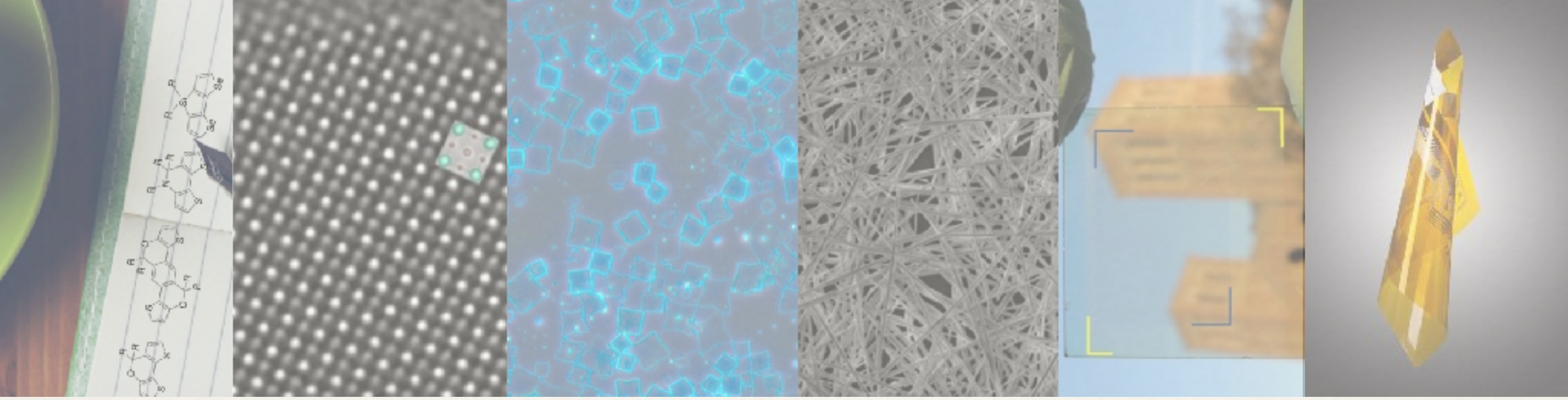

Semiconducting Halide Perovskite Nanomaterials and Heterojunctions

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Brick Nanotechnology Center, April 2018

Next generation Semiconductors

Conventional semiconductors

Si: Czochralski method

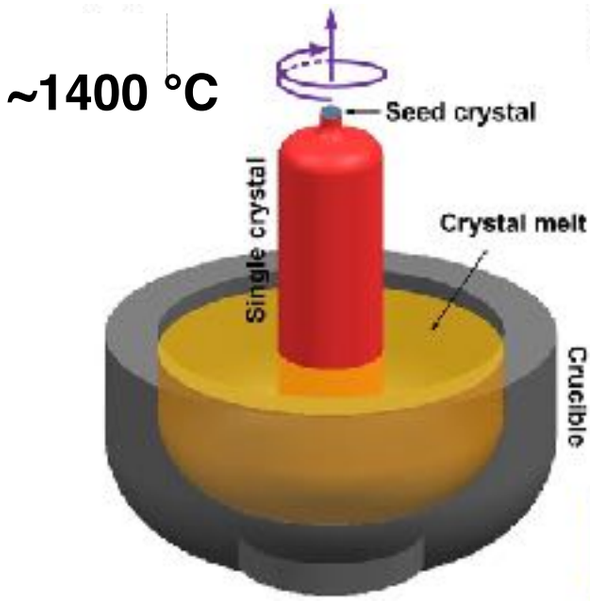
At 1900 °C $SiO_2 + 2\ C \rightarrow Si + 2\ CO$

At 300 °C $Si + 3\ HCl \rightarrow SiHCl_3\ (g) + H_2$

After purification: 99.9999999%

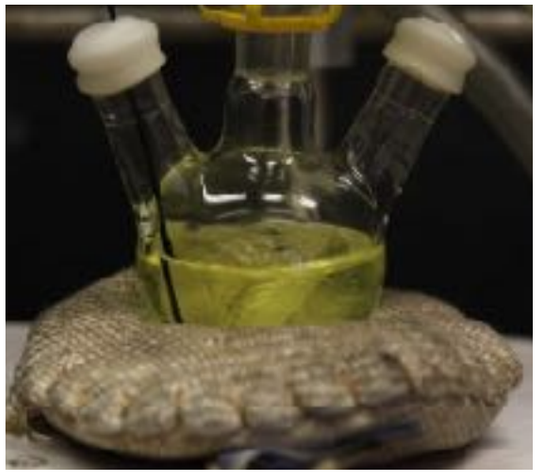
At 1100 °C $SiHCl_3 + H_2 \rightarrow Si + 3\ HCl$

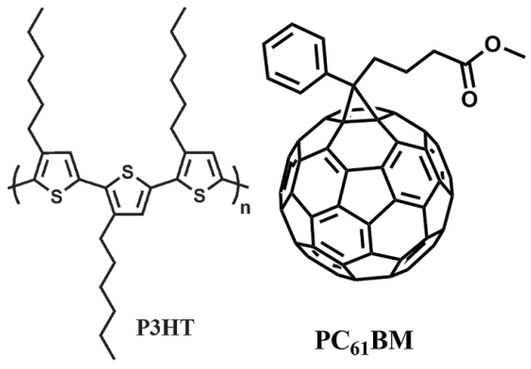
Electronic grade silicon: 99.9999999%

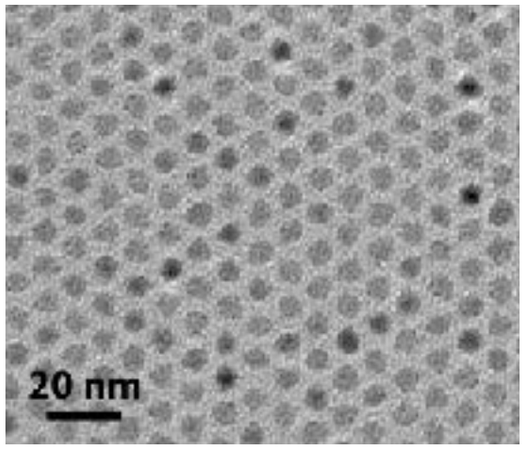


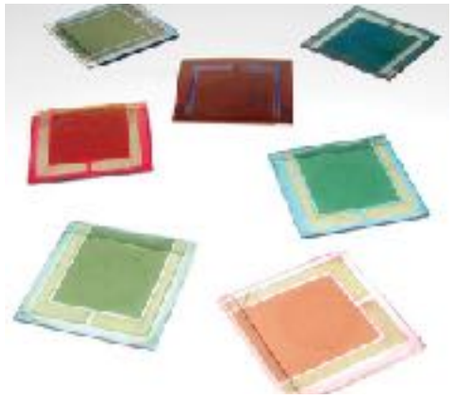
III-V (GaAs):
Metal Organic Chemical Vapor Deposition or
Molecular Beam Epitaxy

Solution-processed semiconductors

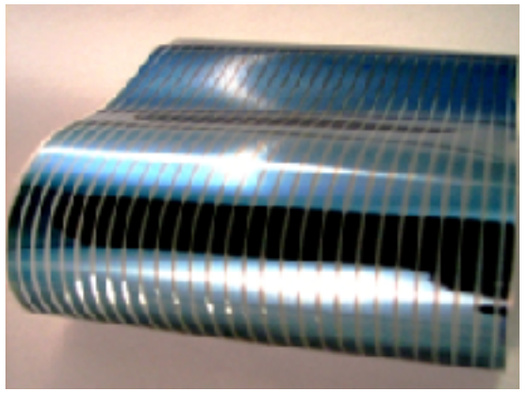




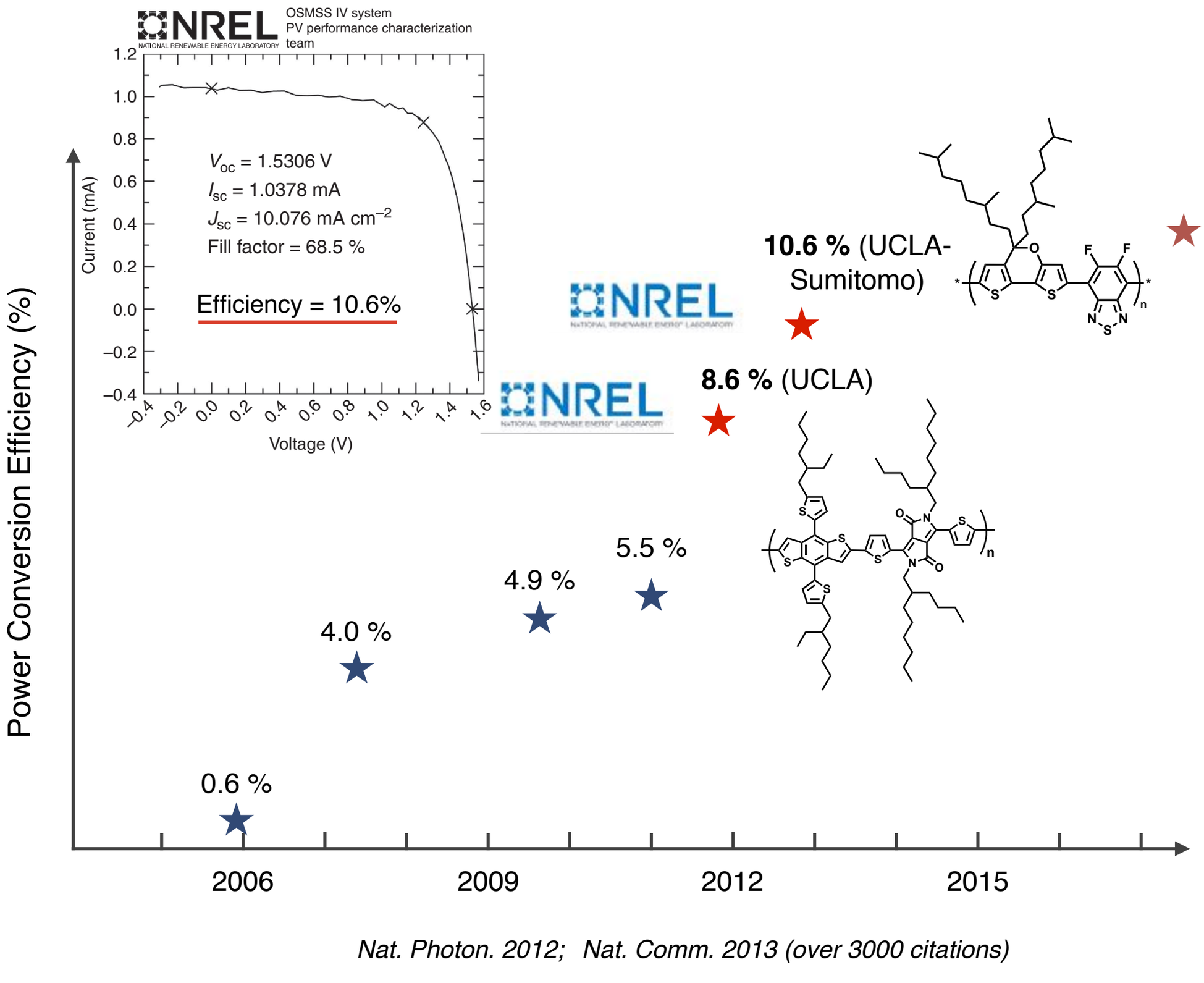




Credit: Solarmer Inc.

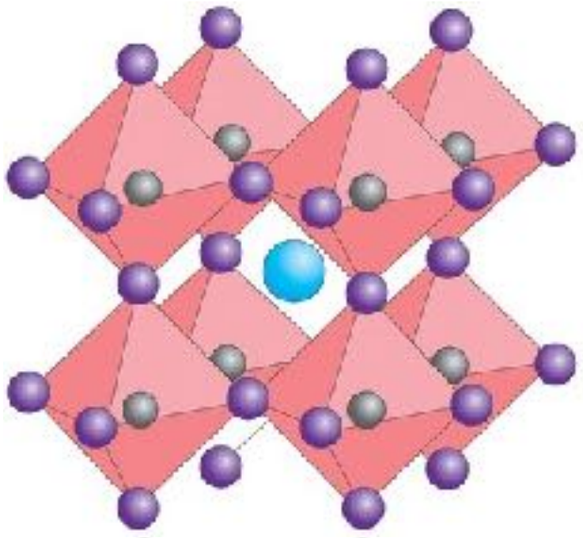


Organic solar cells



Nat. Photon. 2012; Nat. Comm. 2013 (over 3000 citations)

Halide perovskite — $(CH_3NH_3)PbI_3$



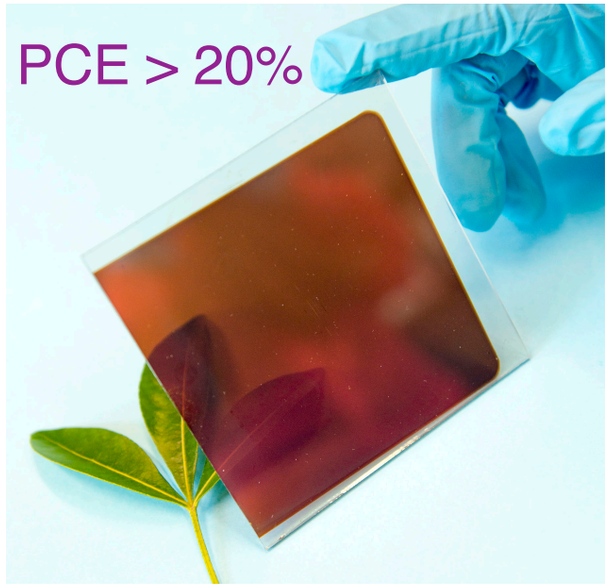
A : Cs^+, $R\text{-}NH_3^+$…
B : Pb^{2+}, Sn^{2+}, Ge^{2+}…
X : Cl^-, Br^-, I^-…

Long carrier diffusion length

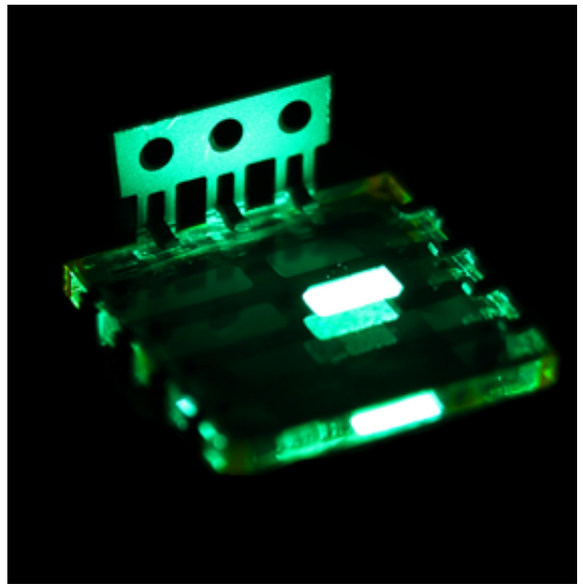
High absorption coefficient

High PL quantum efficiency

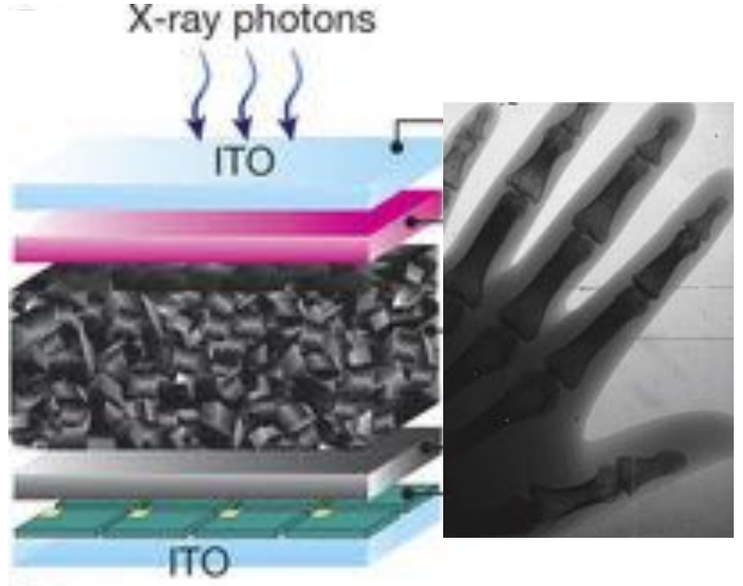
Defect tolerant



Miyasaka, JACS, 2009, 131, 6050
Snaith, Science, 2012, 338, 643
Yang, Science, 2014, 345, 542
Seok, Nature, 2015, 517, 476

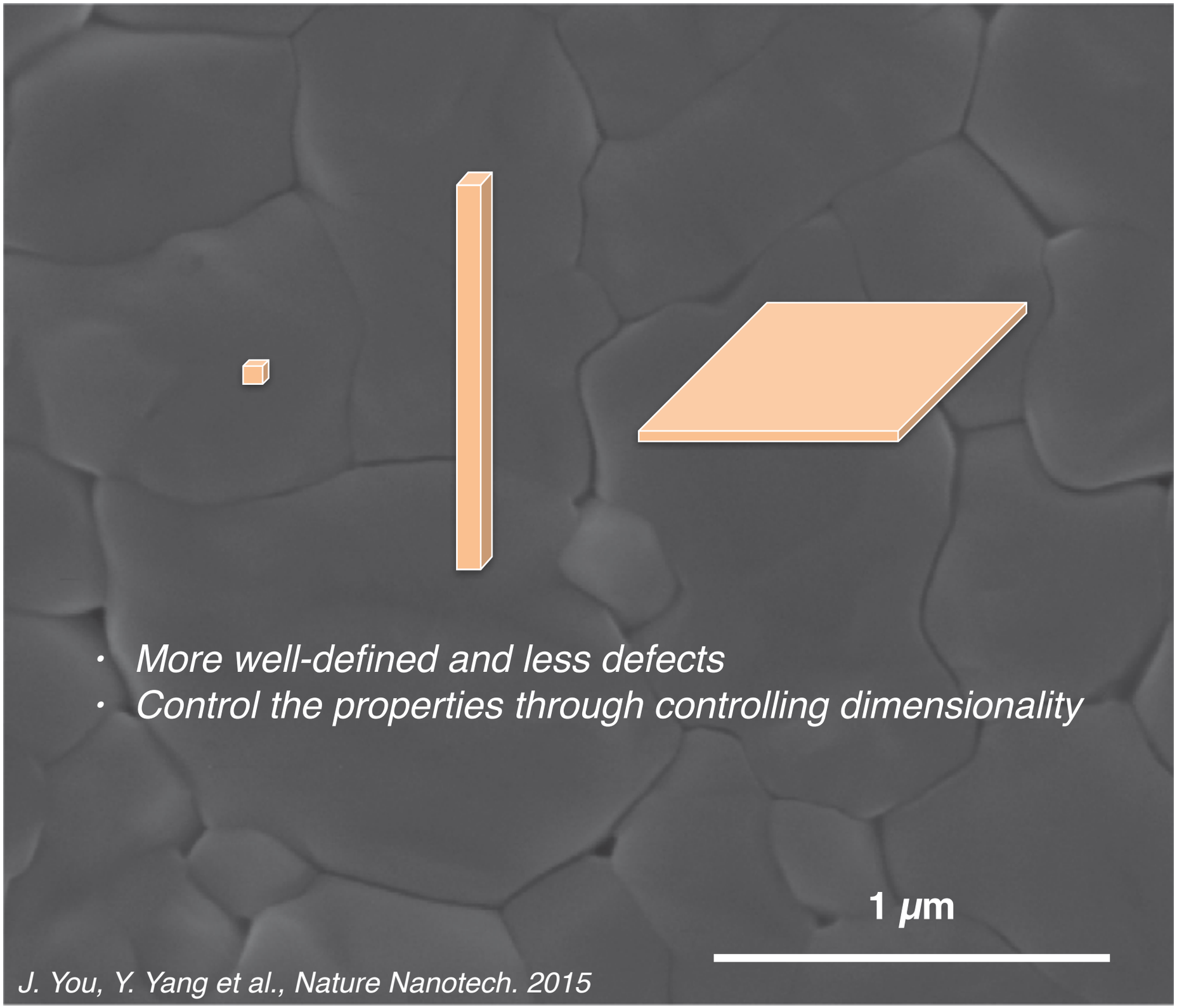


Friend, *Nature Nanotechnology, 2014, 9, 687*
Sargent, Nature Nanotechnology, 2016, 11, 872

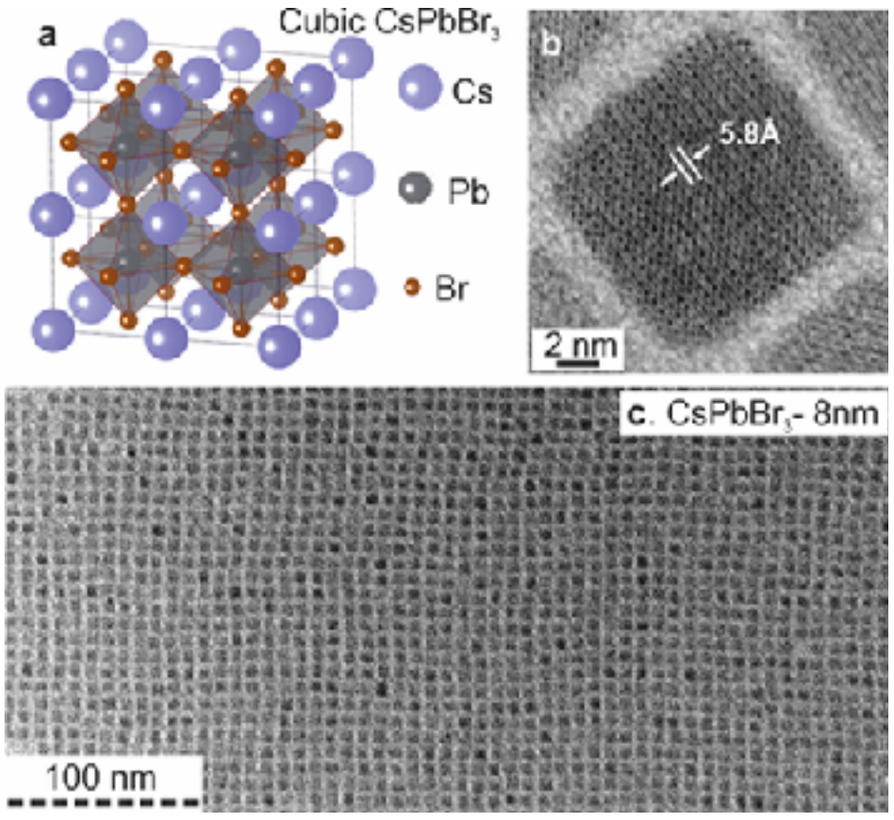


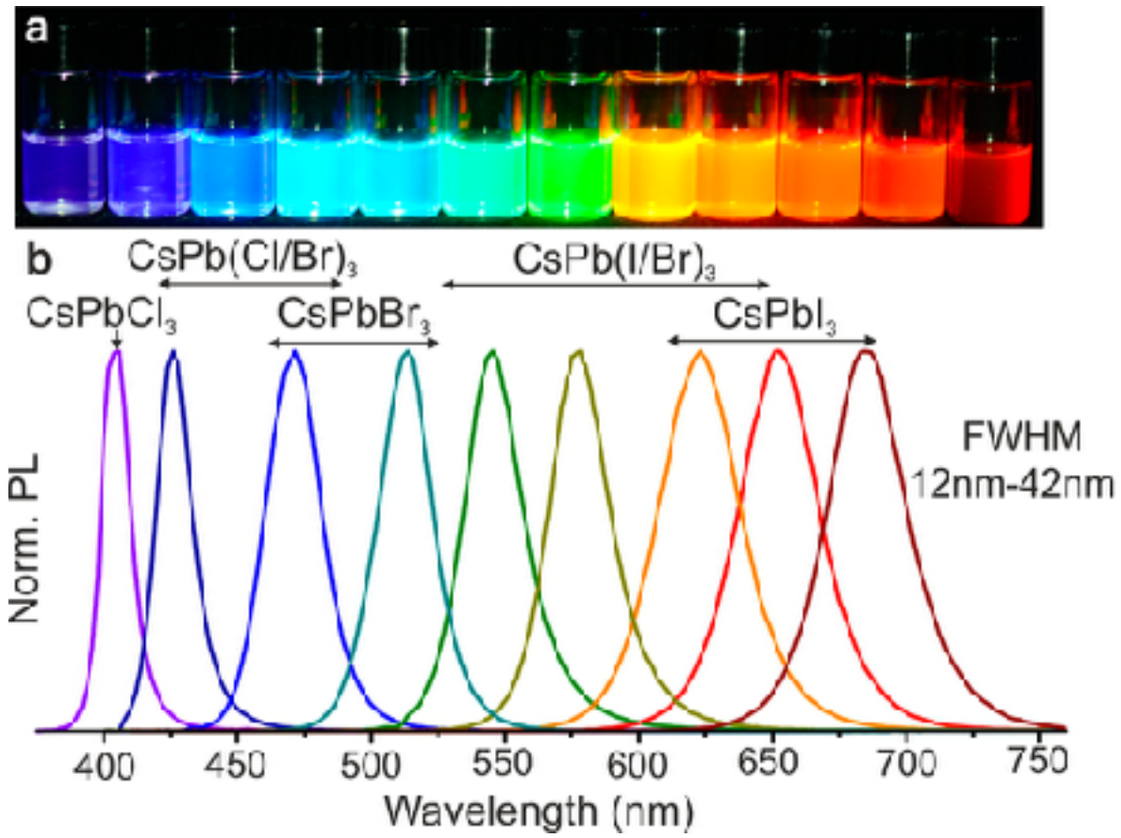
Huang, Nature Photonics, 2016, 9, 679
Park, Nature 2017, 550, 87

Halide perovskite — $(CH_3NH_3)PbI_3$



Halide perovskite nano structures



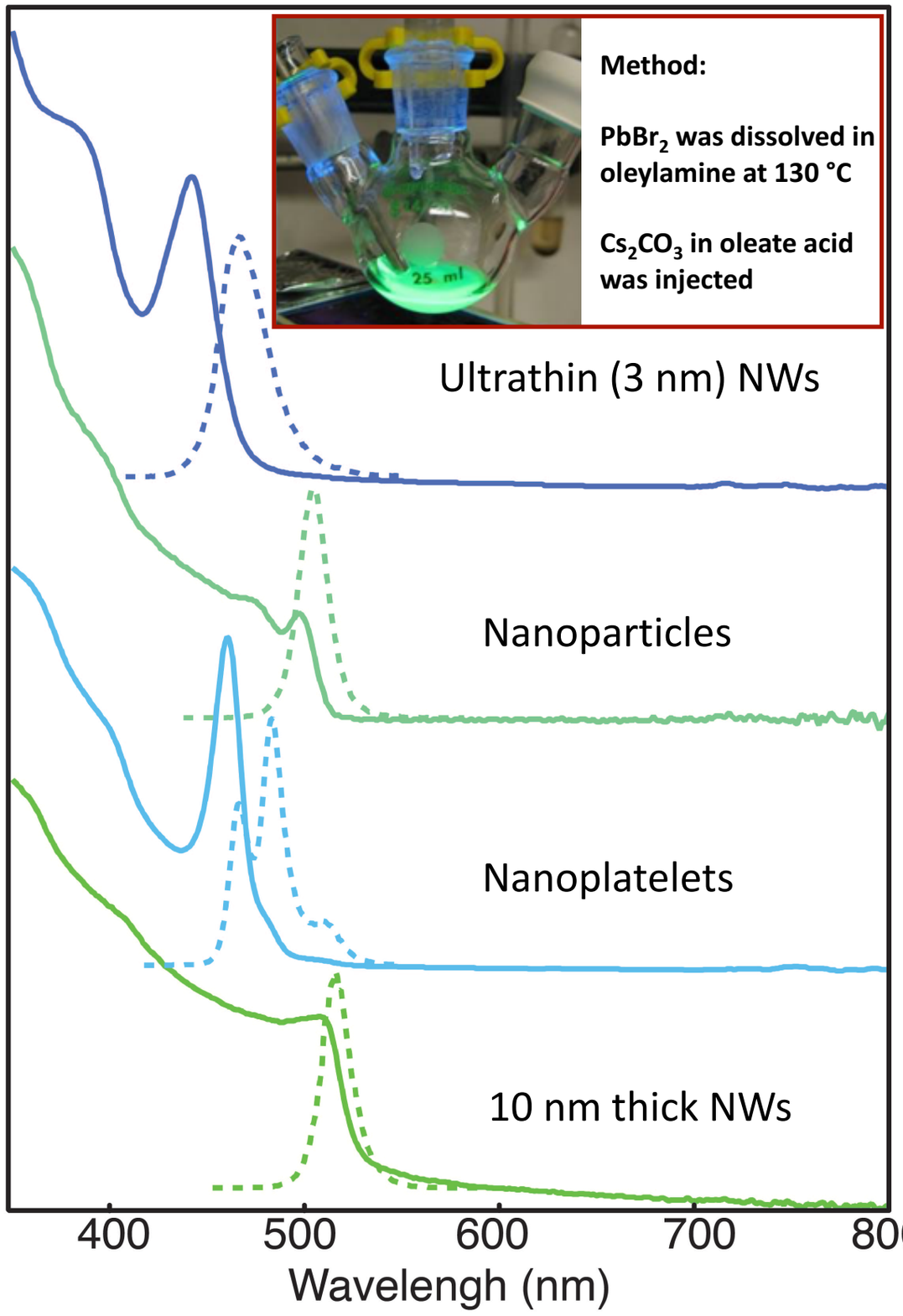


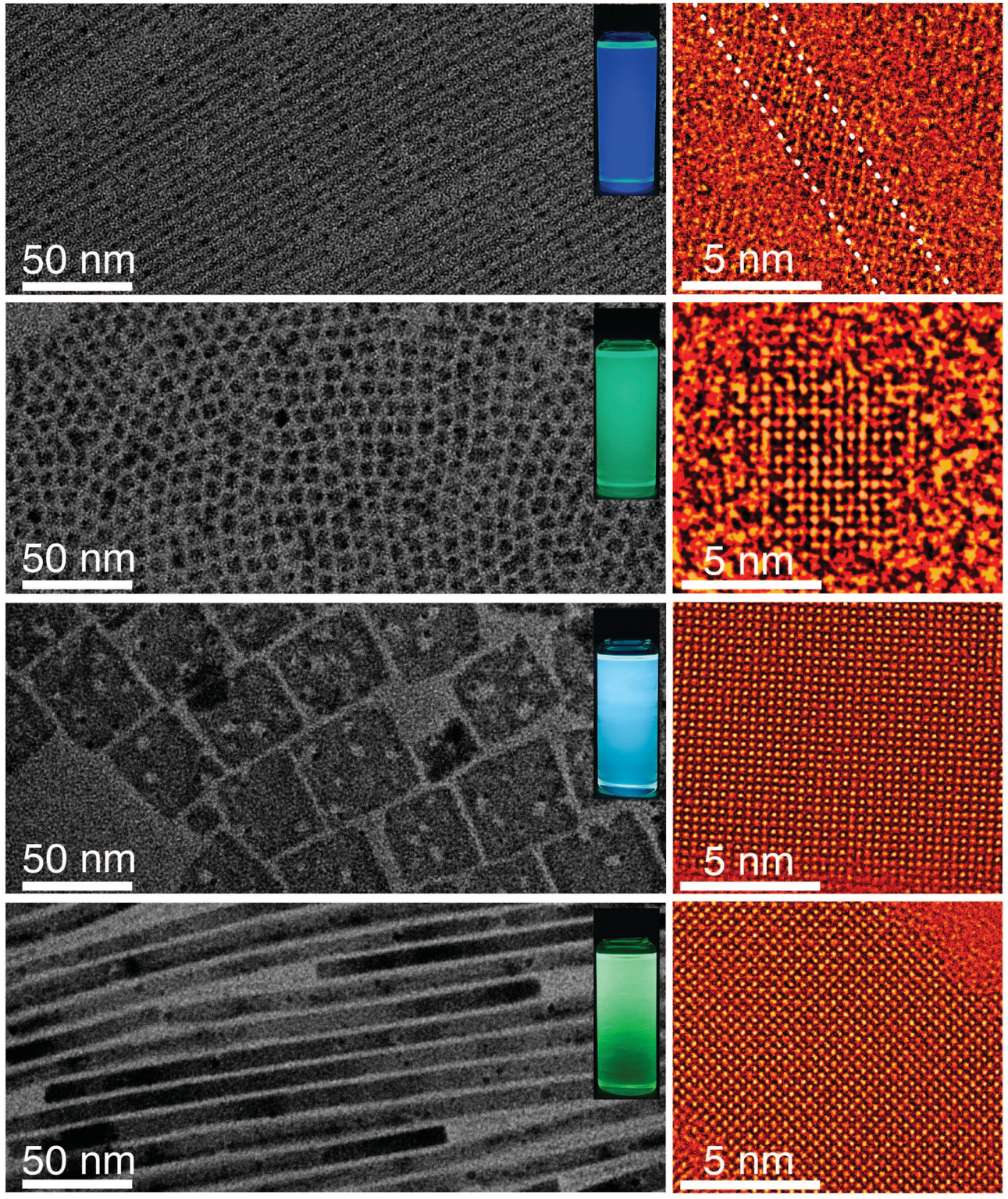
M. Kovalenko et al., Nano Lett. 2015, 15, 3692

Nonconventional Synthesis

New Nanoscale Morphology (1D,2D)

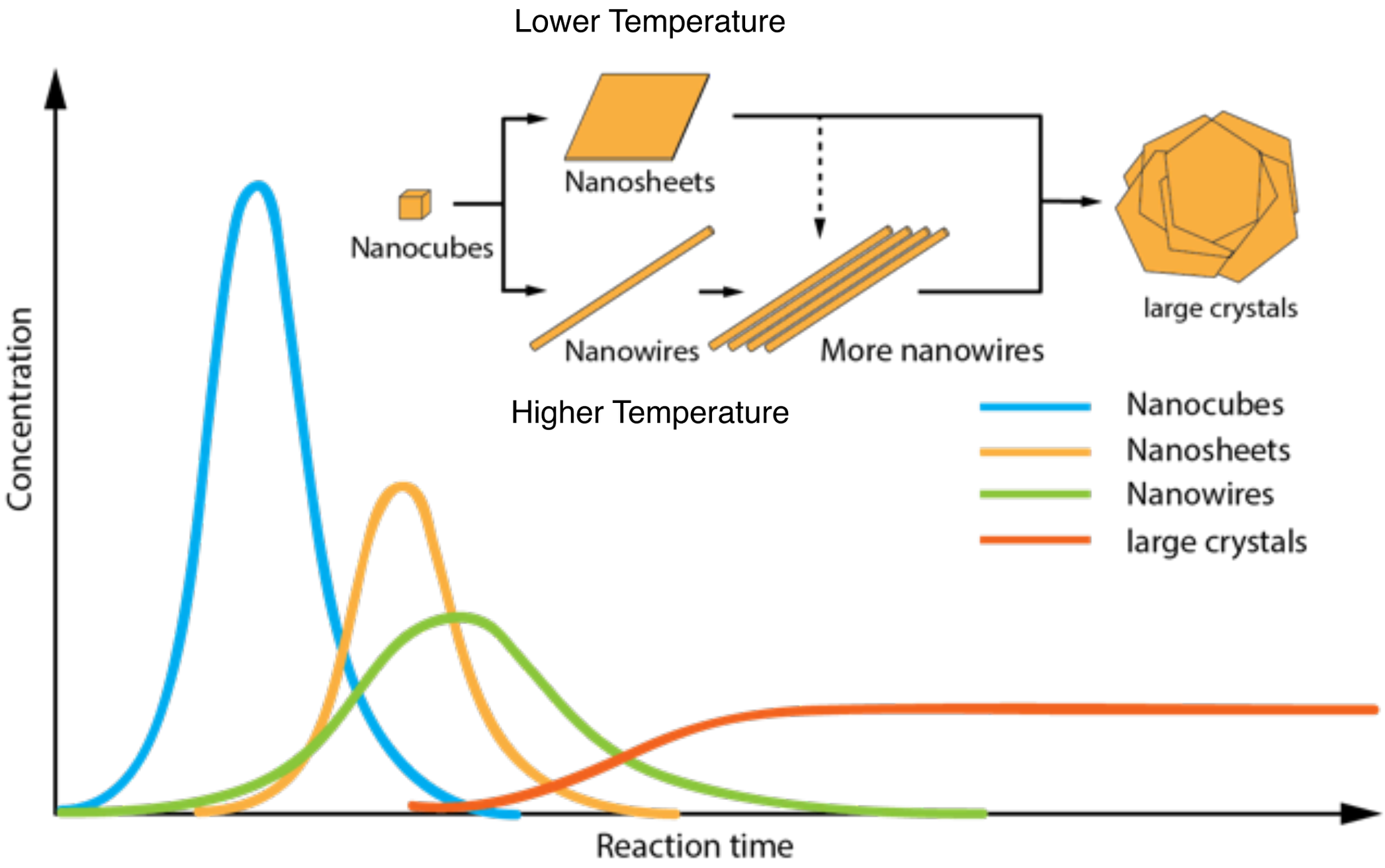
$CsPbBr_3$ Nanowire growth



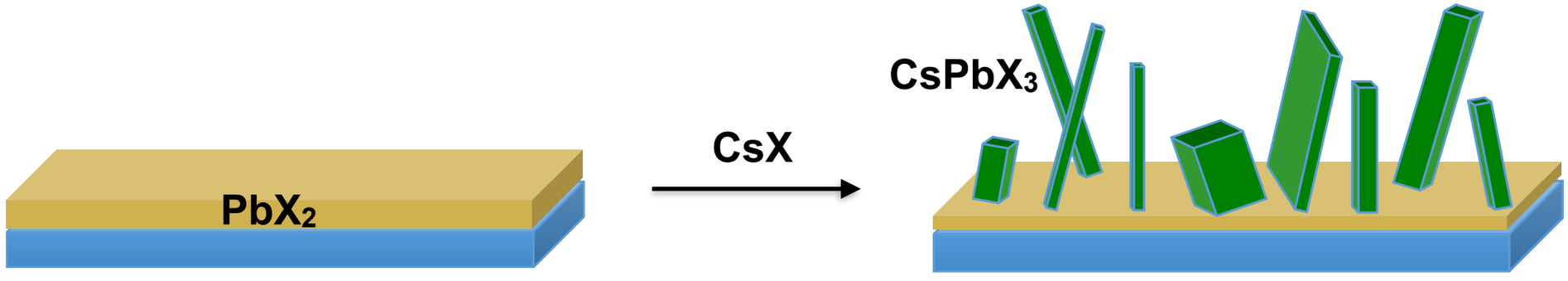


D. Zhang et al. JACS 2016 138, 13155

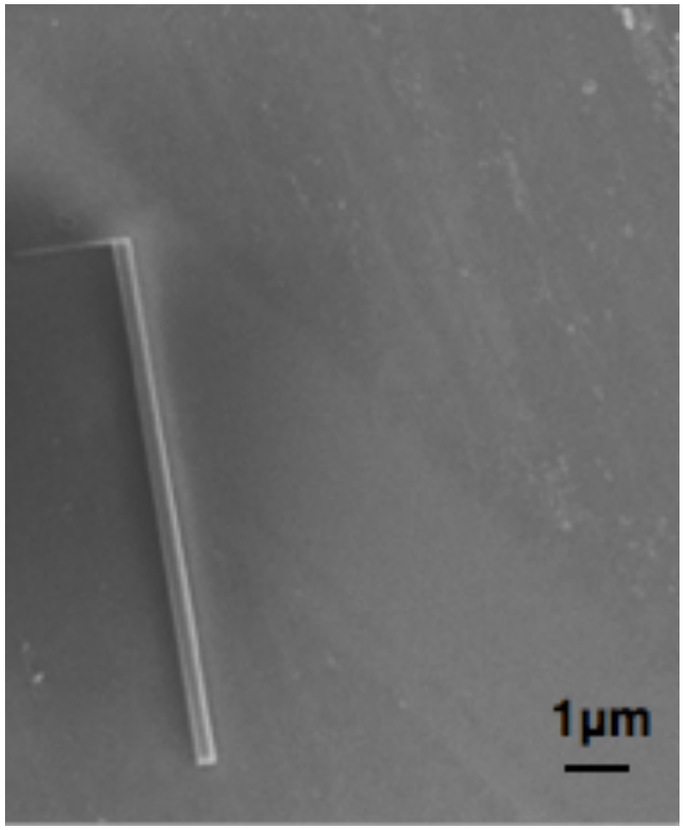
Nanowire growth

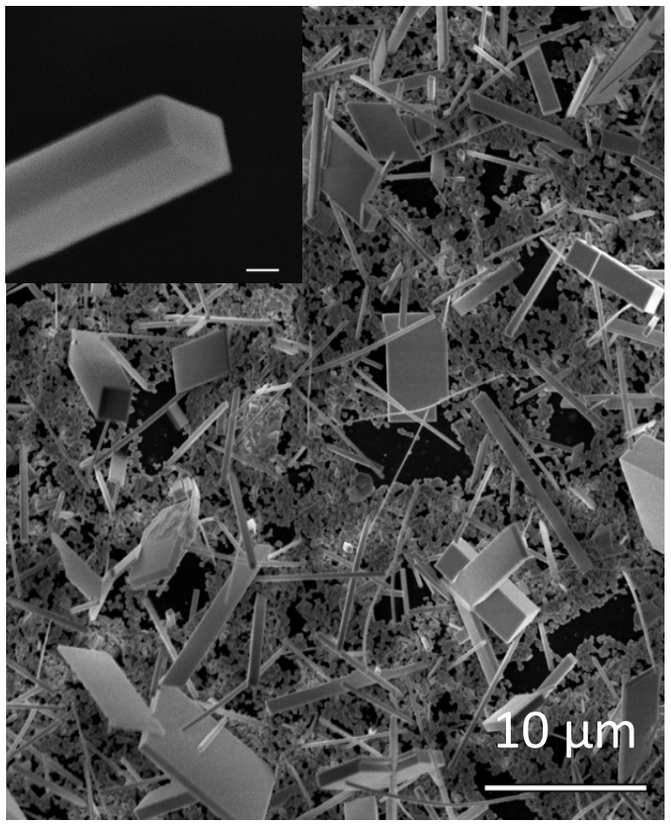


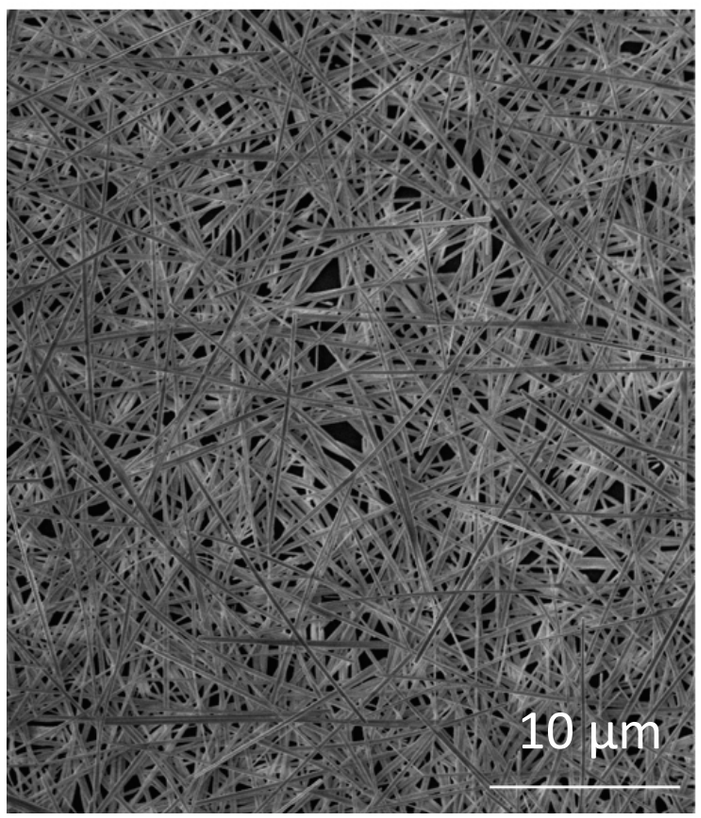
Nanowire growth



$CsPbCl_3$ $CsPbBr_3$ $CsPbI_3$

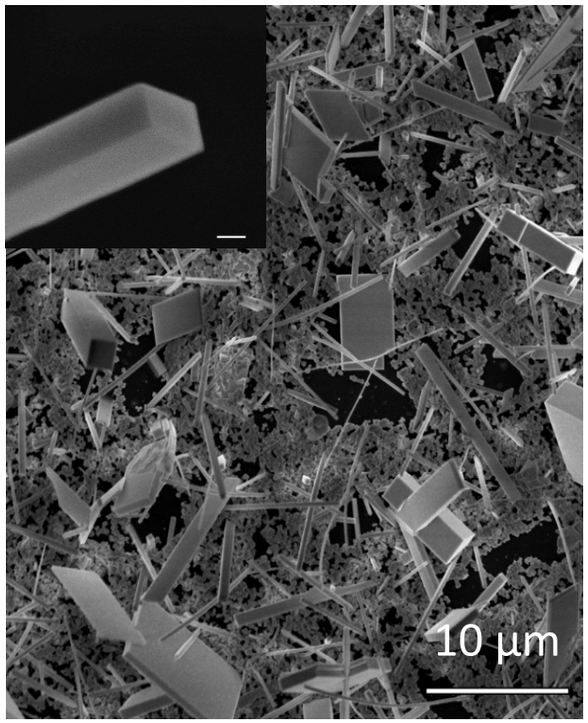


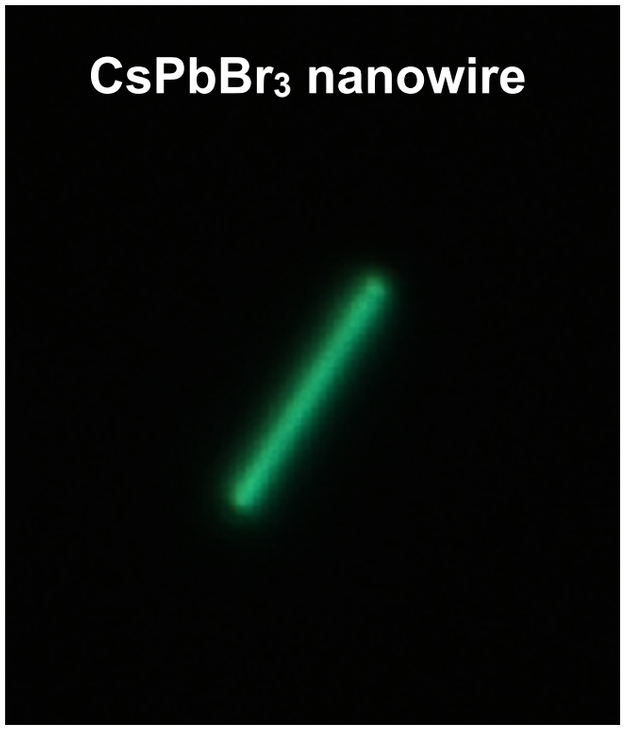


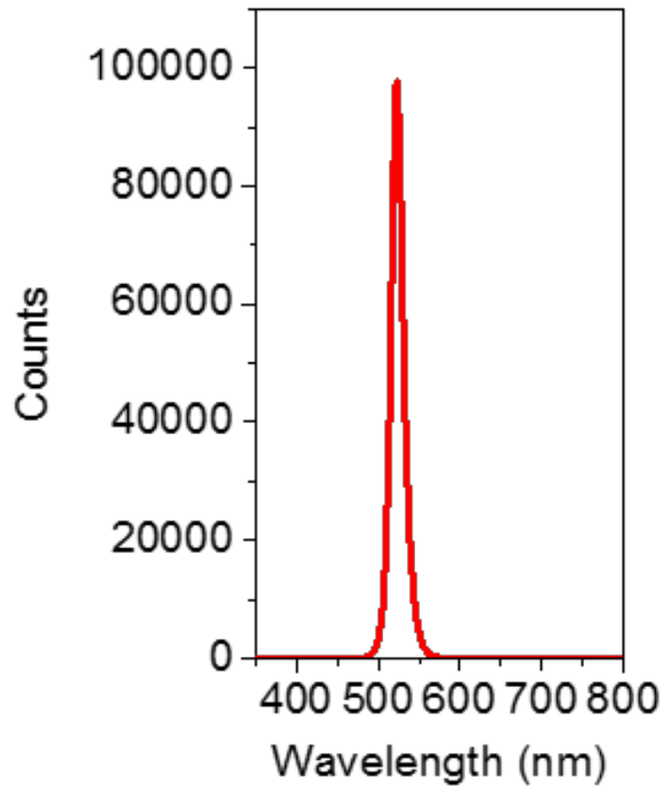


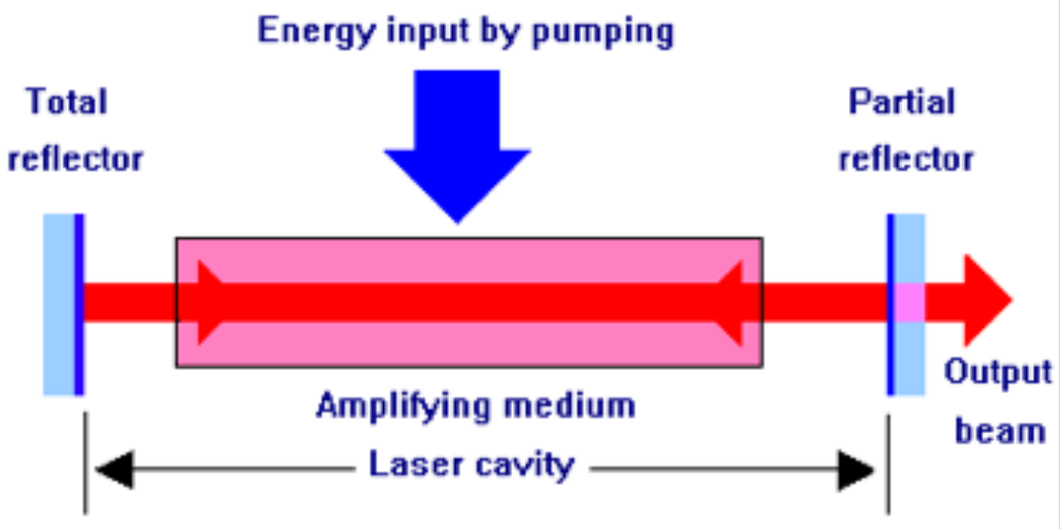
S. Eaton, S. Leone, P. Yang et al. Proc. Natl. Acad. Sci. 2016, 113, 1993

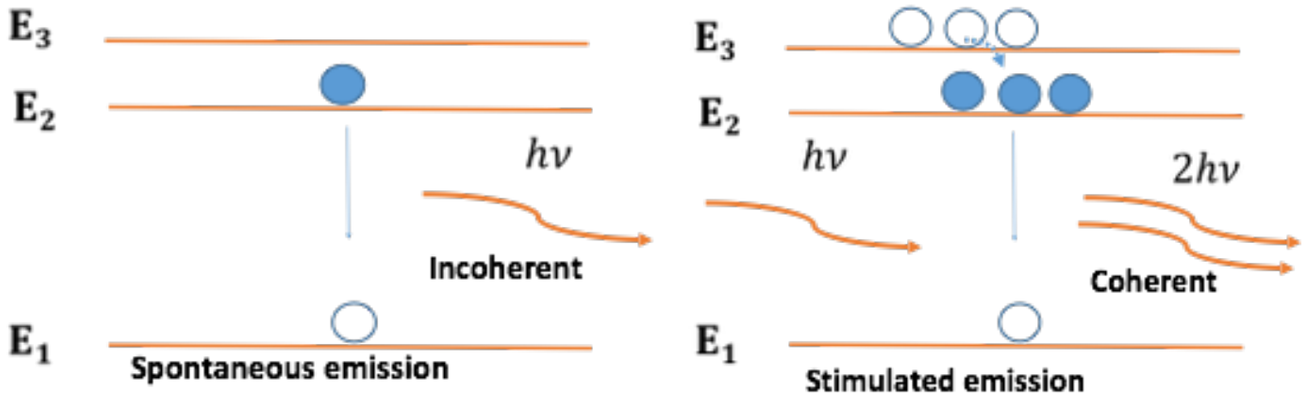
Optical Property



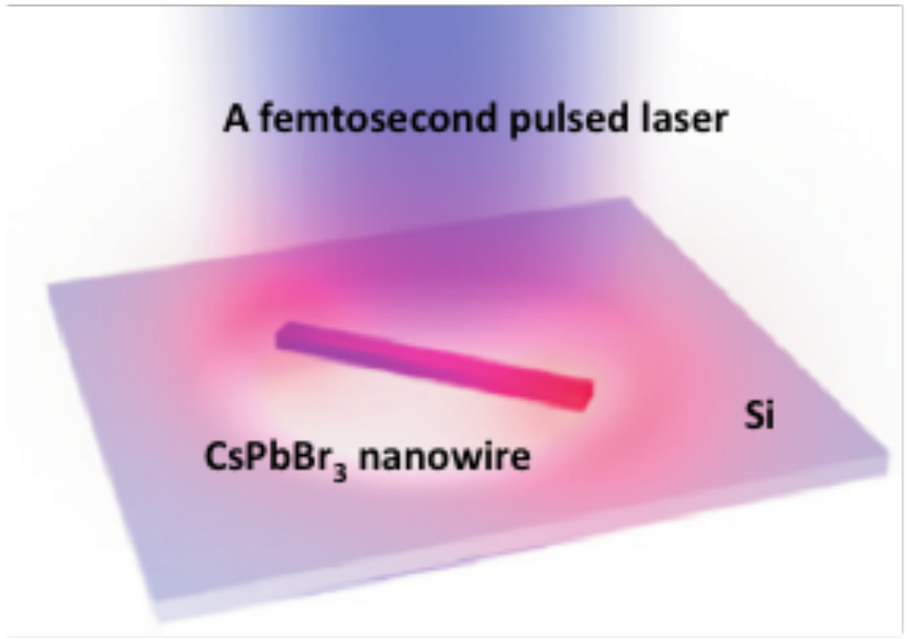


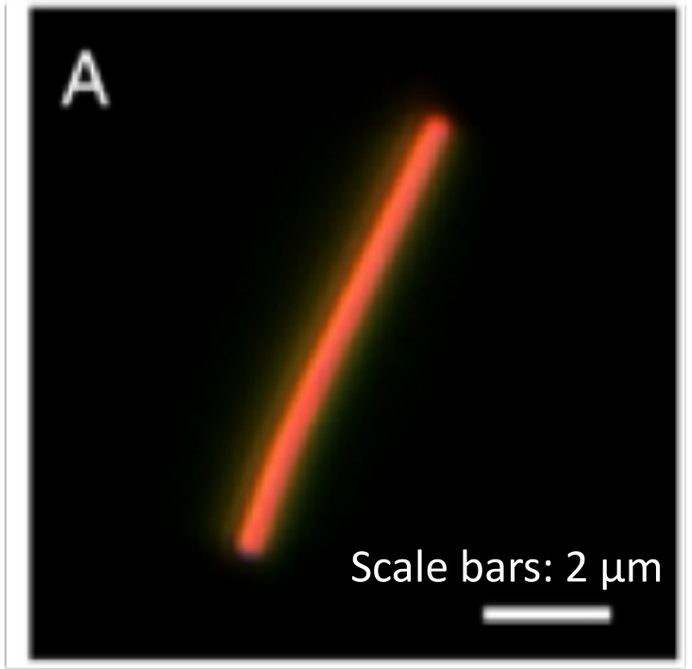


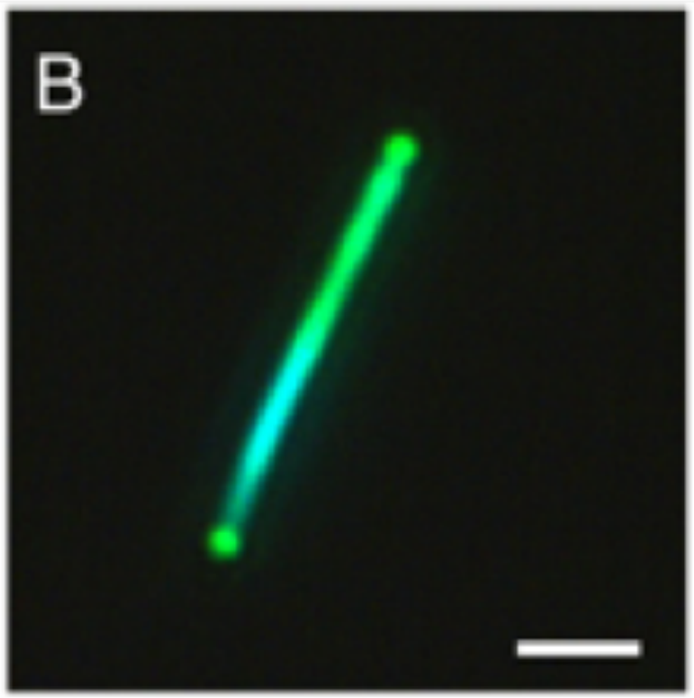


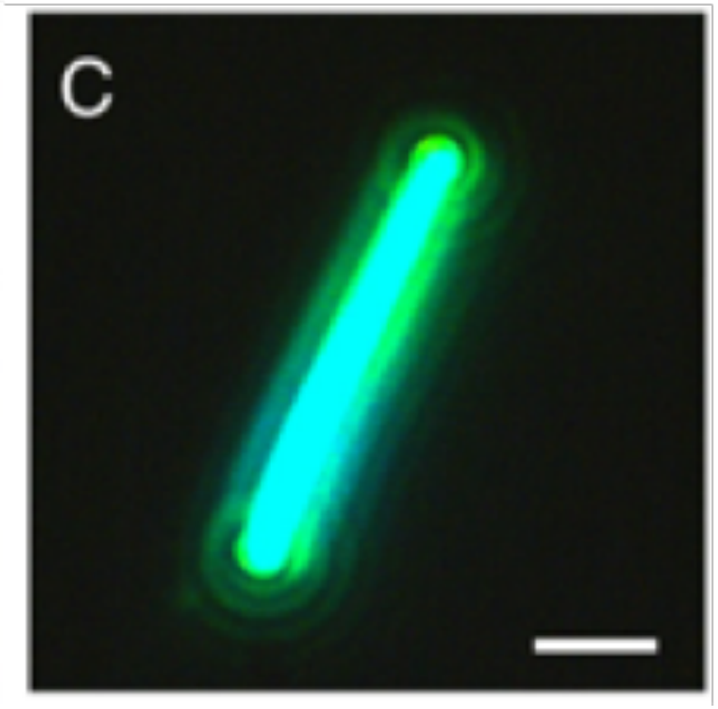


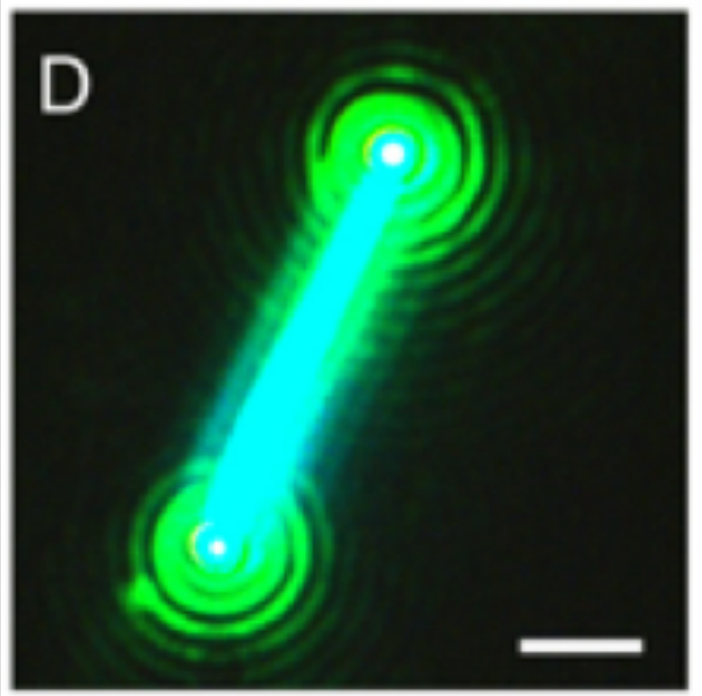
Optically driven $CsPbBr_3$ NW laser









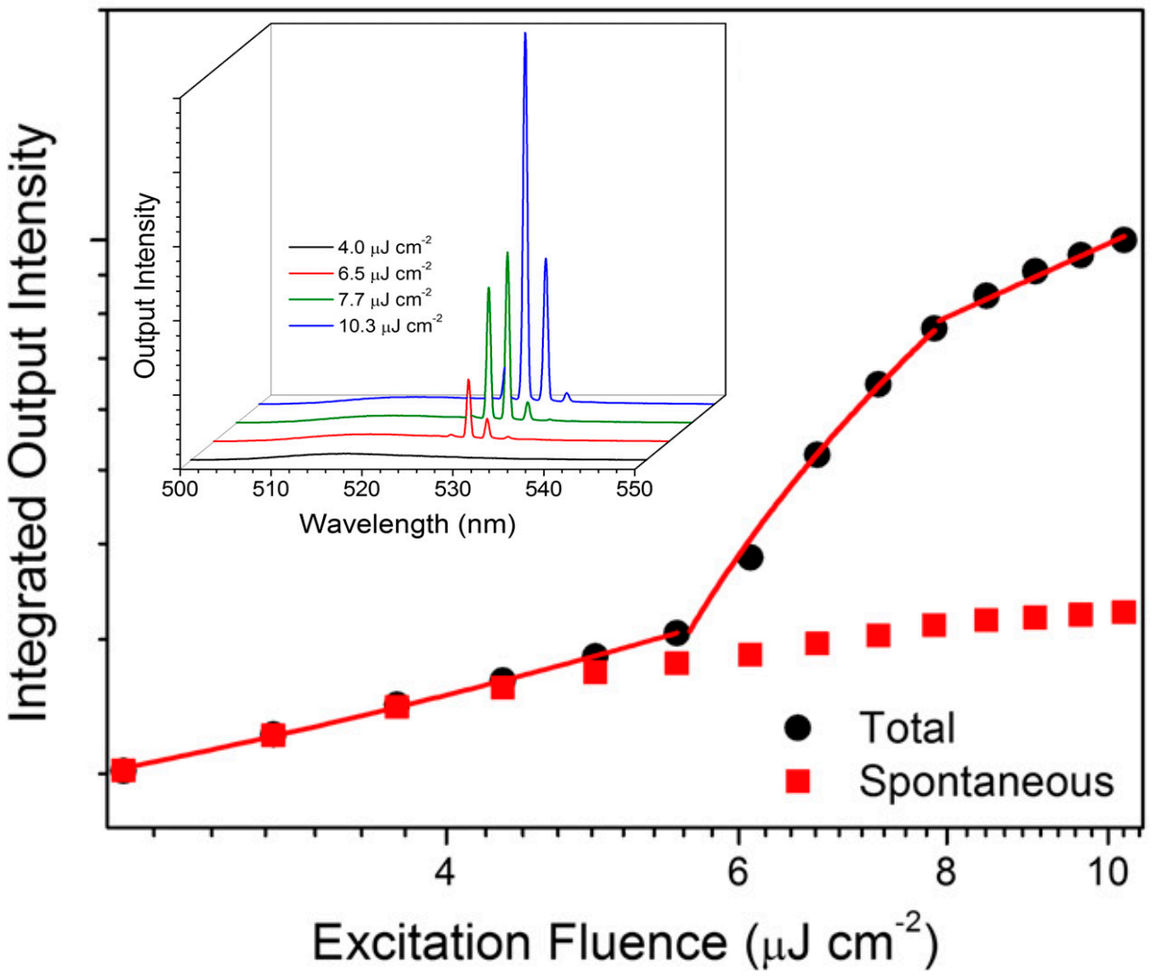


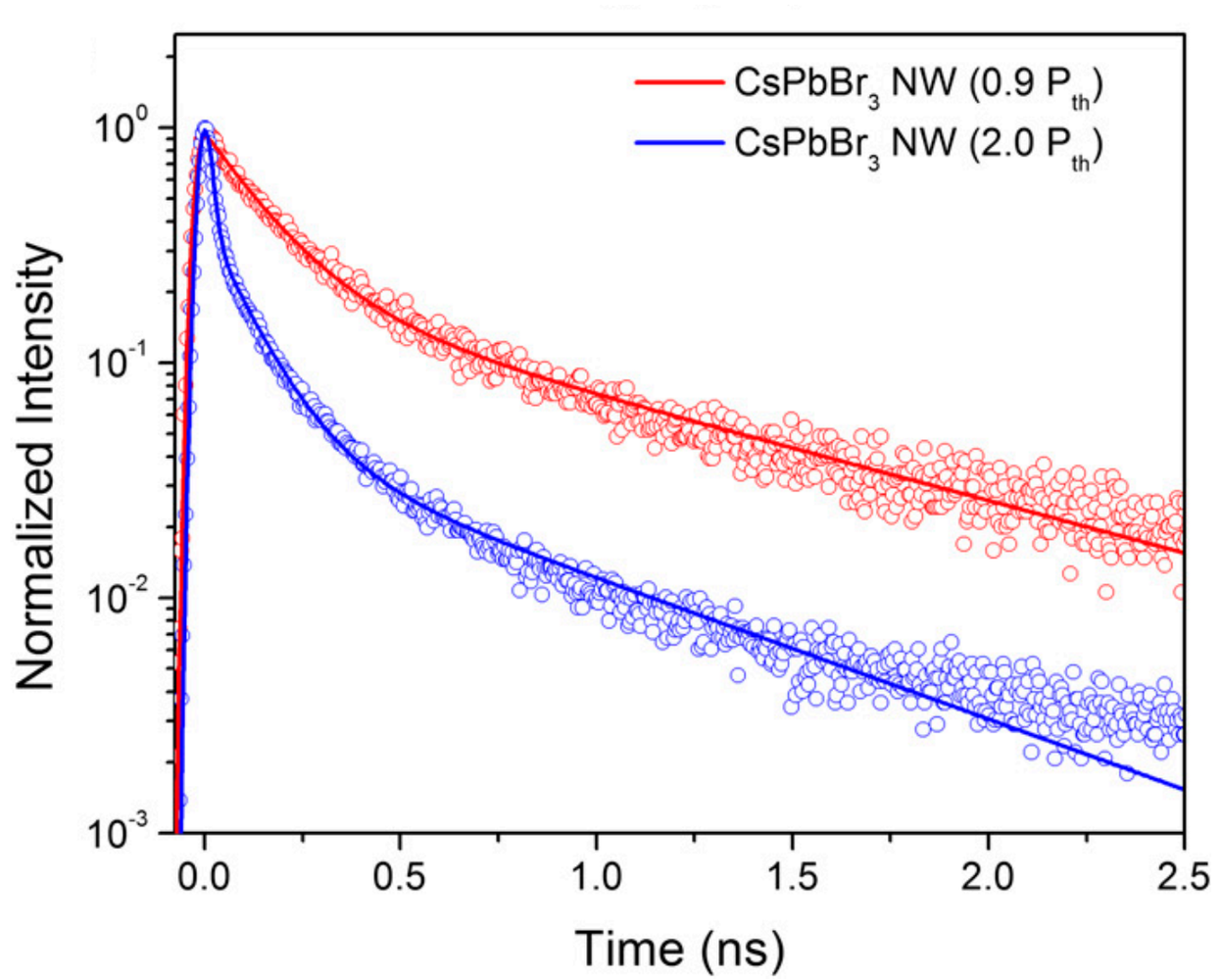
In collaboration with Steve Leone

Optically driven $CsPbBr_3$ NW laser

- Low threshold ~ 5μJ cm^{-2}
- Multi-mode emissions

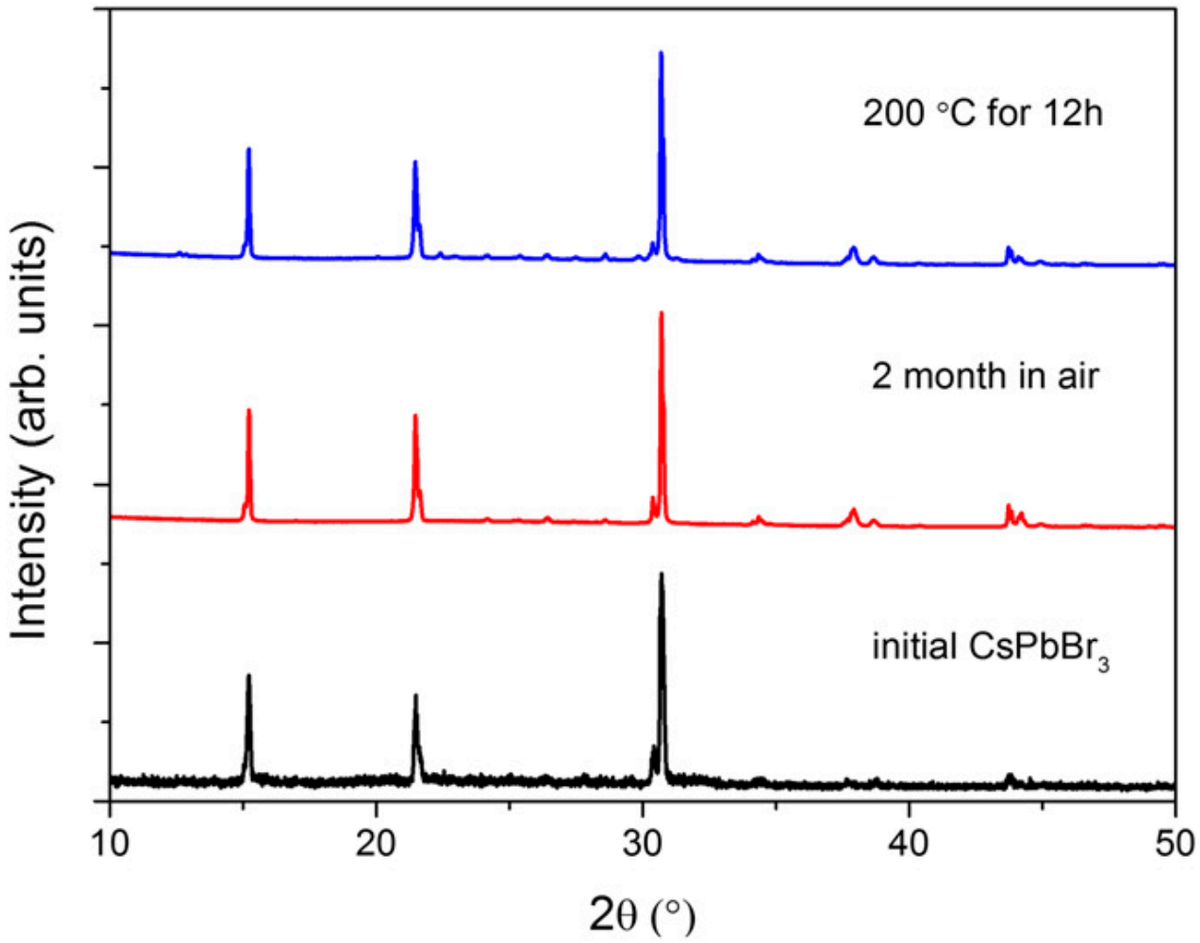
- Carrier lifetime shortened under lasing condition

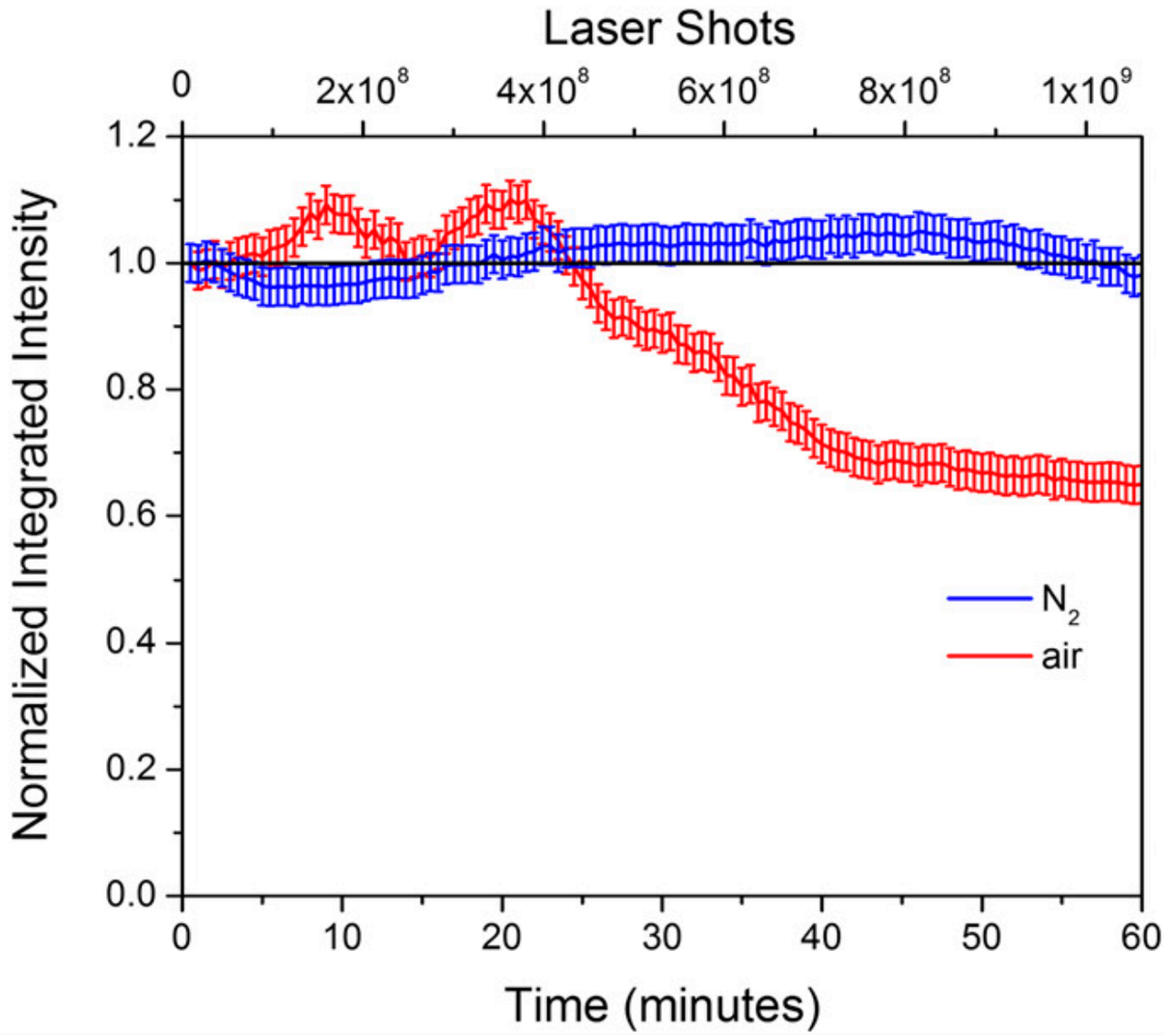




S. Eaton, S. Leone, P. Yang et al. Proc. Natl. Acad. Sci. 2016, 113, 1993

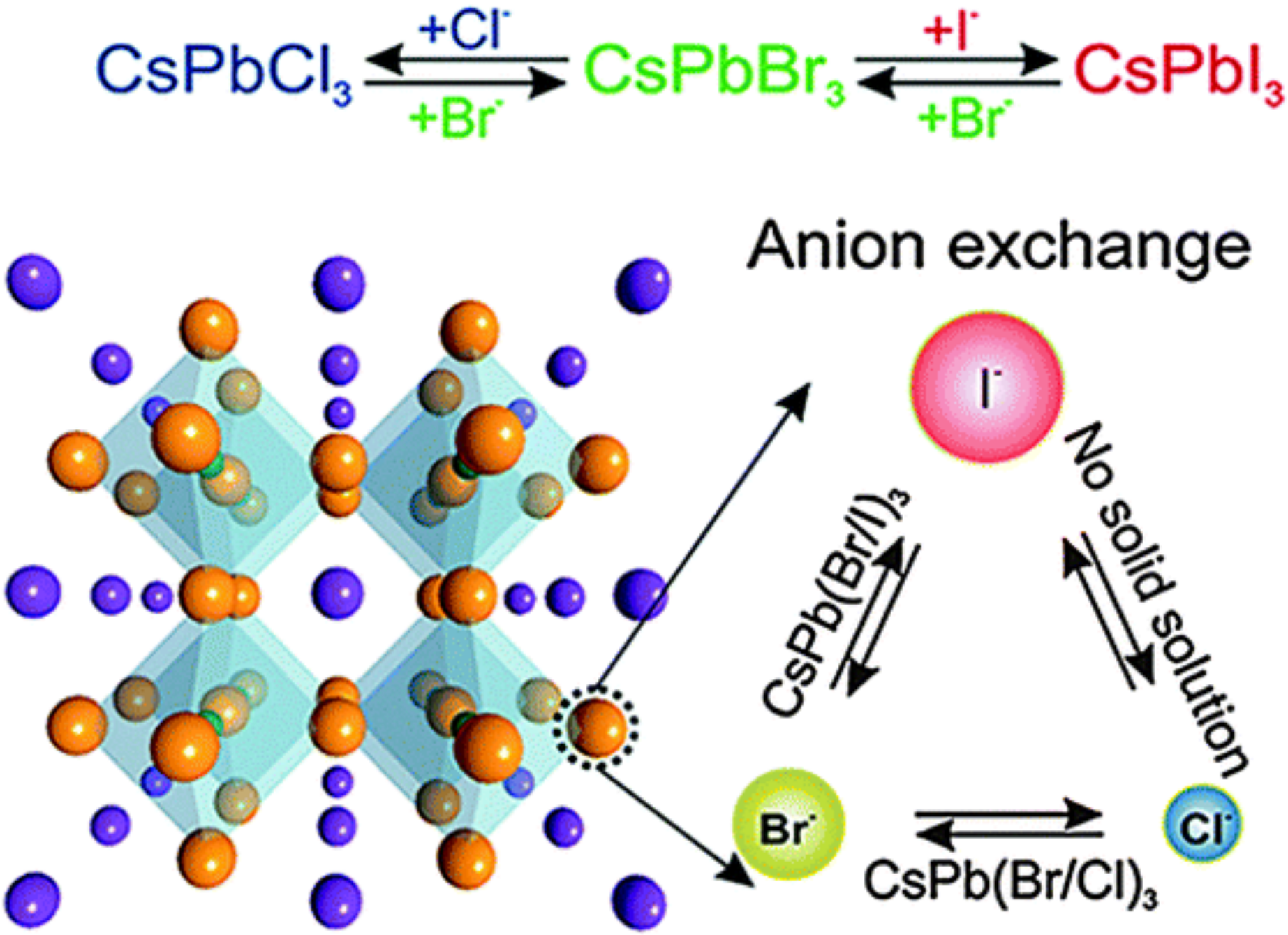
$CsPbBr_3$ NW laser stability





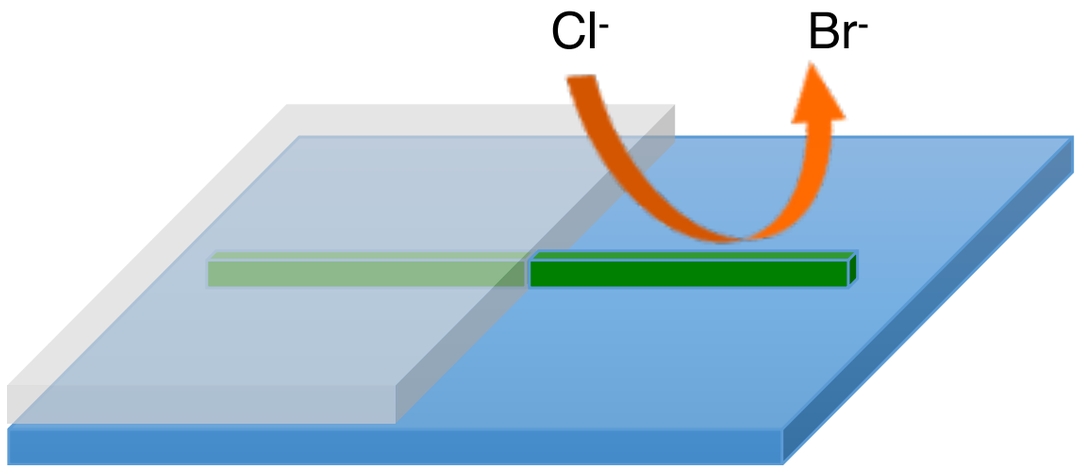
S. Eaton, S. Leone, P. Yang et al. Proc. Natl. Acad. Sci. 2016, 113, 1993

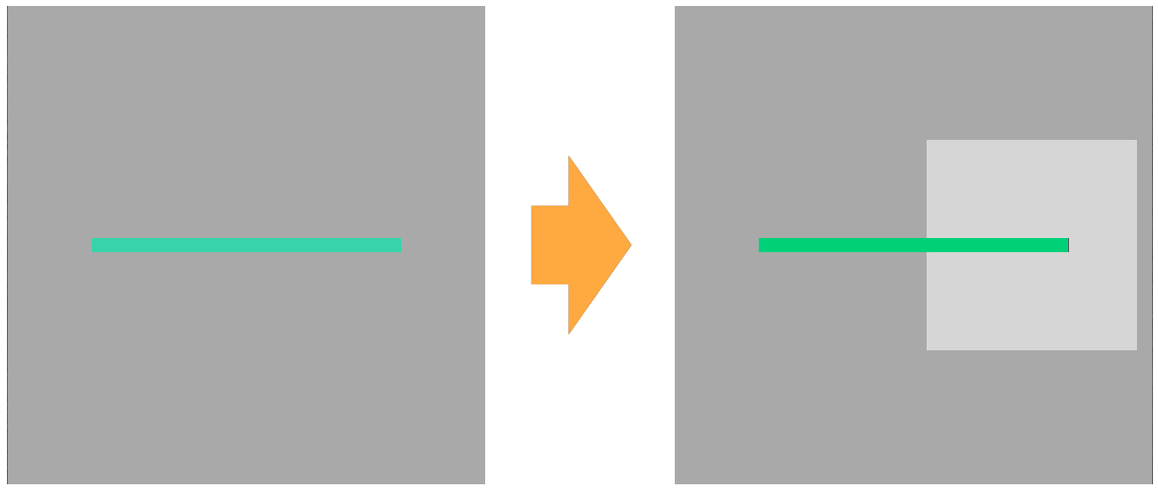
Composition Tuning via Anion Exchange



F. Gao et al. J. Mater. Chem. C, 2016, 4, 3898

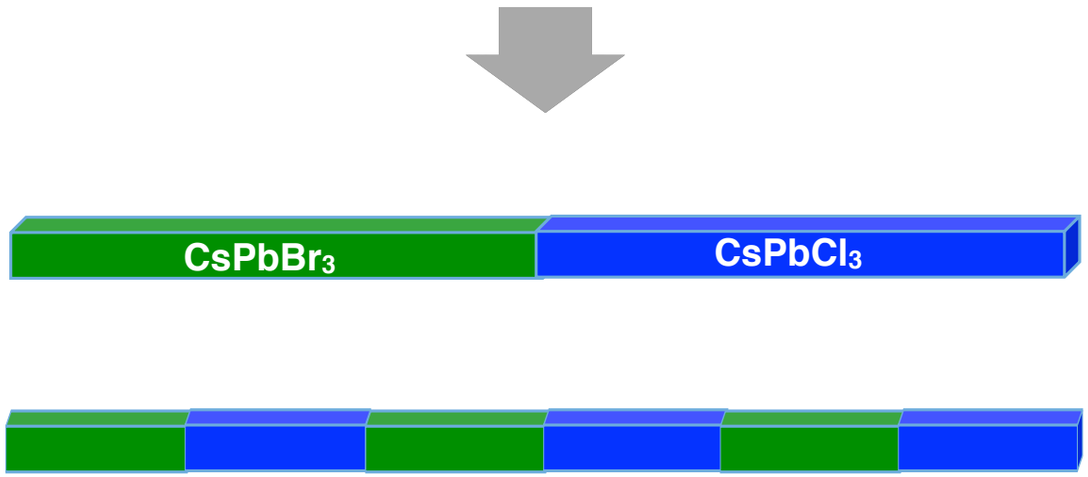
Localized anion exchange

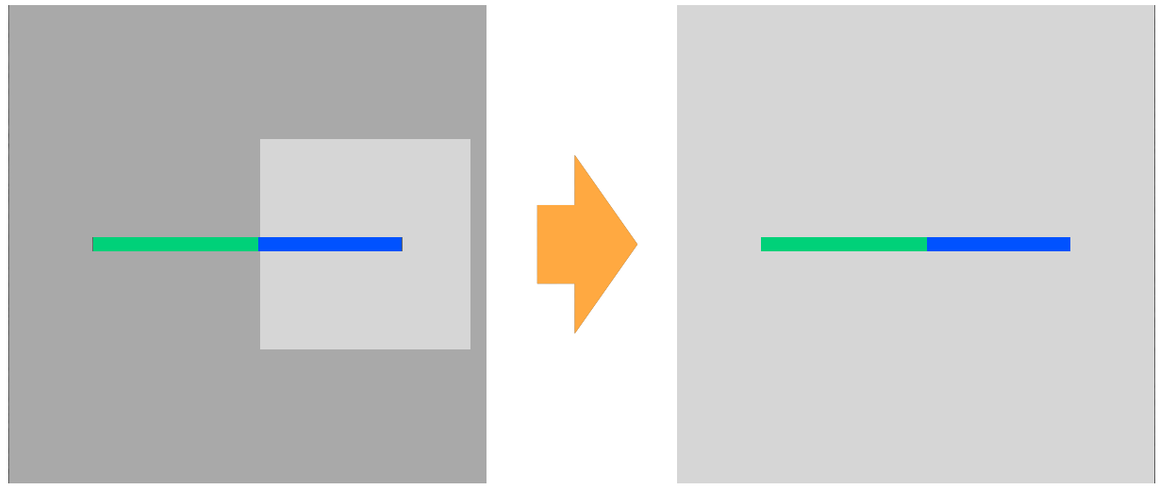




Single nanowire coated with PMMA

e-beam lithography to create an opening

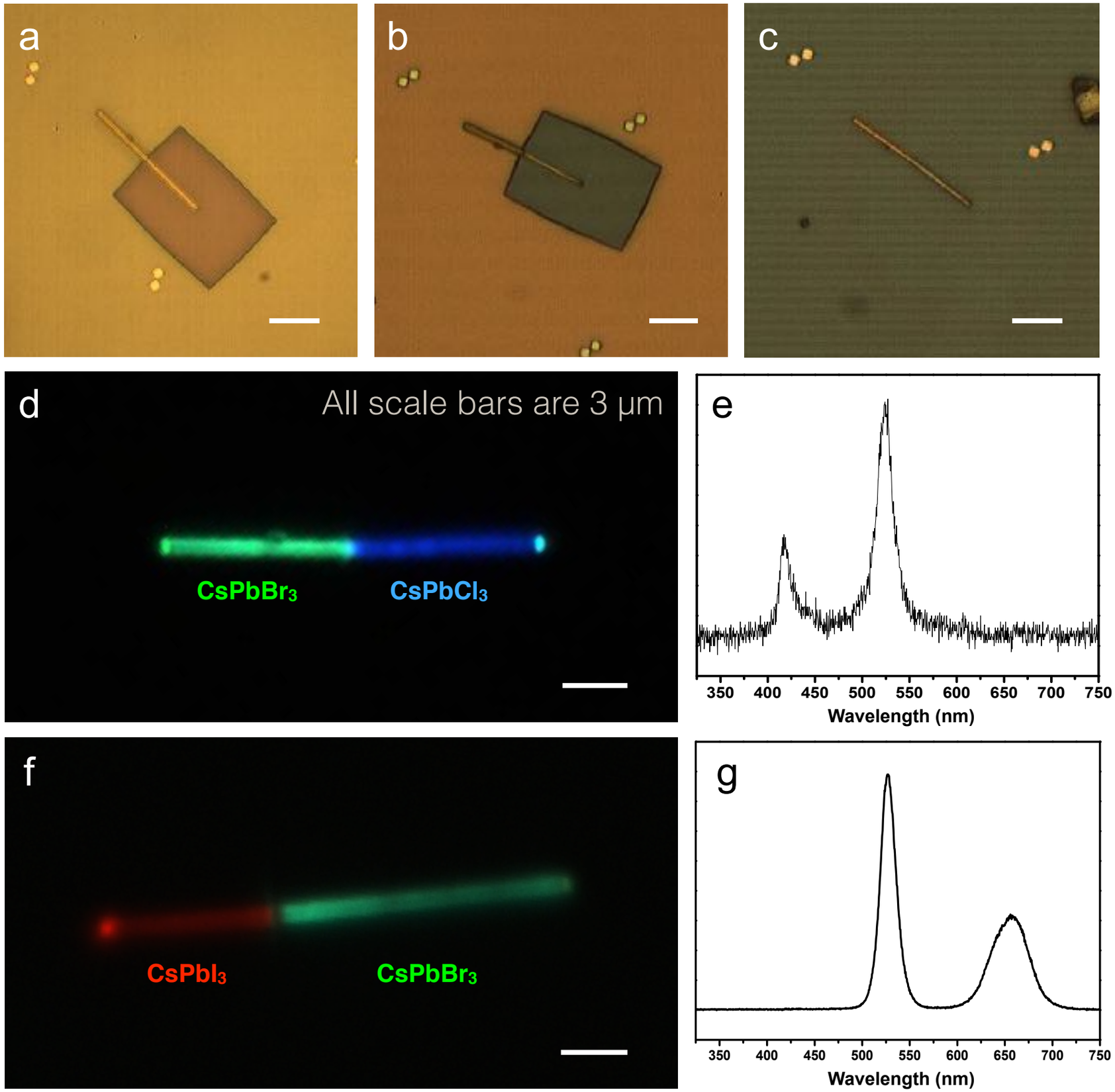




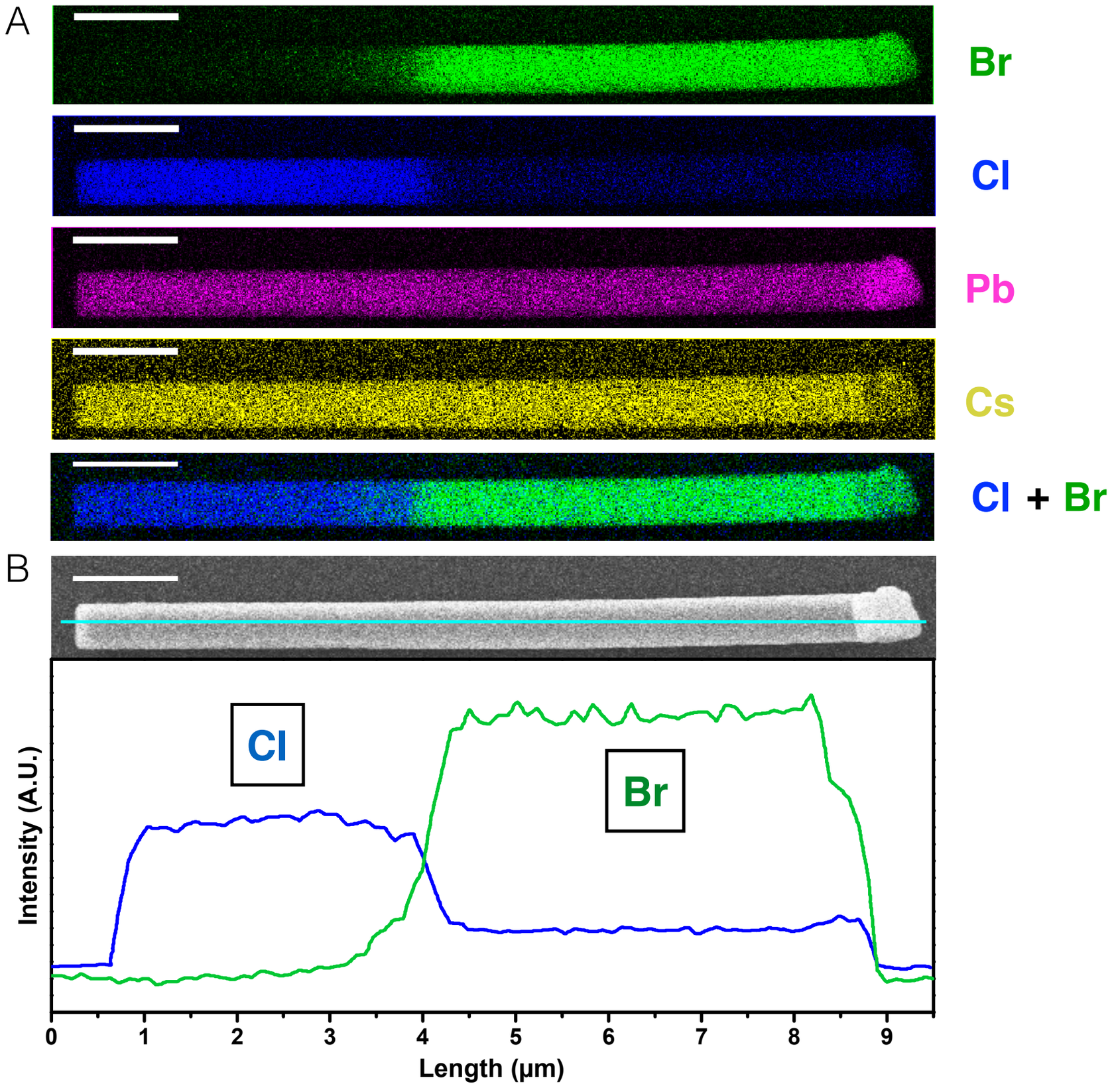
Anion exchange to create a heterojunction

Remove coating

PVSK heterojunctions

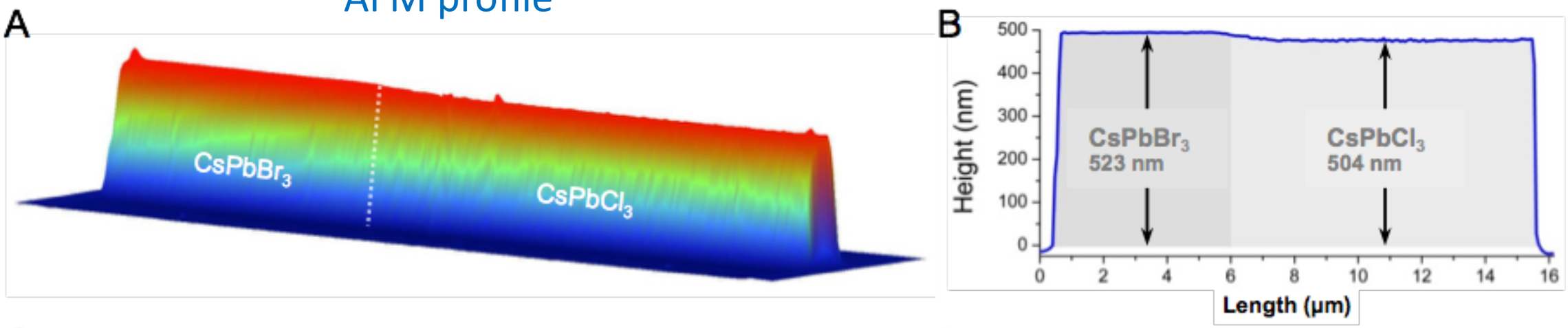


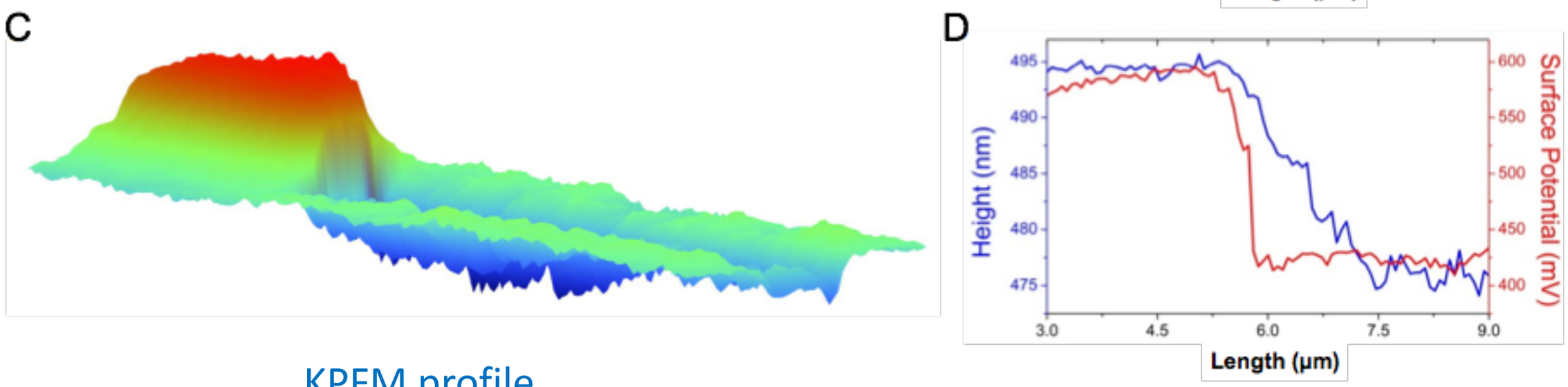
SEM-EDX mapping



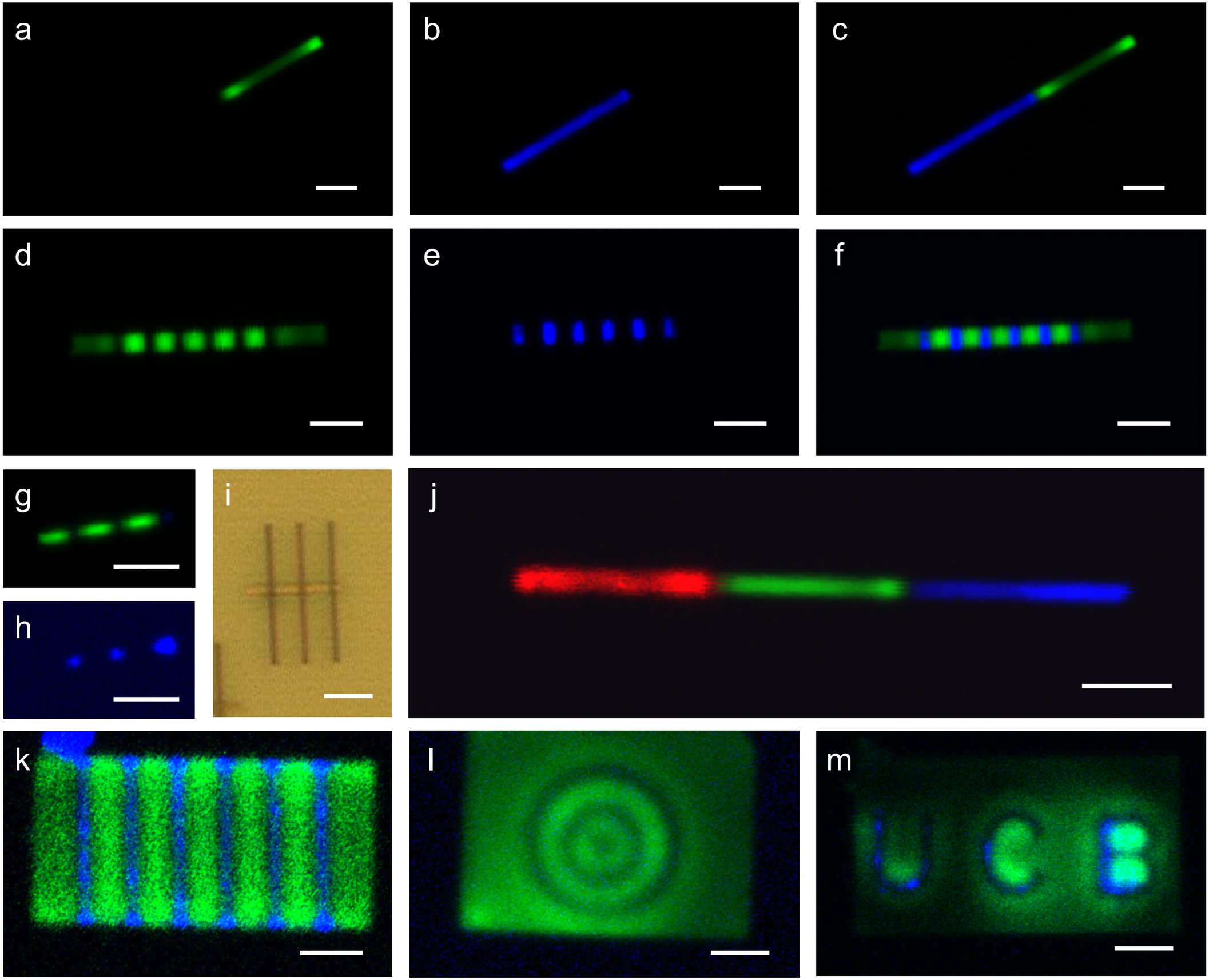
AFM-KPFM study

AFM profile





KPFM profile

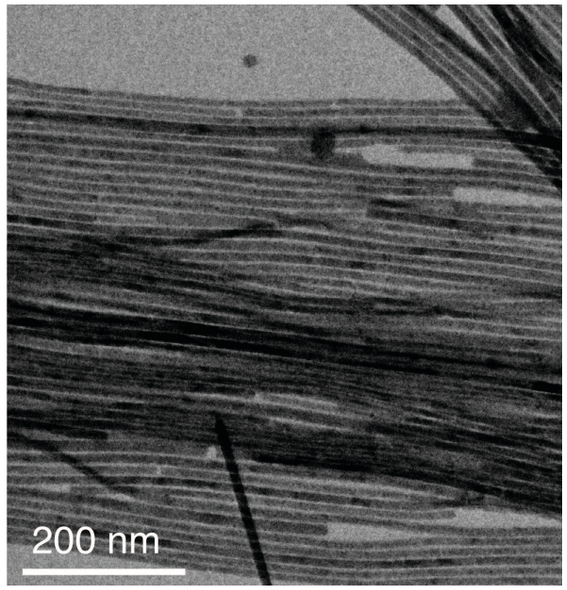


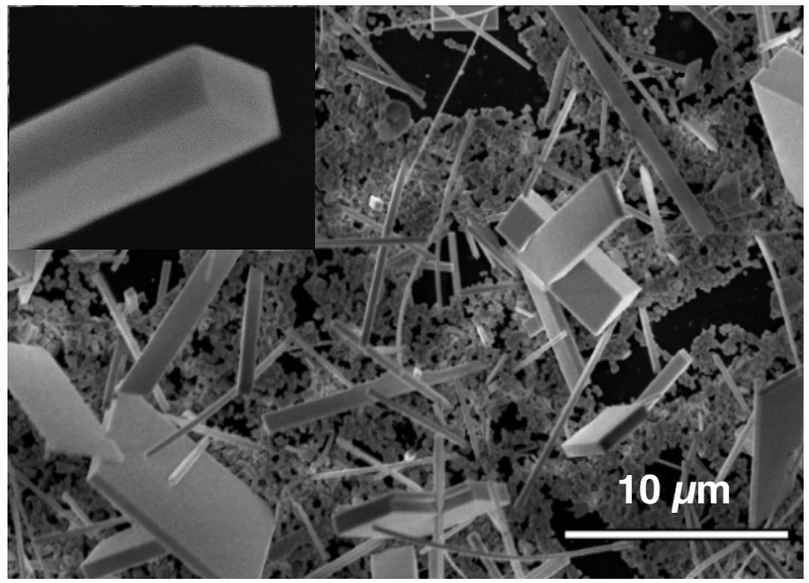
All scale bars are 3 μm

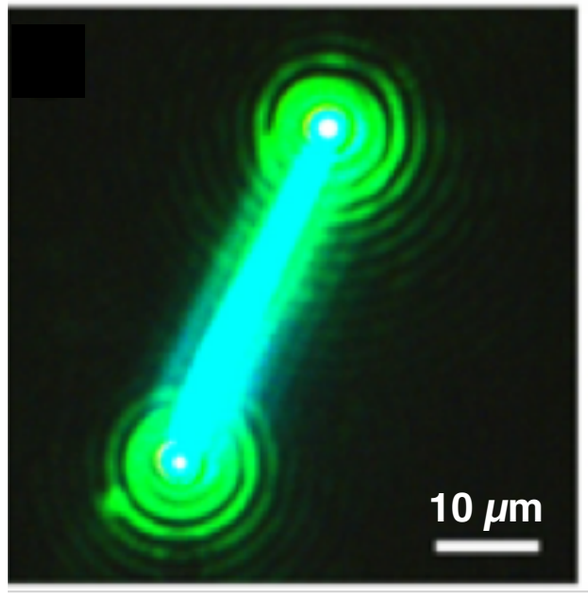
L. Dou, N. S. Ginsburg, P. Yang et al, PNAS 2017

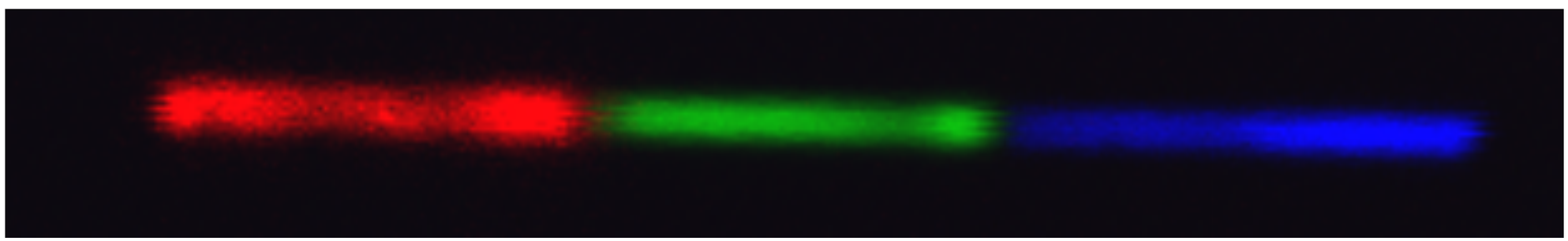
Summary for nanowires

- Colloidal synthesis of ultra thin $CsPbBr_3$ nanowire
- Substrate - crystallization approach to synthesize $CsPbX_3$ nanowire
- Optically - driven $CsPbBr_3$ nanowire laser
- $CsPbX_3$ nanowire heterojunction via localized anion exchange

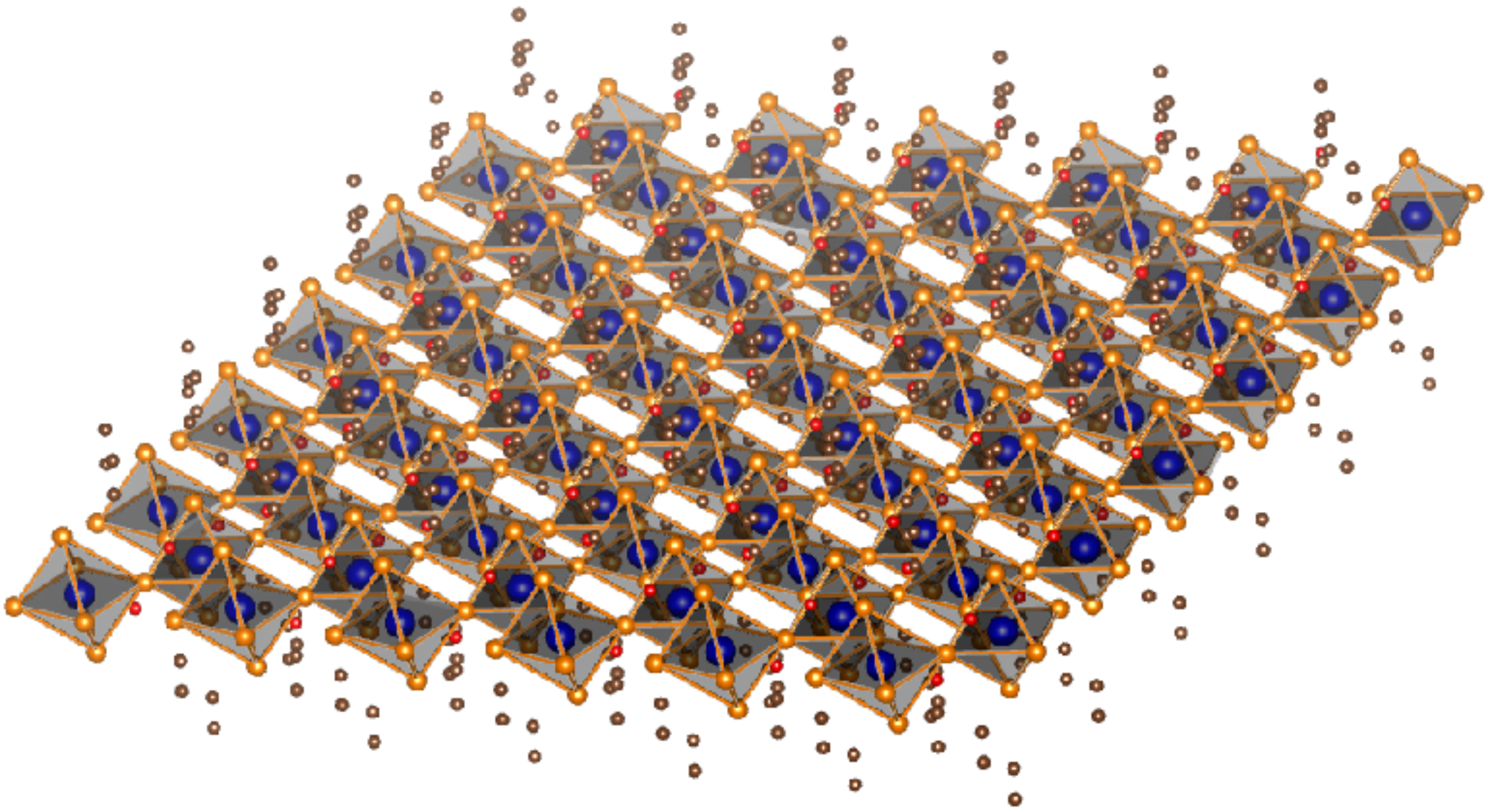








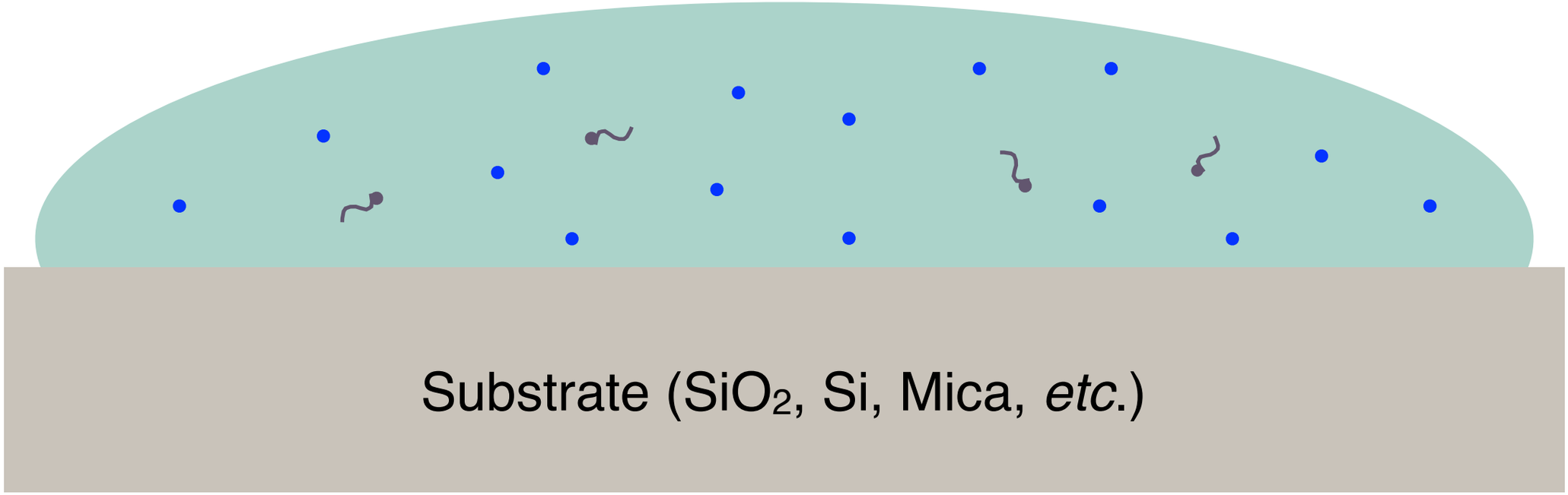
2D sheet growth



$(C_4H_9NH_3)_2PbBr_4$

2D sheet growth

1. Dissolve stoichiometric $PbBr_2$:$C_4H_9NH_3Br$ = 1:2 in DMF
2. Dilute with DMF, chlorobenzene, and **acetonitrile;** concentration ~0.05%
3. Drop casting on SiO_2 substrate under mild heating (70~80 °C)



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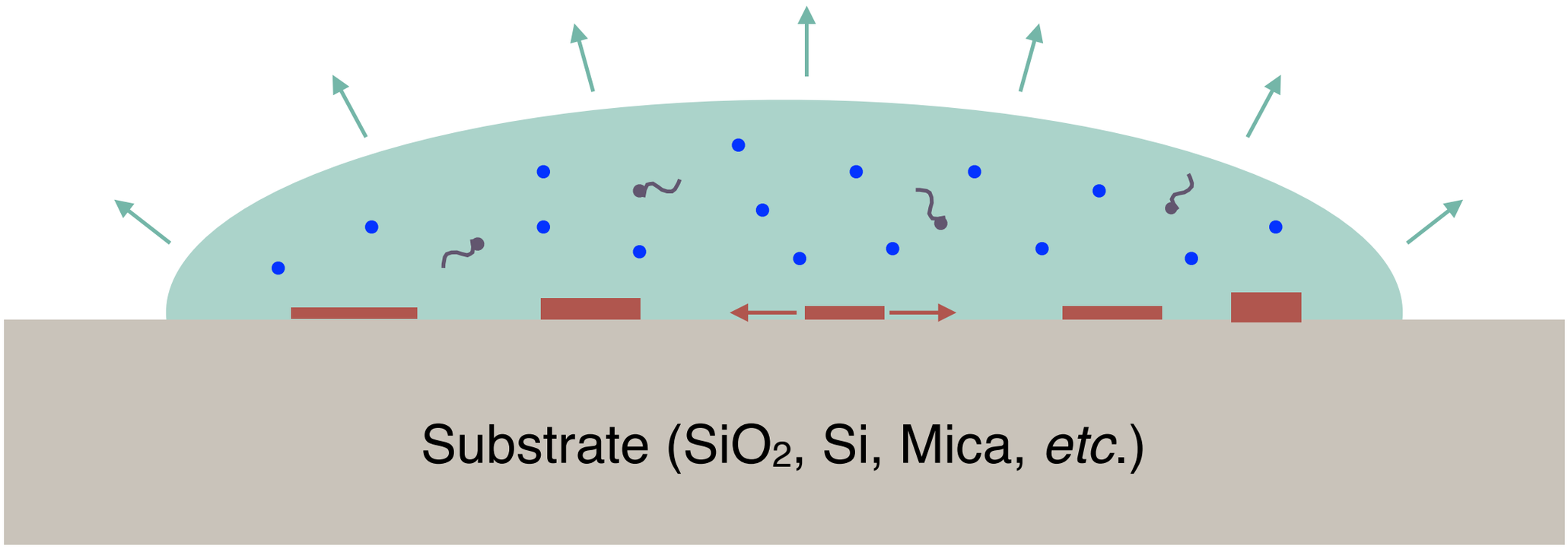
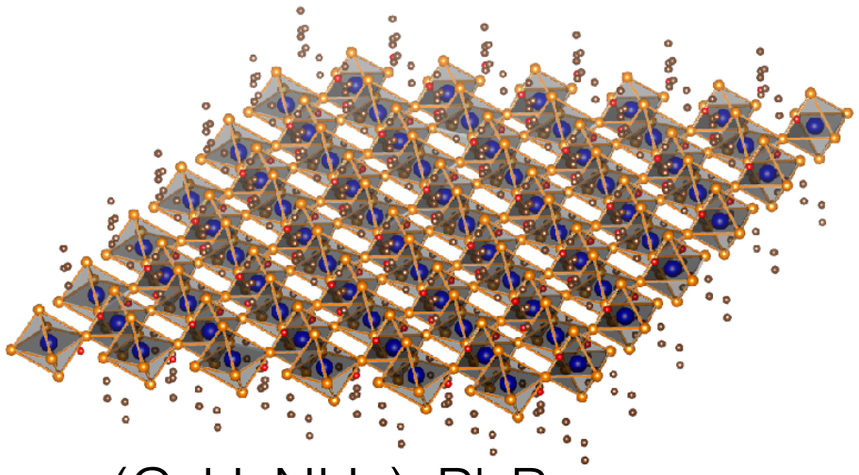
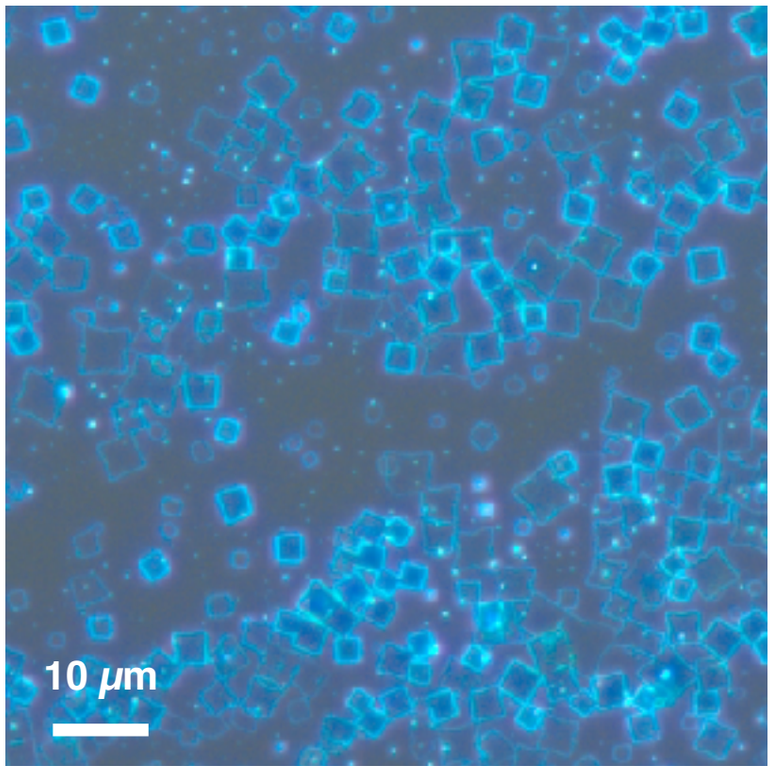
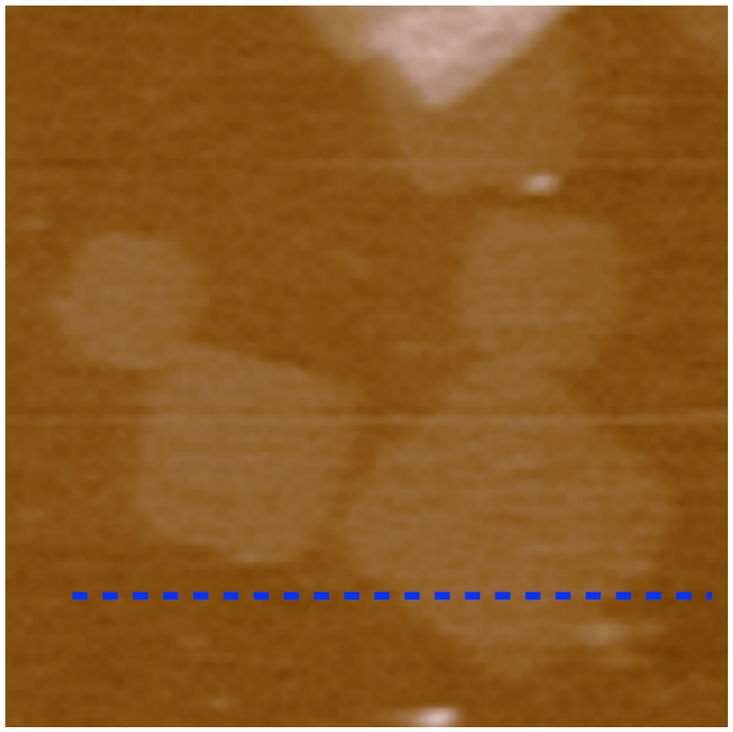


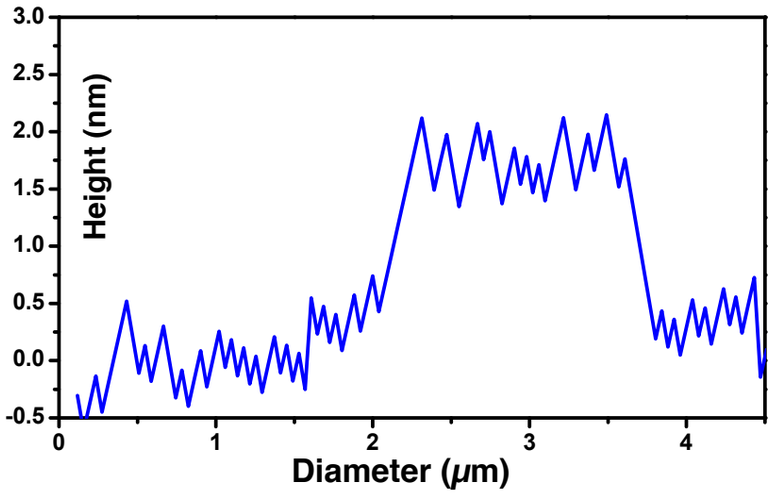
2D sheet growth

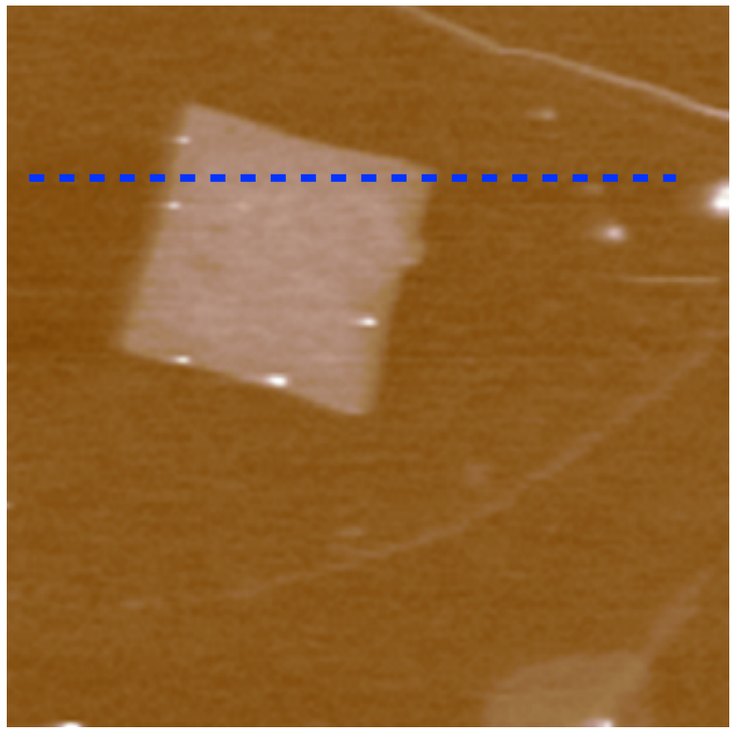


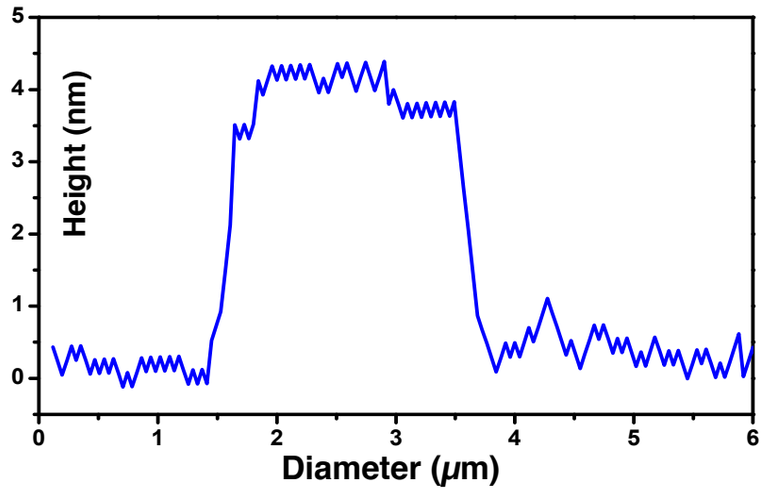
$(C_4H_9NH_3)_2PbBr_4$





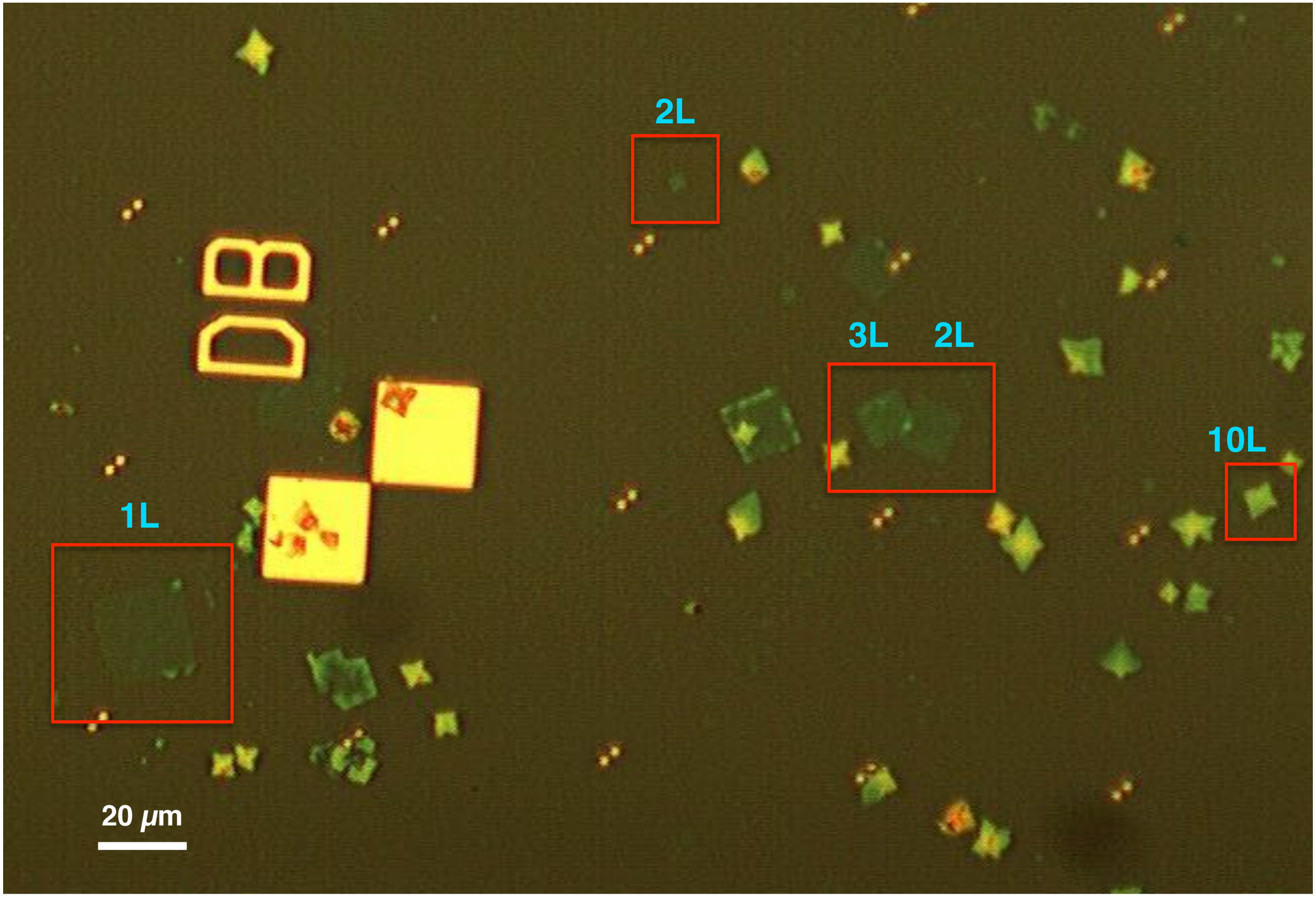




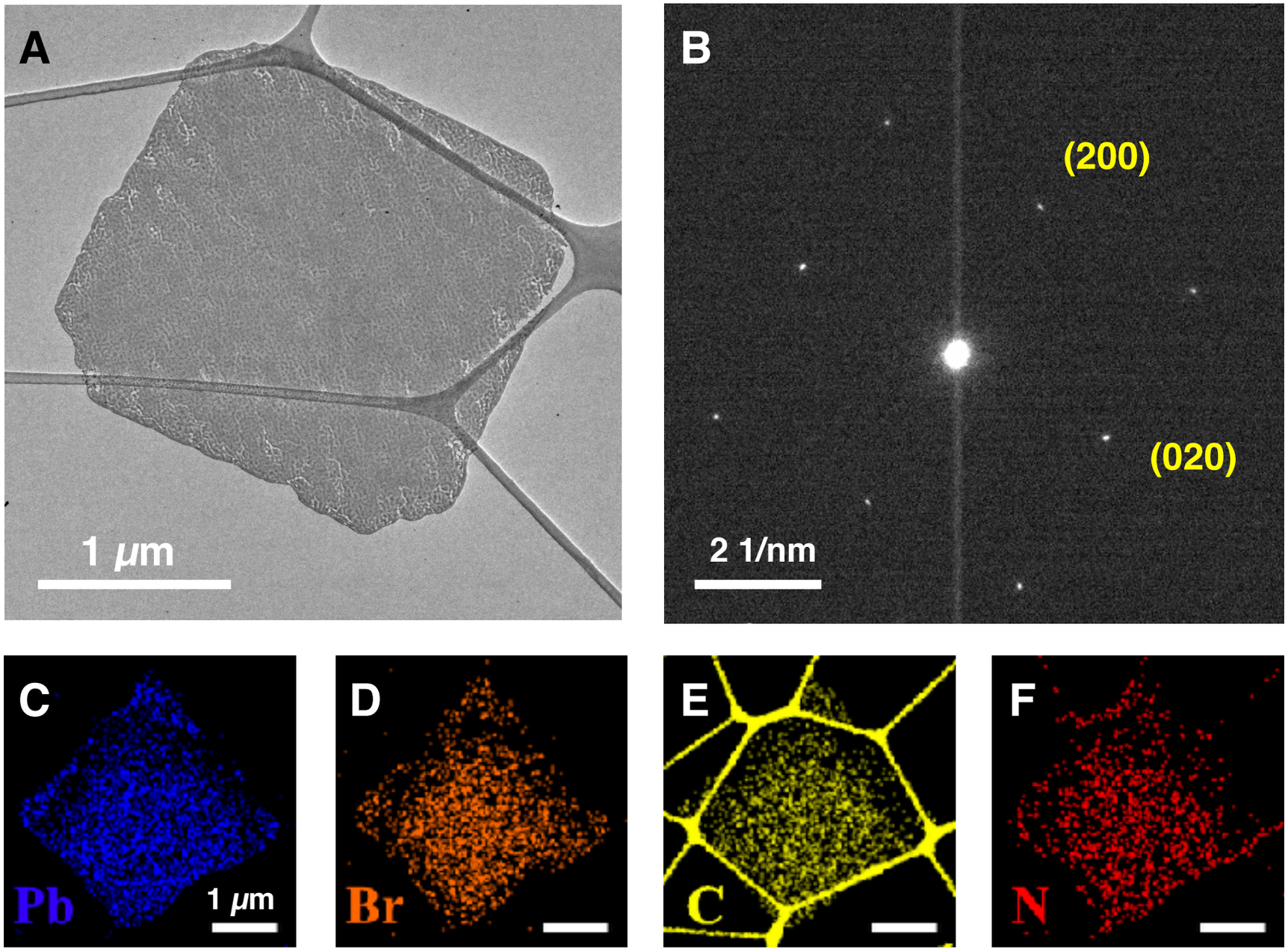


L. Dou, A. Wong, Y. Yu, P. Yang et al. Science 2015, 349, 1518

Optical images



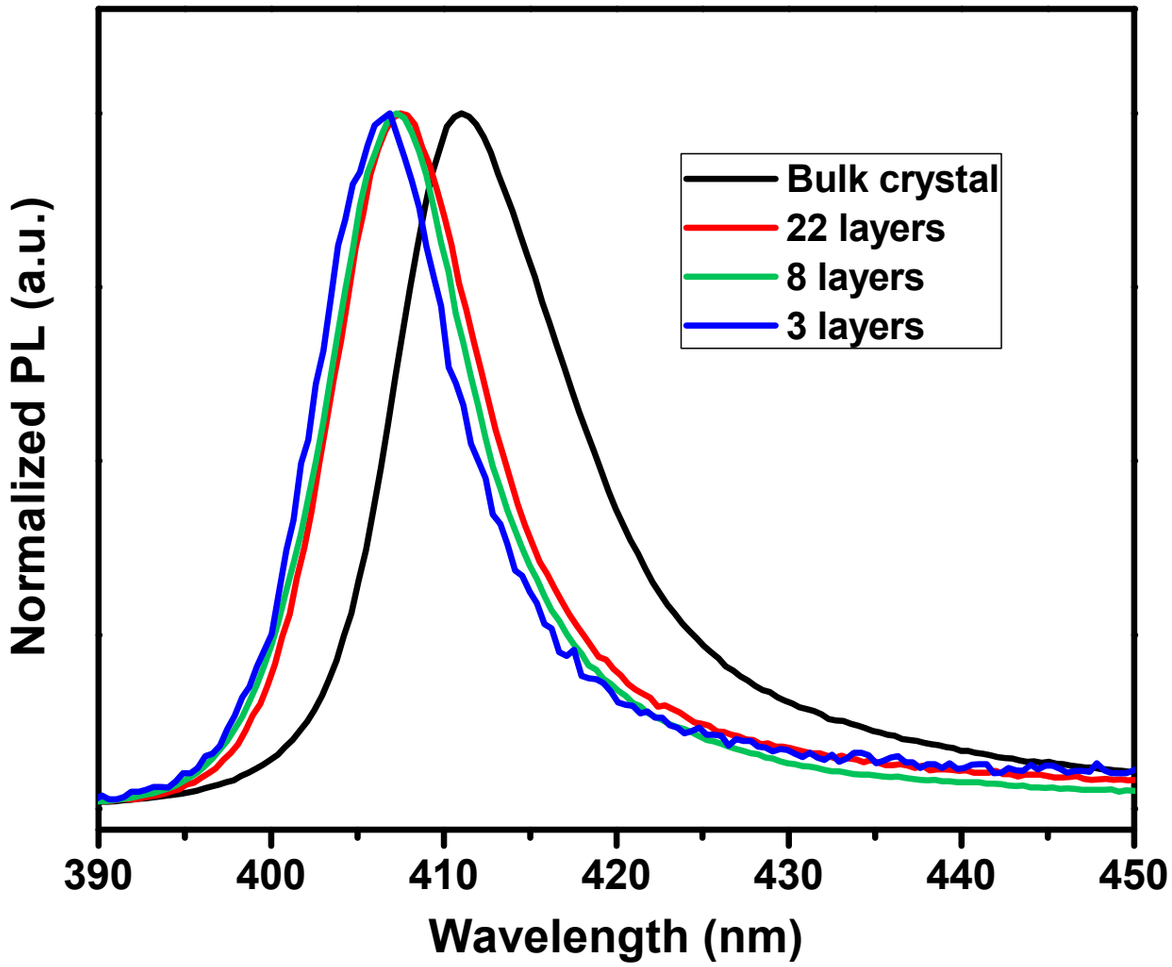
TEM characterization

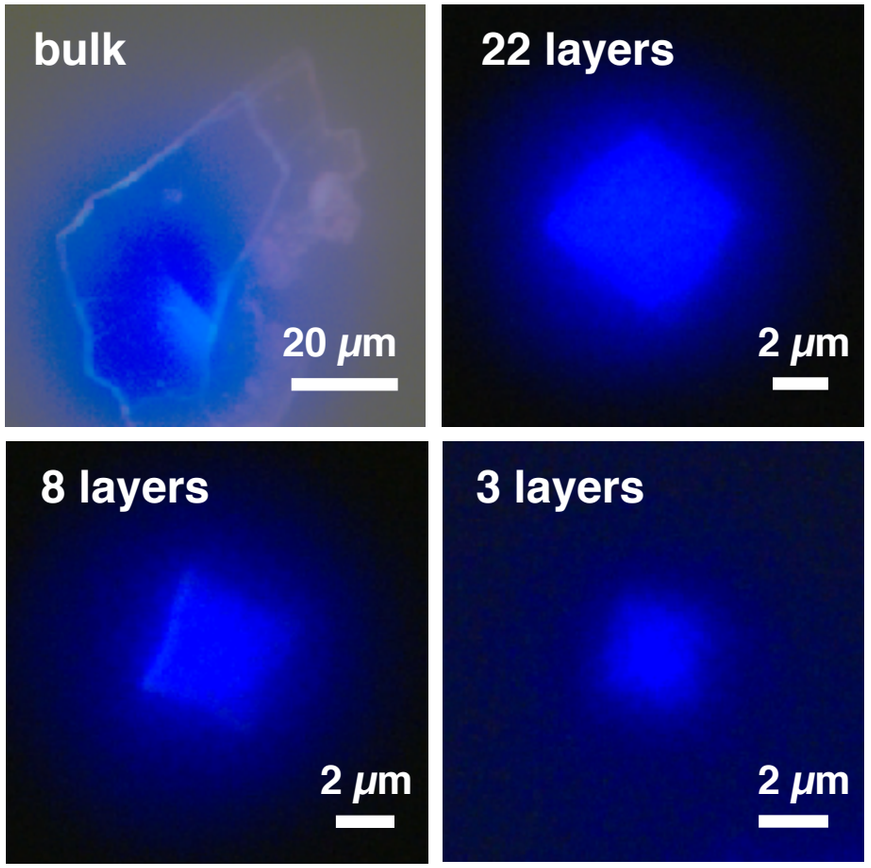


2D sheets lattice constant: a = 8.45 Å, b = 8.67 Å

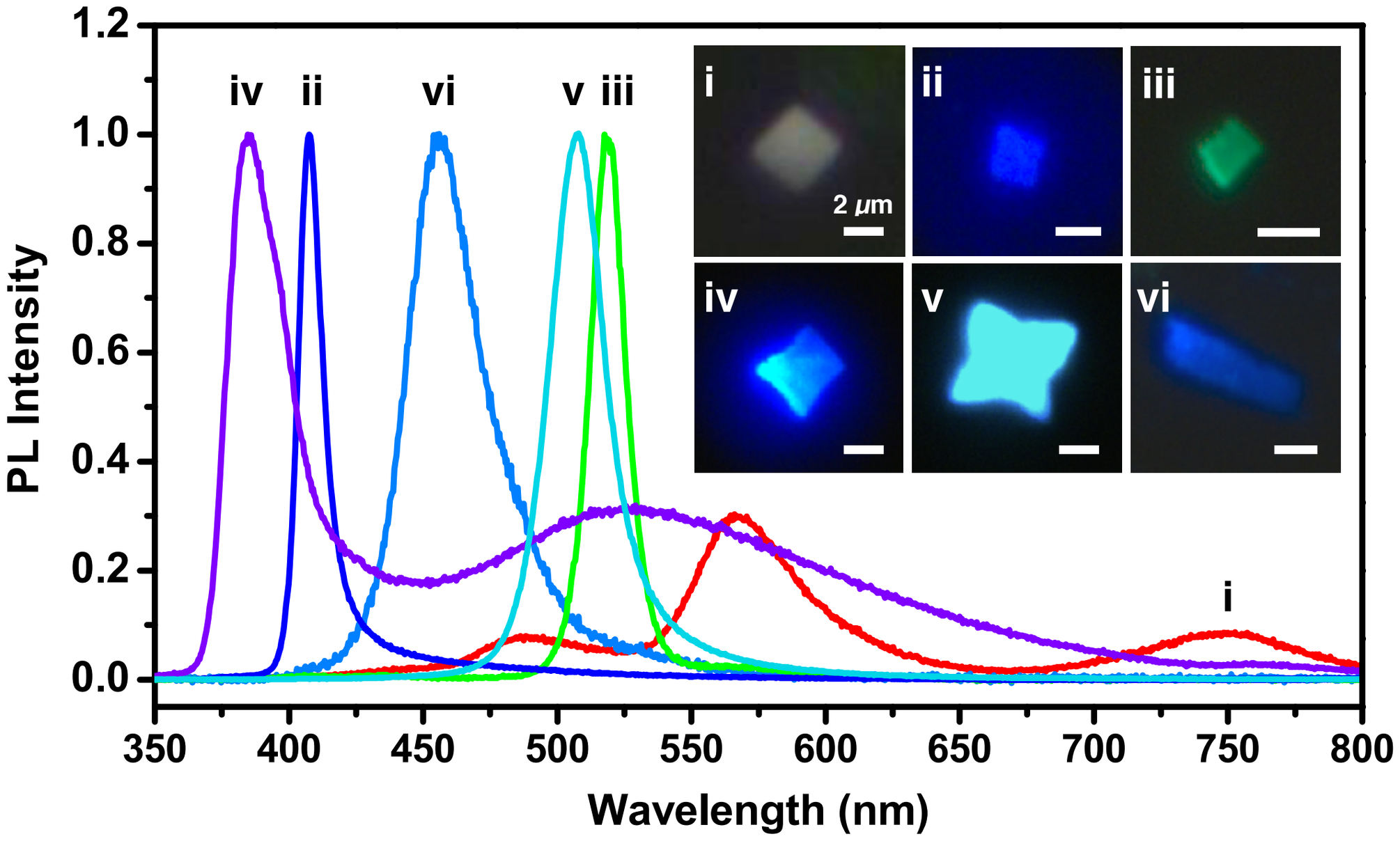
Bulk: a = 8.22 Å, b = 8.33 Å

Single sheet PL study





Composition and color tunability



$(C_4H_9NH_3)_2PbCl_4$ (i), $(C_4H_9NH_3)_2PbBr_4$ (ii), $(C_4H_9NH_3)_2PbI_4$ (iii),
$(C_4H_9NH_3)_2PbCl_2Br_2$ (iv), $(C_4H_9NH_3)_2PbBr_2I_2$ (v), $(C_4H_9NH_3)_2(CH_3NH_3)Pb_2Br_7$ (vi)

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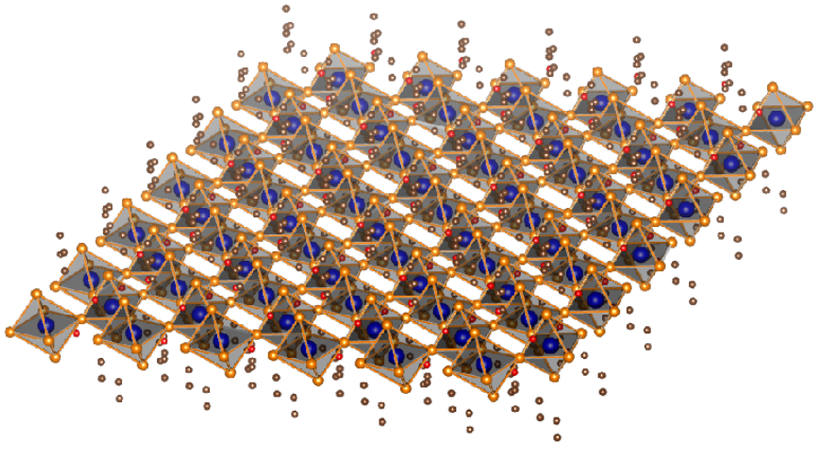
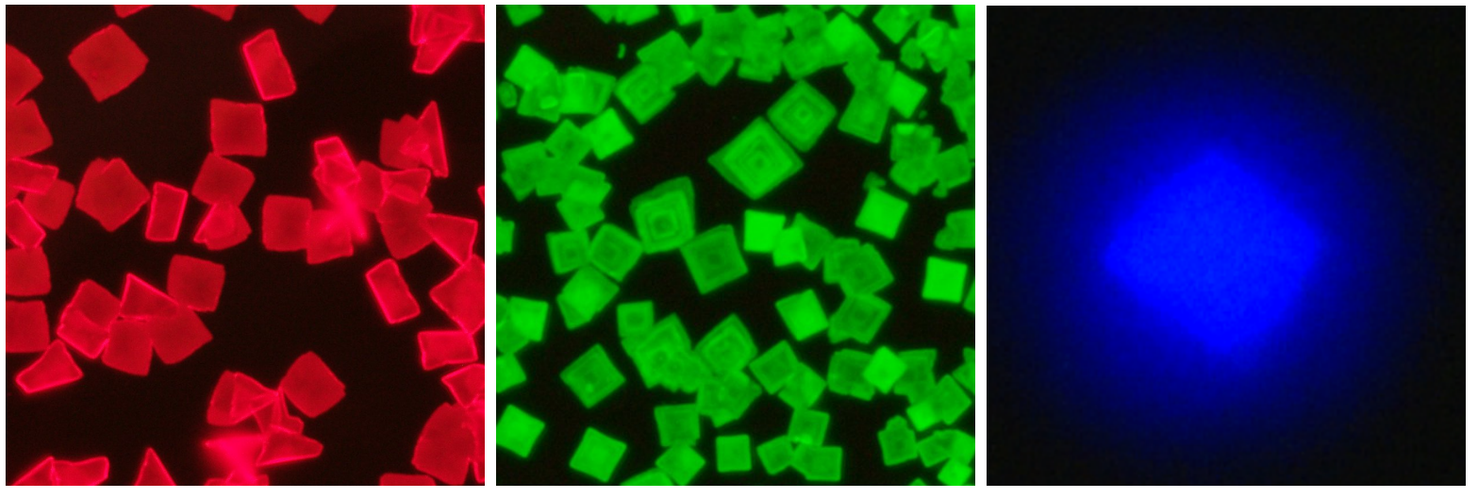
Summary for 2D structures

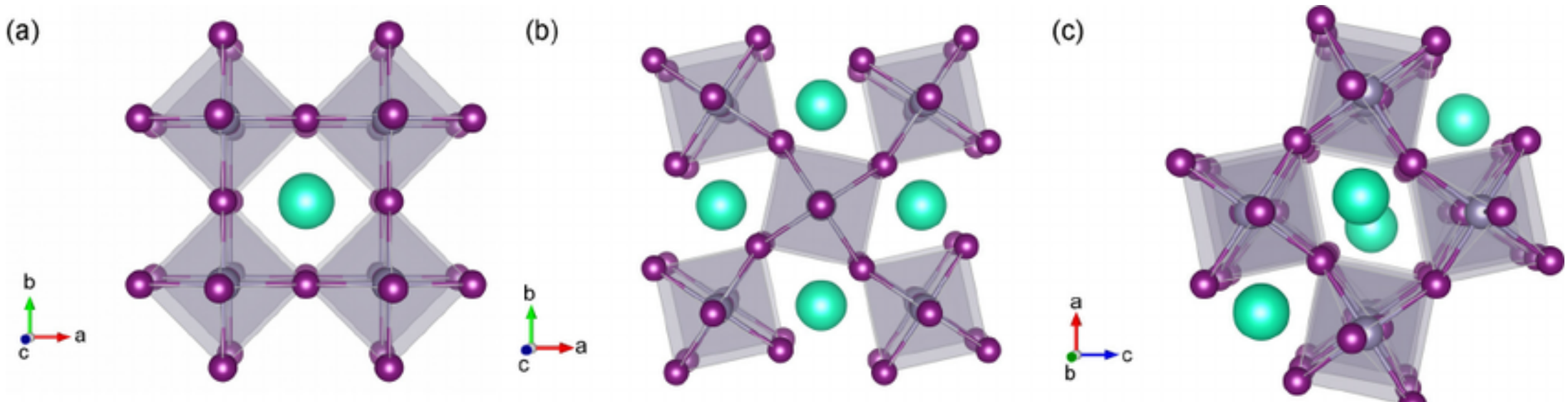
- Substrate-guided solvent evaporation method to grow atomically-thin 2D perovskites
- Weak electronic coupling between layers
- Tunable optical properties by varying inorganic and organic parts
- Electron transport properties to be explored more



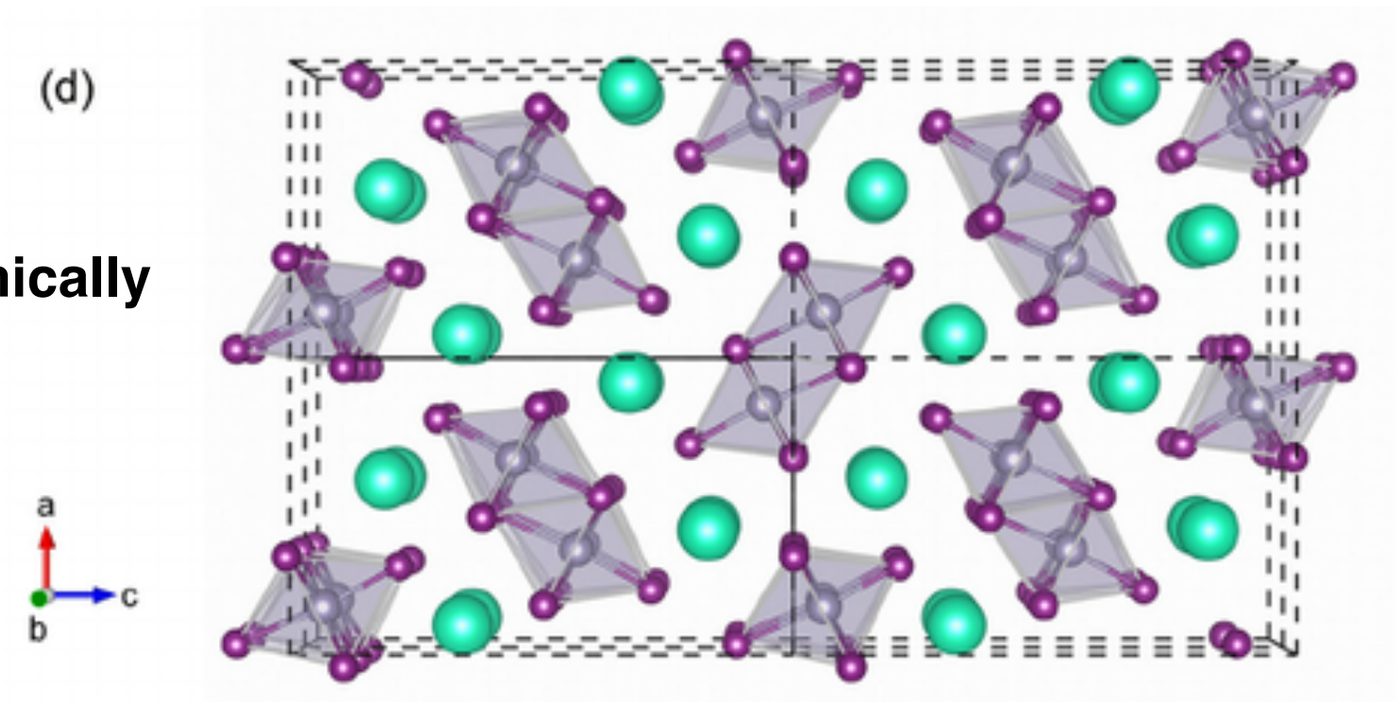


Phase transition of $CsPbI_3$

$(CH_3NH_3)PbX_3 \longrightarrow CsPbX_3$

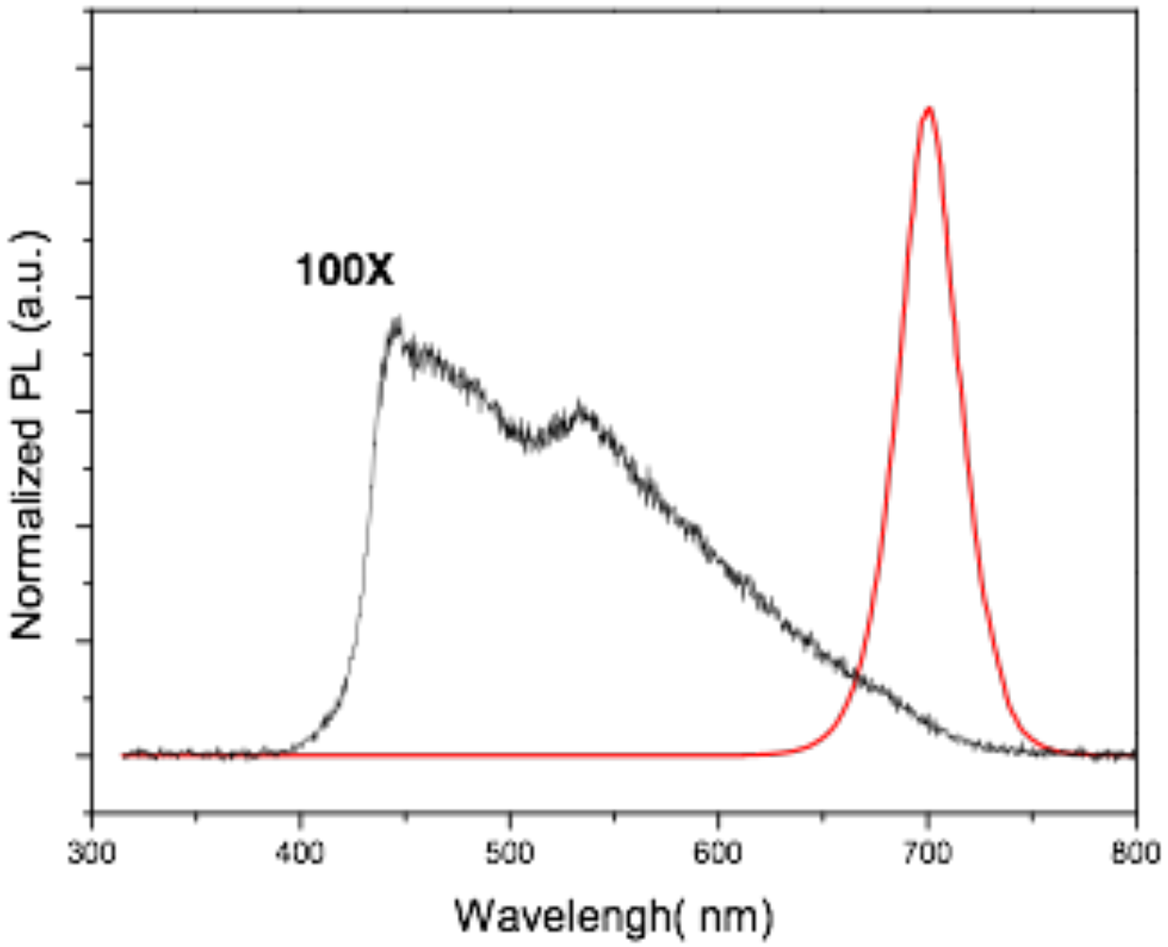


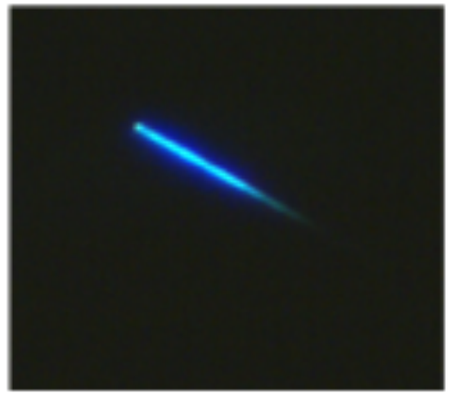
Thermodynamically stable at RT



A. Walsh et al. Phys. Rev. B 2015, 91, 144107

Optical properties of $CsPbI_3$



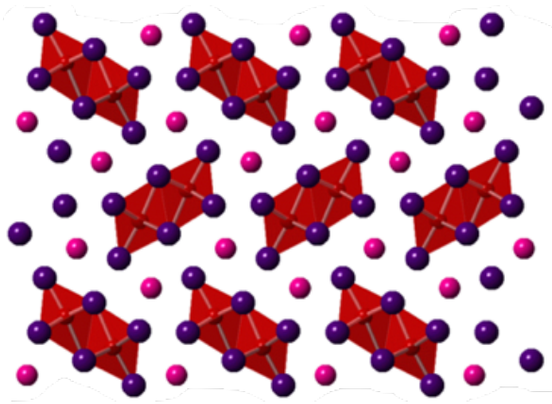


Heated up to 320 C and quench to RT

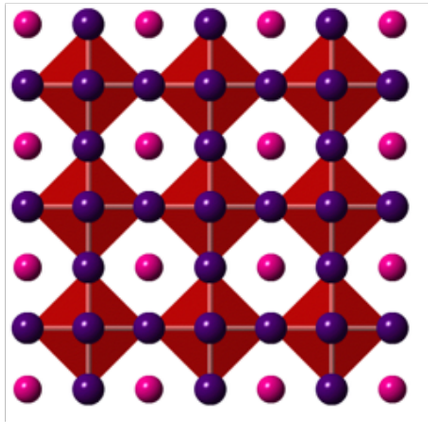
How to make solar cells?

Phase transition of $CsPbI_3$

$(CH_3NH_3)PbI_3$ ⟶ $CsPbI_3$



$CsPbI_3$
reversible transition



Thermodynamically stable at RT

Thermodynamically unstable at RT

Heating (300 C)

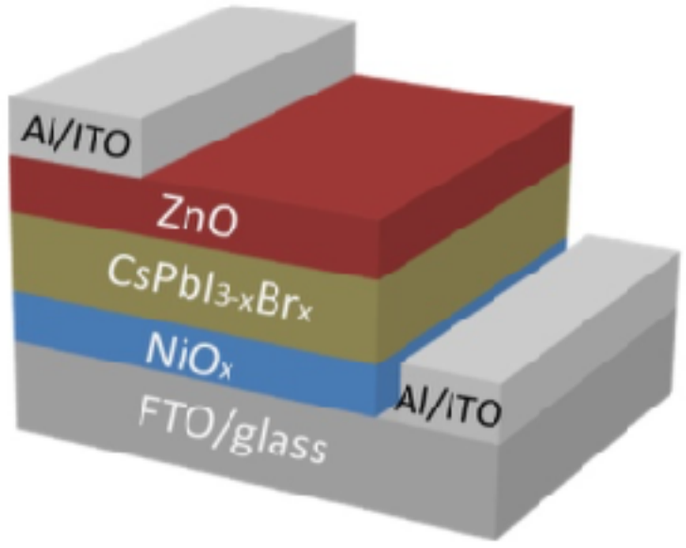
Moisture

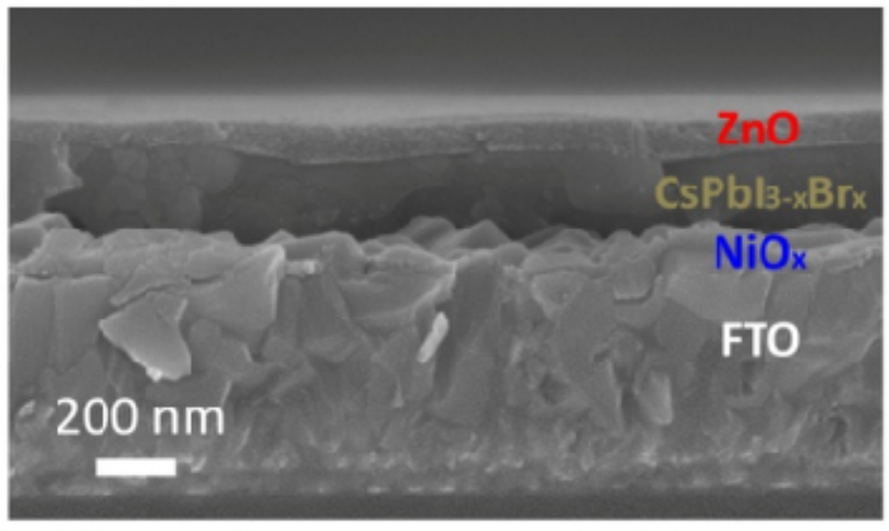
Transparent state

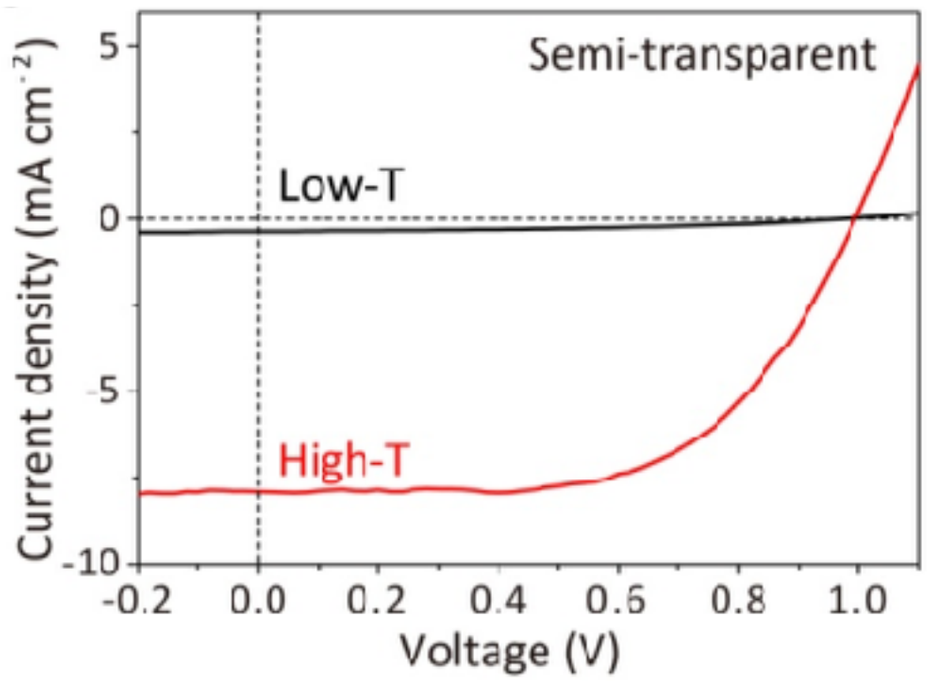
Photovoltaic state

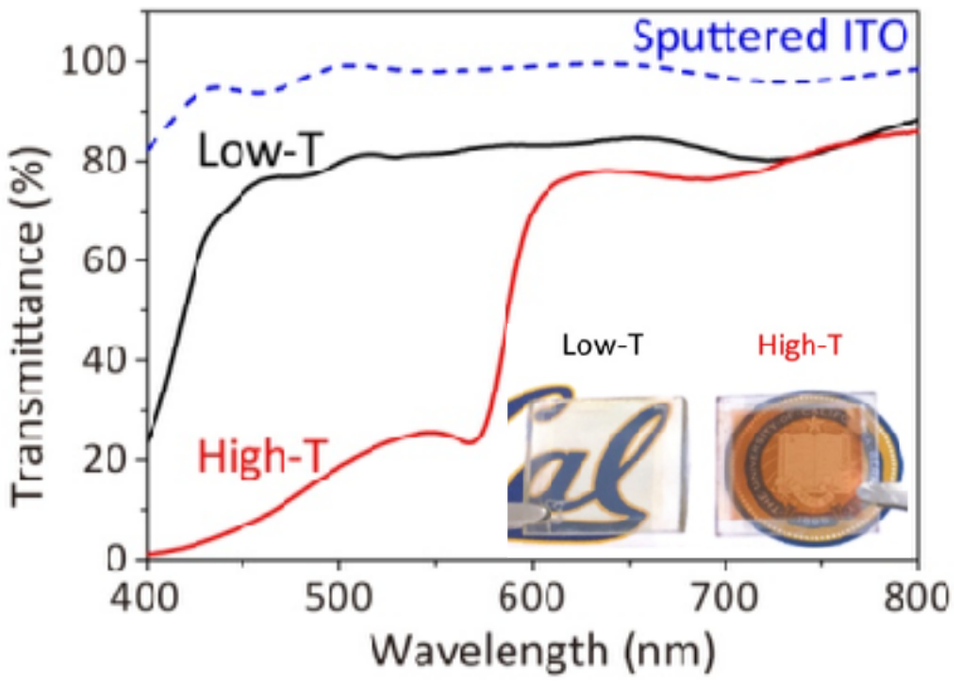
Smart PV windows

Device performance



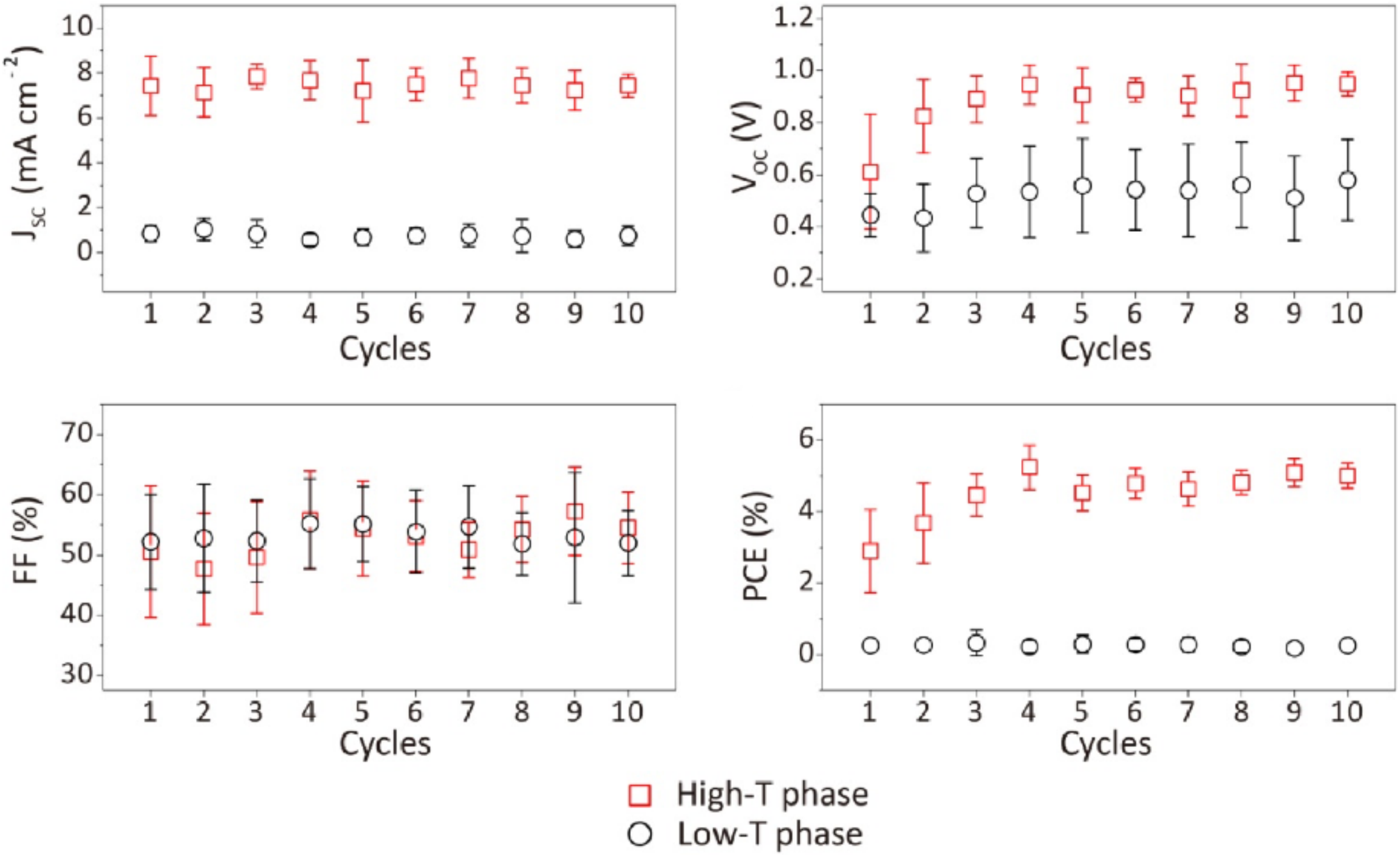






J. Lin, M. Lai, L. Dou, P. Yang et al. Nature Materials 2018

Reversibility



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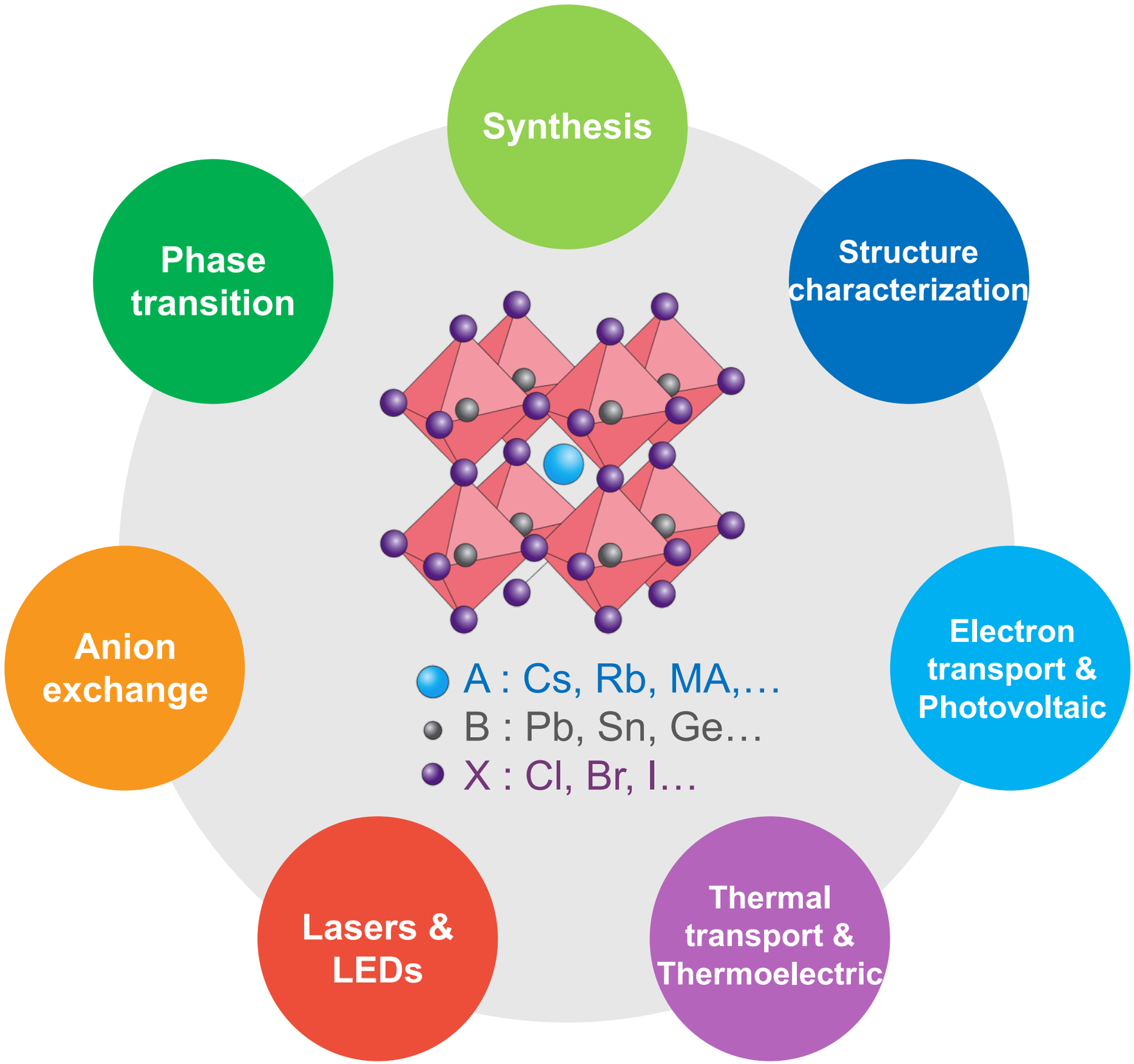
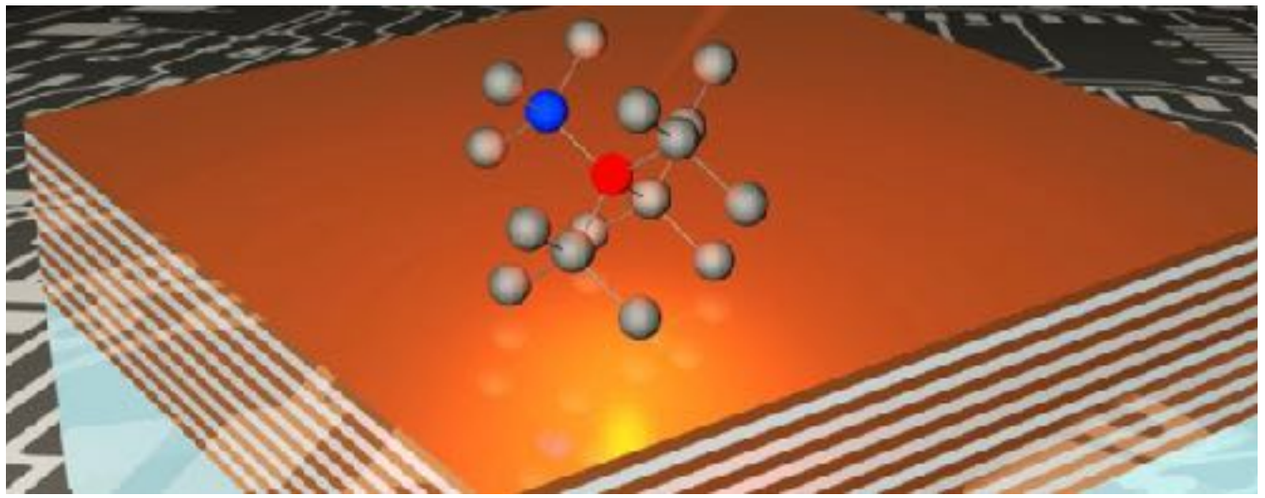
Summary

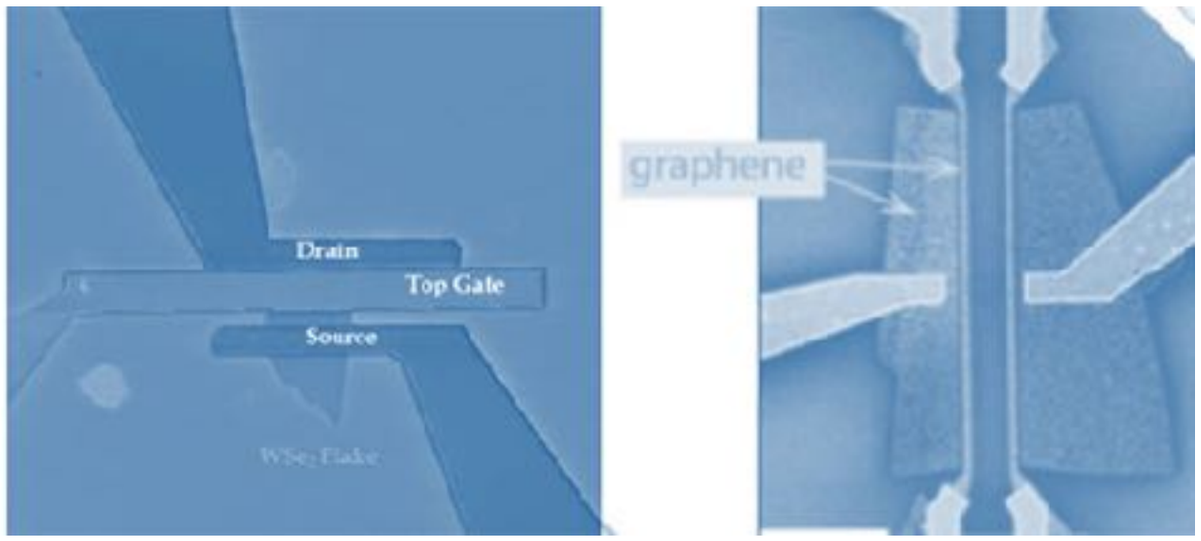

Synthesis
Phase transition
Structure characterization
A : Cs, Rb, MA,…
B : Pb, Sn, Ge…
X : Cl, Br, I…
Anion exchange
Electron transport & Photovoltaic
Lasers & LEDs
Thermal transport & Thermoelectric

Synergistic interests with BNC

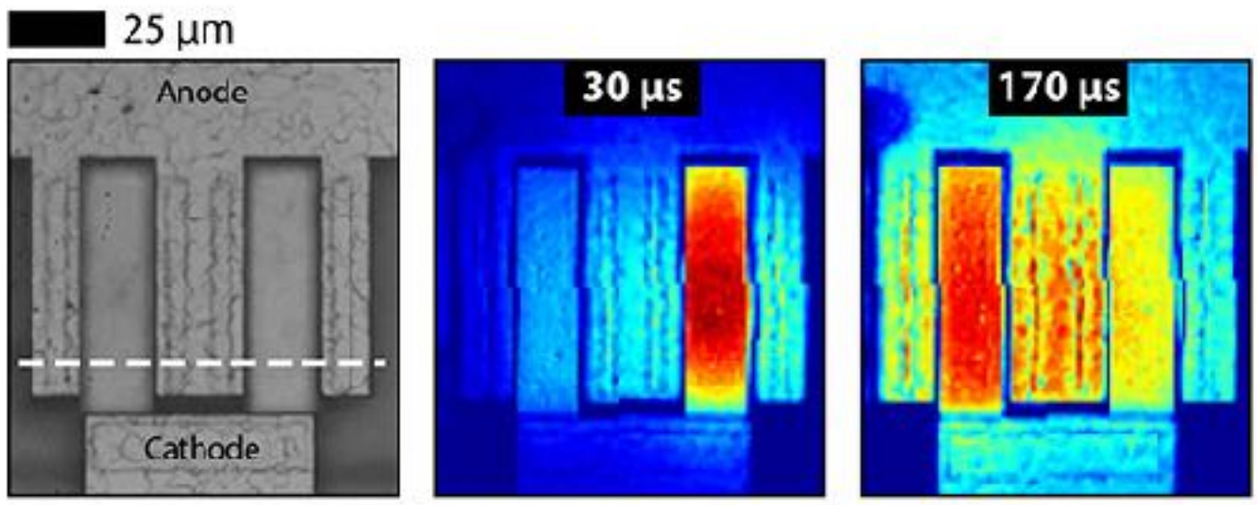
Scalable Manufacturing of Aware and Responsive Thin Films



Nanophotonics and Quantum Optics



Nanoelectronics and Semiconductor Devices



Energy Conversion and Heat Transfer

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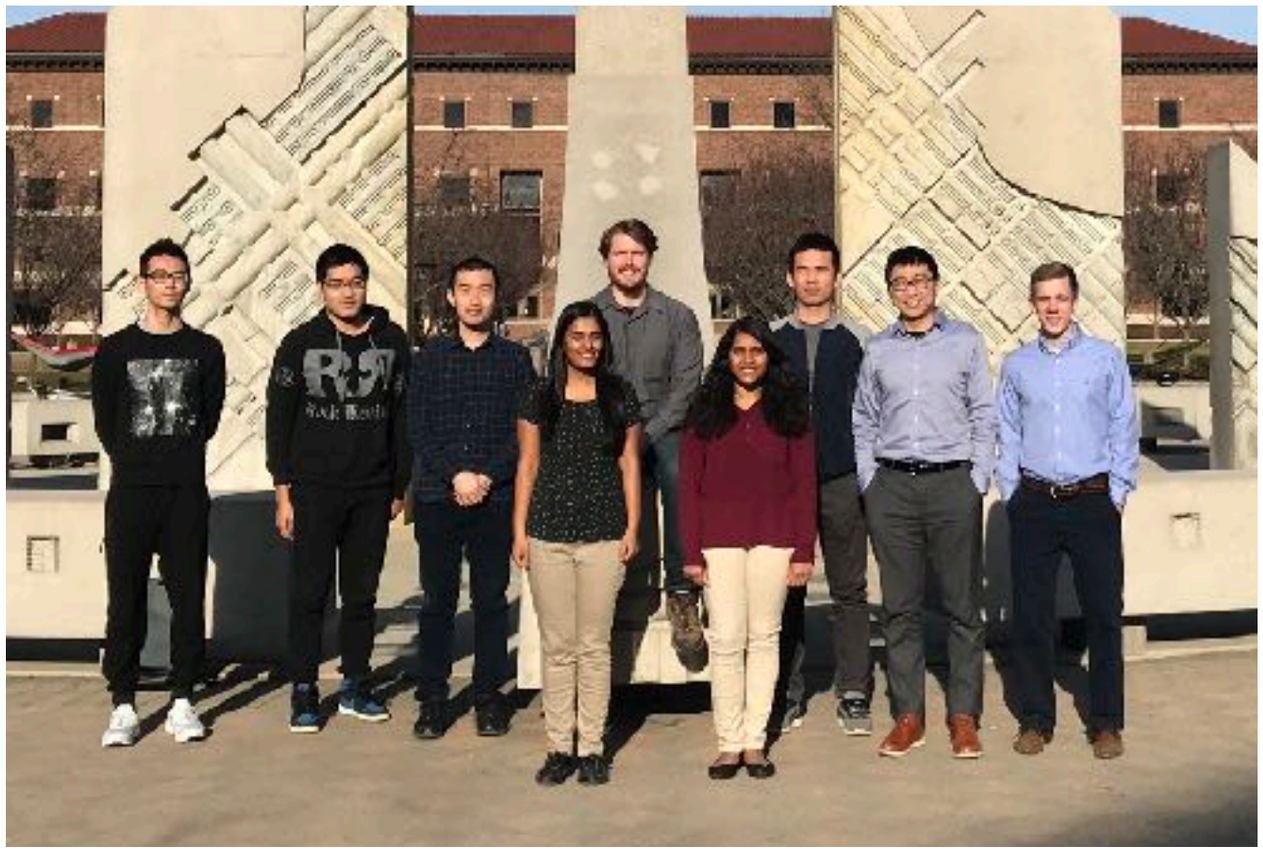
- Prof. Peidong Yang
- Ms. Akriti
- Mr. Aidan Coffey
- Mr. Blake Finkenauer
- Dr. Yao Gao
- Dr. Enzheng Shi
- Dr. Dmitry Zemlyanov
- Dr. Shibin Deng
- Prof. Libai Huang



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