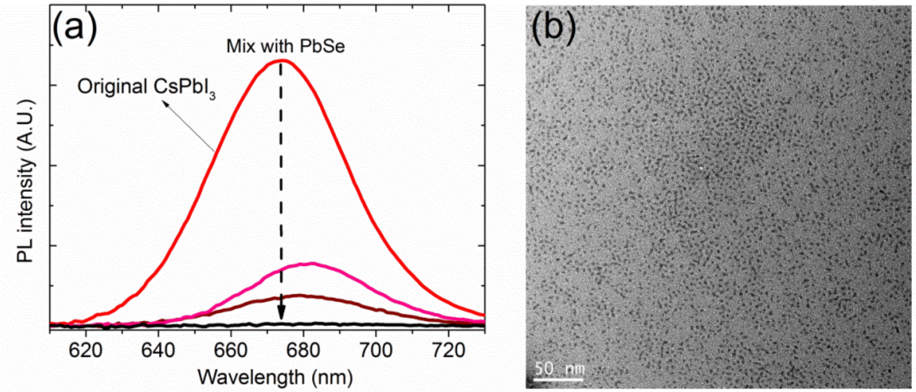
$CsPbBr_3$ → $CsPbCl_xBr_{3-x}$

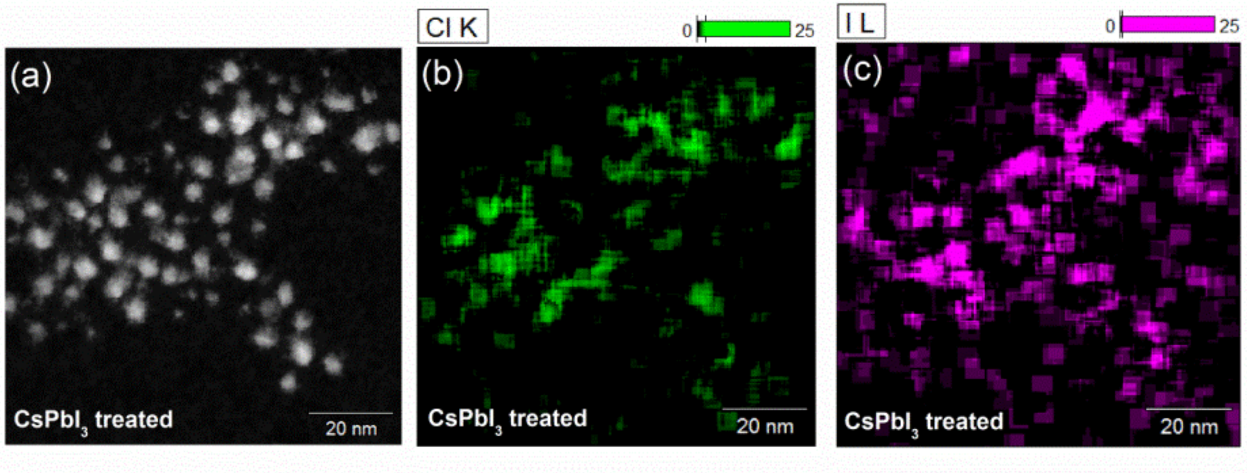
PbSe (Cl) → PbSe (Cl+Br)

Zhang et.al., Adv. Mat., 2017

Ion Exchange between PbSe QDs and Perovskite NPs







$CsPbI_3$ → Degraded products

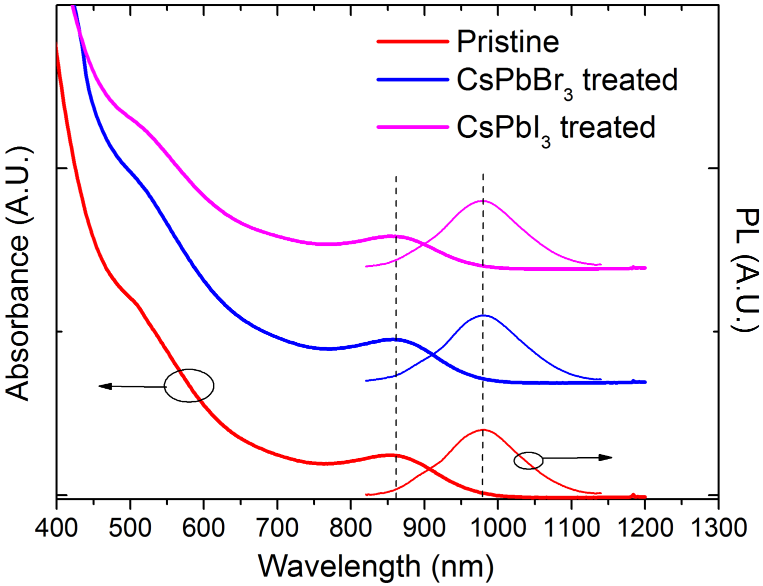
PbSe (Cl) → PbSe (Cl+I)

***$CsPbI_3$ cannot be converted to $CsPbCl_3$ directly**

Akkerman et.al., J. Am. Chem. Soc., 2015

Zhang et.al., Adv. Mat., 2017

Ion Exchange between PbSe QDs and Perovskite NPs



Treatment	$CsPbX_3/PbSe$ (upon mixing)	Cl/Pb	X/Pb (X = Br, I)	(Cl+X)/Pb (X = Br, I)	PLQY [%]
Pristine	–	0.19	–	0.19	38
$CsPbBr_3$	0.07	0.17	0.14	0.31	38
$CsPbBr_3$	0.13	0.14	0.16	0.30	42
$CsPbBr_3$	0.26	0.10	0.22	0.32	35
$CsPbI_3$	0.01	0.16	0.02	0.18	37
$CsPbI_3$	0.03	0.15	0.04	0.19	52
$CsPbI_3$	0.16	0.10	0.18	0.28	5

PLQY of PbSe QDs

Purification:

1. **Intentional degradation of perovskite NPs (by adding polar solvents)**
2. **Well-dispersed PbSe QDs are separated from the degraded products (powder)**

$$\mathbf{PLQY} = \frac{\#\ \mathbf{photons\ emitted}}{\#\ \mathbf{photons\ absorbed}}$$

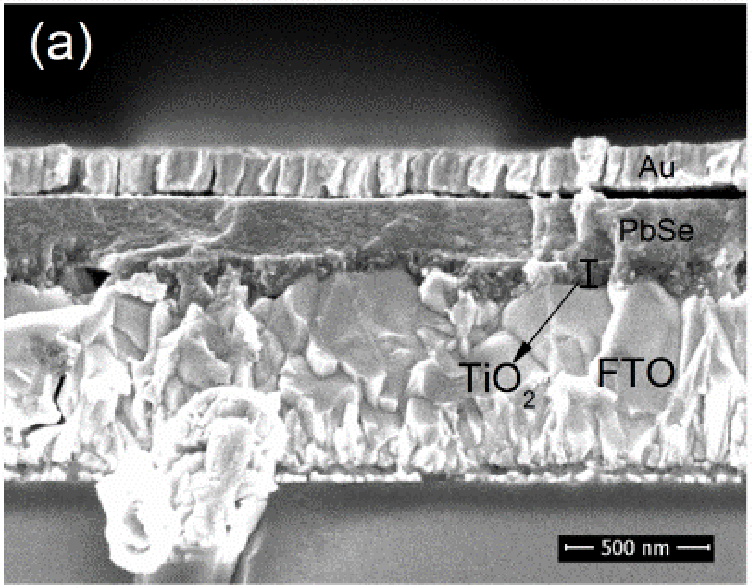
***Indication of # defects in the QDs**

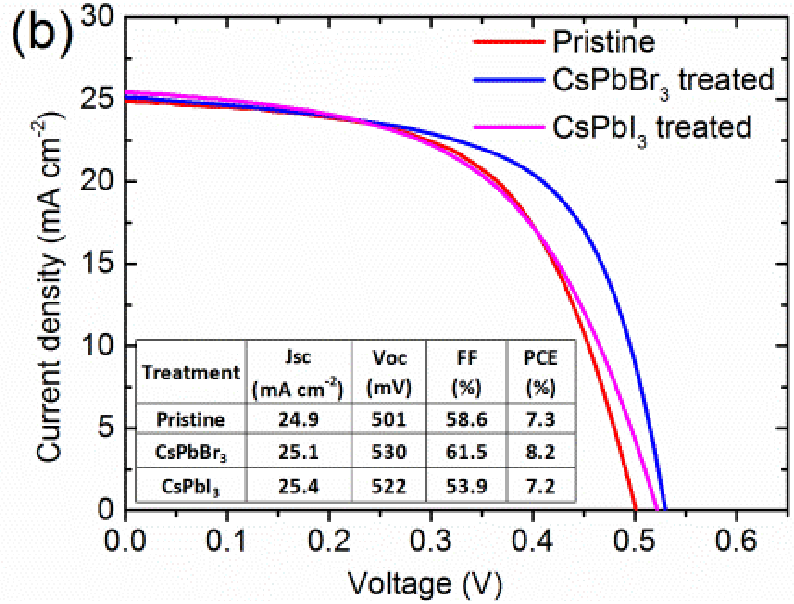
***Measured using integrating sphere**

Zhang et.al., Adv. Mat., 2017

Ion Exchange between PbSe QDs and Perovskite NPs

Now solar cells:

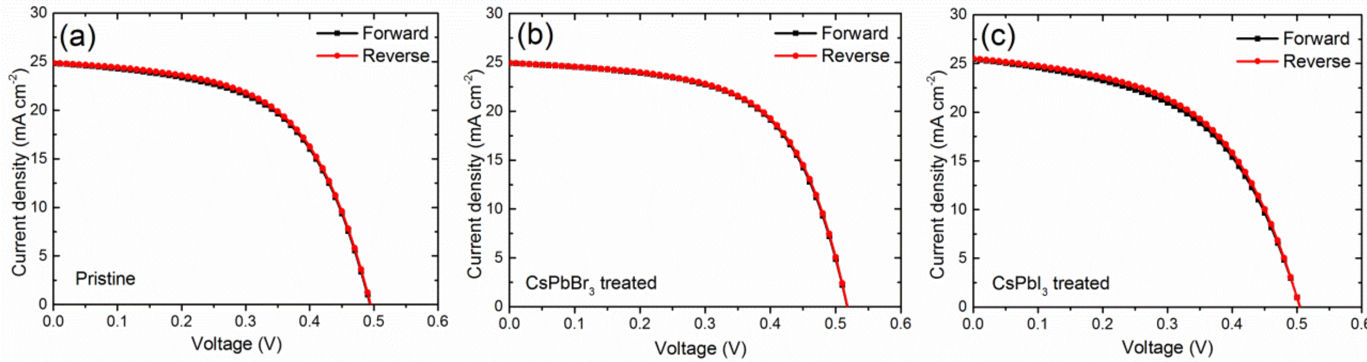




Treatment	Jsc (mA cm^{-2})	Voc (mV)	FF (%)	PCE (%)
Pristine	24.9	501	58.6	7.3
CsPbBr$_3$	25.1	530	61.5	8.2
CsPbI$_3$	25.4	522	53.9	7.2

- **Highest PCE 8.2%**
- Previously 7.2%

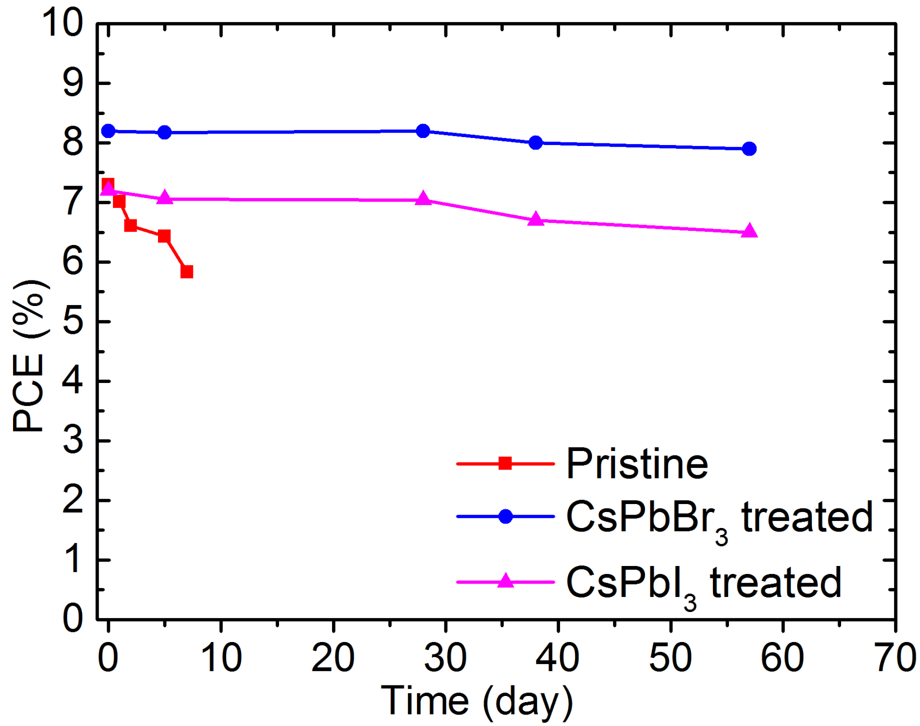
UNSW SYDNEY



Zhang et.al., Adv. Mat., 2017

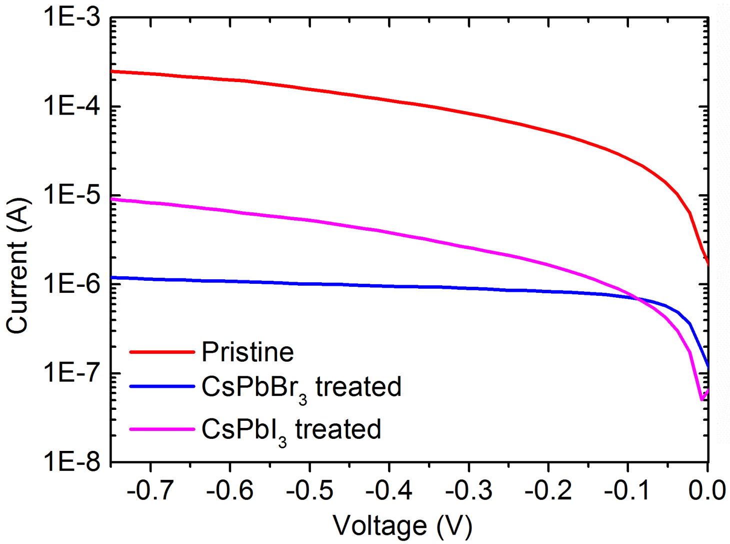
Ion Exchange between PbSe QDs and Perovskite NPs

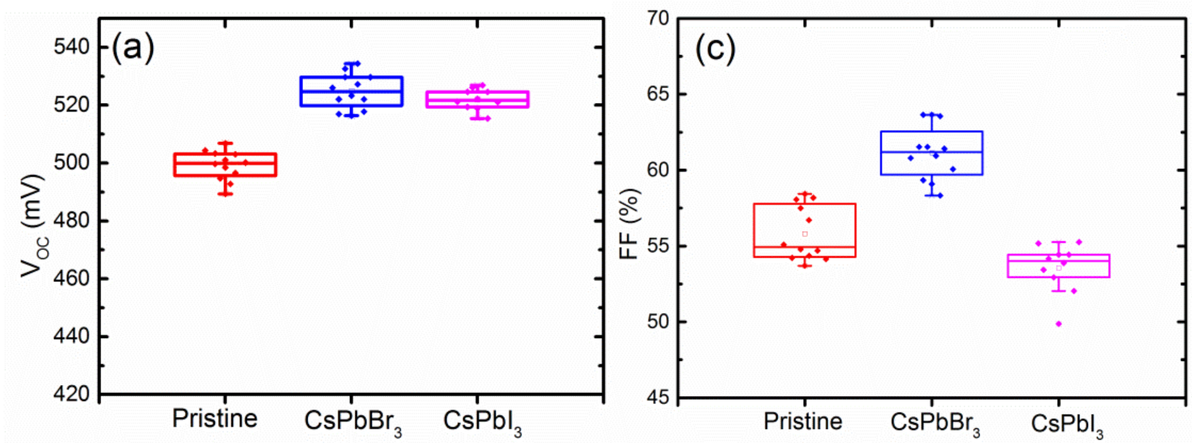
Air-stability:

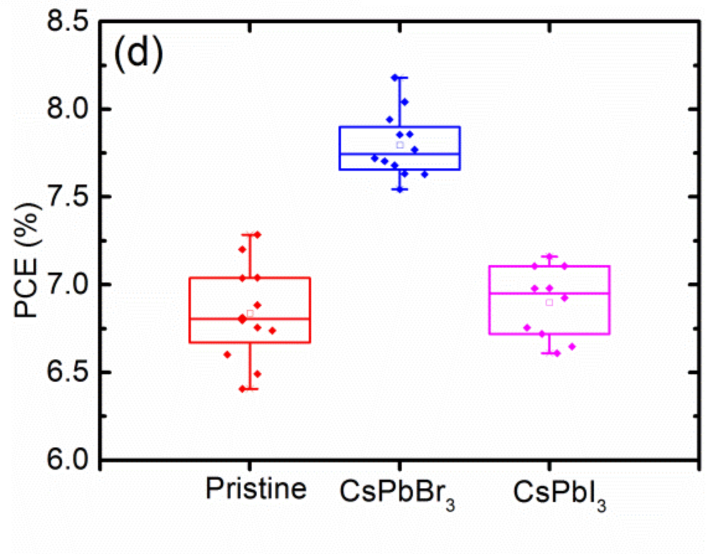


Zhang et.al., Adv. Mat., 2017

Ion Exchange between PbSe QDs and Perovskite NPs



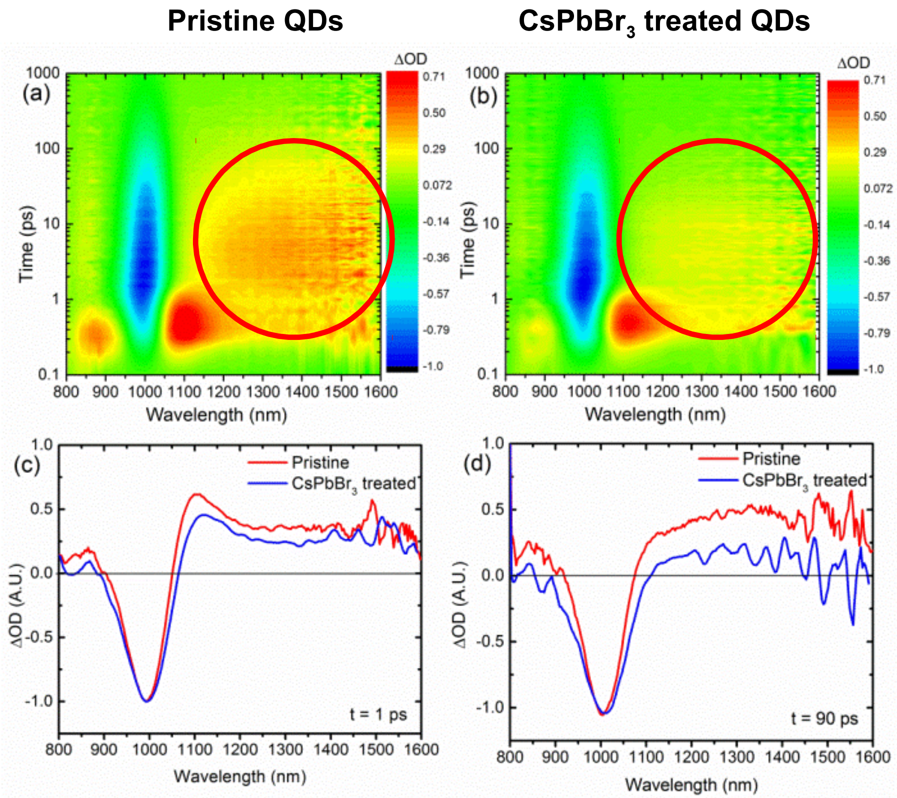


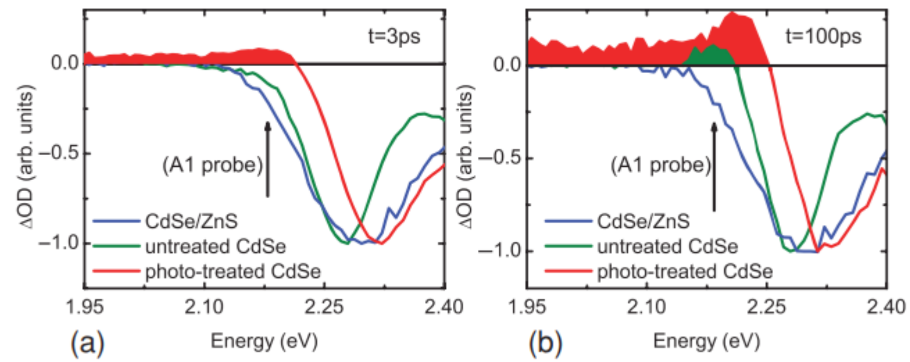


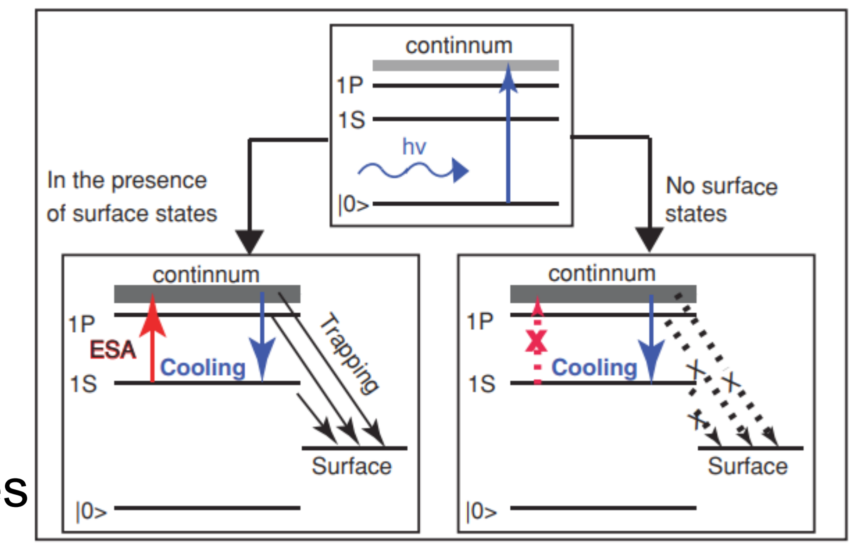
- Highly reproducible
- Voc consistently higher

Zhang et.al., Adv. Mat., 2017

Ion Exchange between PbSe QDs and Perovskite NPs







- Suppressed "red" signal from TA indicates less surface defect states
- Improvements arise from better QD surface passivation

Zhang et.al., Adv. Mat., 2017

Tyagi et.al., J. Chem. Phys. 094706, 2011

Ion Exchange between PbSe QDs and Perovskite NPs

PbSe QD solar cells reported in literature:

UNSW SYDNEY

7.2% in 2016

UNSW SYDNEY

8.2% in 2017

COMMUNICATION
Quantum-Dot Solar Cells
ADVANCED MATERIALS
www.advmat.de

A New Passivation Route Leading to Over 8% Efficient PbSe Quantum-Dot Solar Cells via Direct Ion Exchange with Perovskite Nanocrystals

Zhilong Zhang, Zihan Chen, Lin Yuan, Weijian Chen, Jianfeng Yang, Bo Wang, Xiaoming Wen, Jianbing Zhang, Long Hu, John A. Stride, Gavin J. Conibeer, Robert J. Patterson, and Shujuan Huang**

Colloidal quantum dots (QDs) are promising candidate materials for photovoltaics (PV) owing to the tunable bandgap and low-cost solution process-

and efficient multiple-exciton generation (MEG),[22–24] a significant amount of research has been conducted particularly

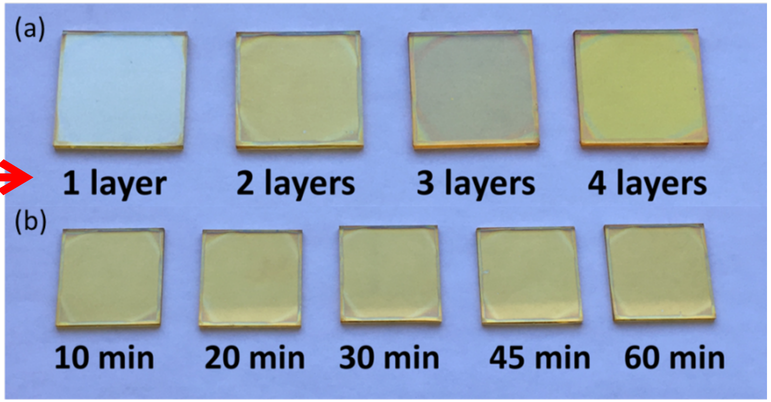
Other works from the CQD group

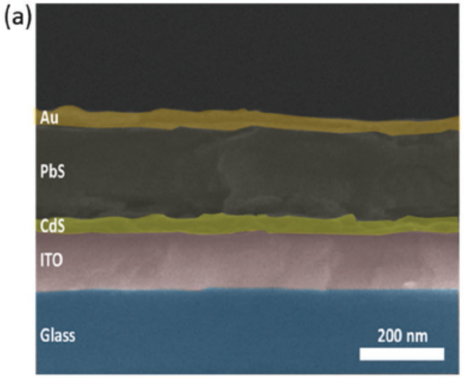
- PbS QD solar cells
  - Improved CdS layer as electron layer
  - Ag doping in hole transport layer
  - One-step deposition
  - QD/QD, QD/perovskite tandems

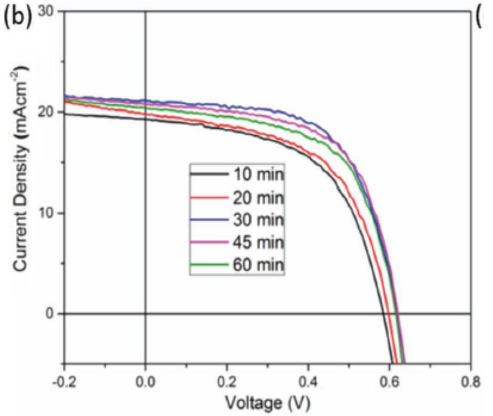
- Perovskite QD devices

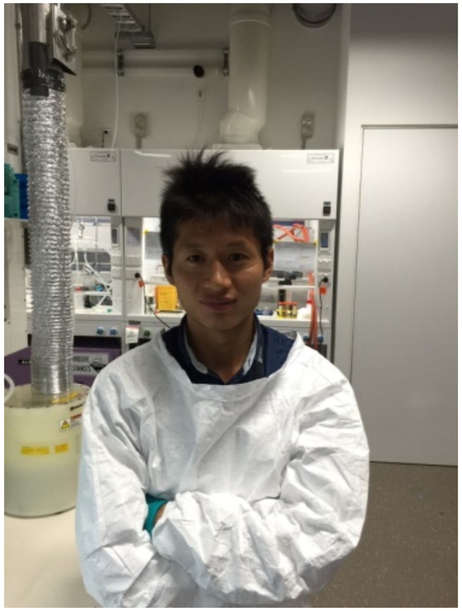
- Low-toxicity materials:
  - Silver bismuth sulfide ($AgBiS_2$) NP solar cells
  - $CuInS_2$ NP solar cells

Improved CdS electron-transport layer: sol-gel deposition



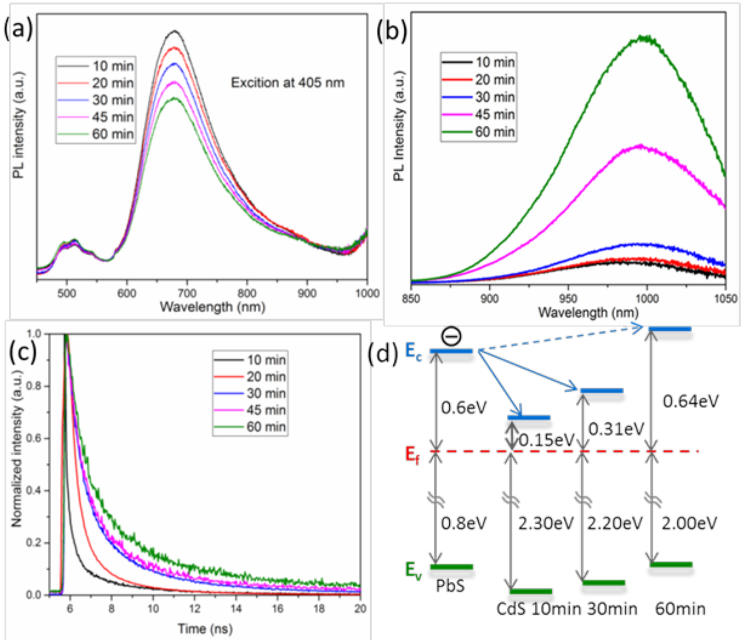






Time [min]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	*FF* [%]	Best PCE [%]	Average PCE [%]
10	0.58	19.8	57	6.5	6.2 ± 0.3
20	0.60	20.6	59	7.3	7.1 ± 0.2
30	0.62	21.5	62	8.3	8.1 ± 0.2
45	0.63	20.3	60	7.7	7.4 ± 0.3
60	0.64	19.5	58	7.2	6.9 ± 0.3

Improved CdS electron-transport layer



Conclusion:

(1) Performance optimized through annealing time

(2) Performance comparable to those with TiO_2 or ZnO

(3) Suitable for spray, dip-coating etc. for other cell types e.g. $Cu(In,Ga)Se_2$, $Cu_2ZnSn(S,Se)_4$ and CdTe

FULL PAPER

ADVANCED FUNCTIONAL MATERIALS

Quantum Dots

www.afm-journal.de

High Performance PbS Colloidal Quantum Dot Solar Cells by Employing Solution-Processed CdS Thin Films from a Single-Source Precursor as the Electron Transport Layer

Long Hu, Robert J. Patterson, Yicong Hu, Weijian Chen, Zhilong Zhang, Lin Yuan, Zihan Chen, Gavin J. Conibeer, Gang Wang, and Shujuan Huang**

CdS thin films are a promising electron transport layer in PbS colloidal

optimal ligands for CQD thin film surface passivation have evolved from organic

Contents soon to be published

Silver bismuth sulfide ($AgBiS_2$) NP solar cells

nature photonics

LETTERS

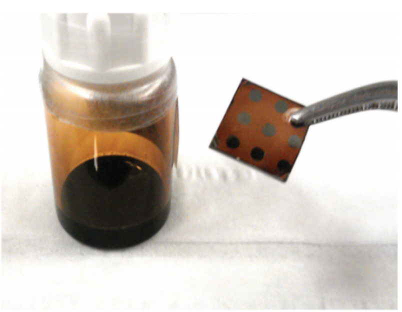
PUBLISHED ONLINE: 20 JUNE 2016 | DOI: 10.1038/NPHOTON.2016.108

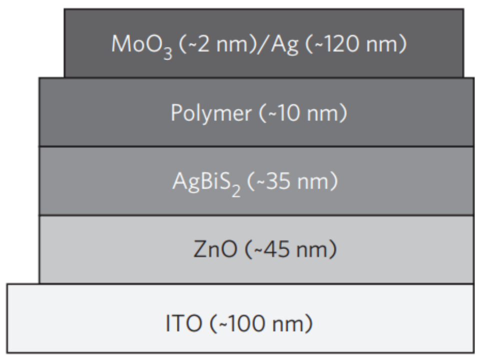
Solution-processed solar cells based on environmentally friendly $AgBiS_2$ nanocrystals

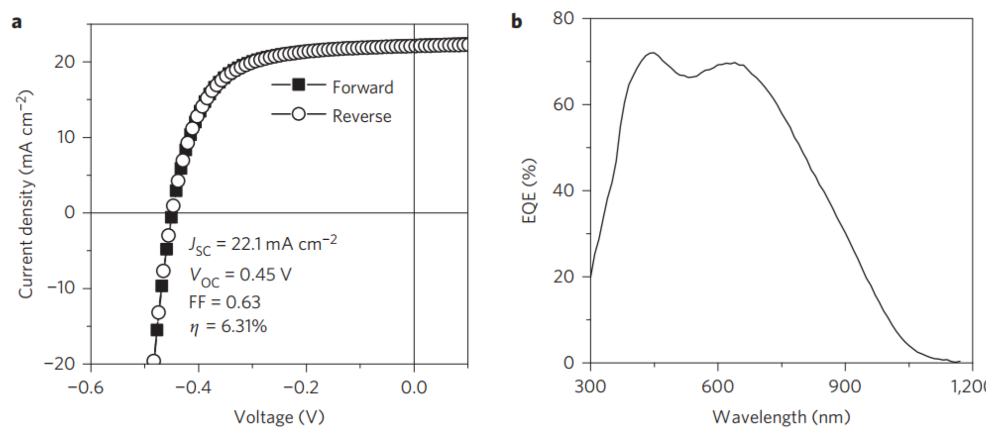
María Bernechea[1†], Nichole Cates Miller[1†], Guillem Xercavins[1], David So[1], Alexandros Stavrinadis[1] and Gerasimos Konstantatos[1,2*]

Solution-processed inorganic solar cells are a promising low- comparable to that of $CuIn_xGa_{(1-x)}Se_2$ (CIGS) (Supplementary

a







Bernechea et.al., Nature Photonics, 10.1038/NPHOTON.2016.108

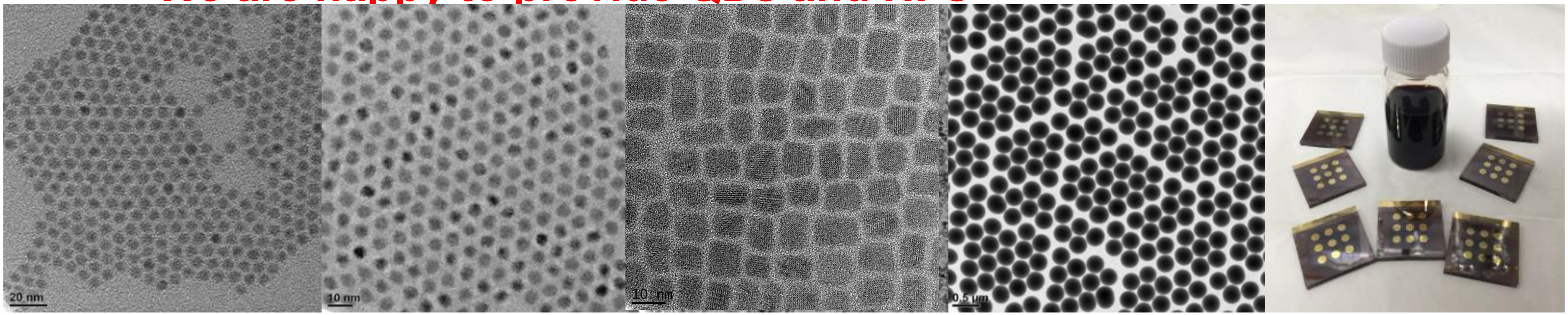
Silver bismuth sulfide ($AgBiS_2$) NP solar cells

Manuscript in preparation

Conclusion

- We can synthesise CQDs here and fabricate device
- Simple and scalable solution-processes for low cost cells
- PbSe QD cell 8.2%, highest reported to date
- PbS QD cell >10%
- Low-toxicity $AgBiS_2$ NP cells ~5%
- **We definitely can fabricate high efficiency CQD devices**

- **We are happy to provide QDs and NPs**



Thank you very much!