Probing the Synthesis and Conversion of Perovskite Single Crystals

Presenter: Freddy A. Rodríguez-Ortiz
Cahoon Group
University of North Carolina at Chapel Hill
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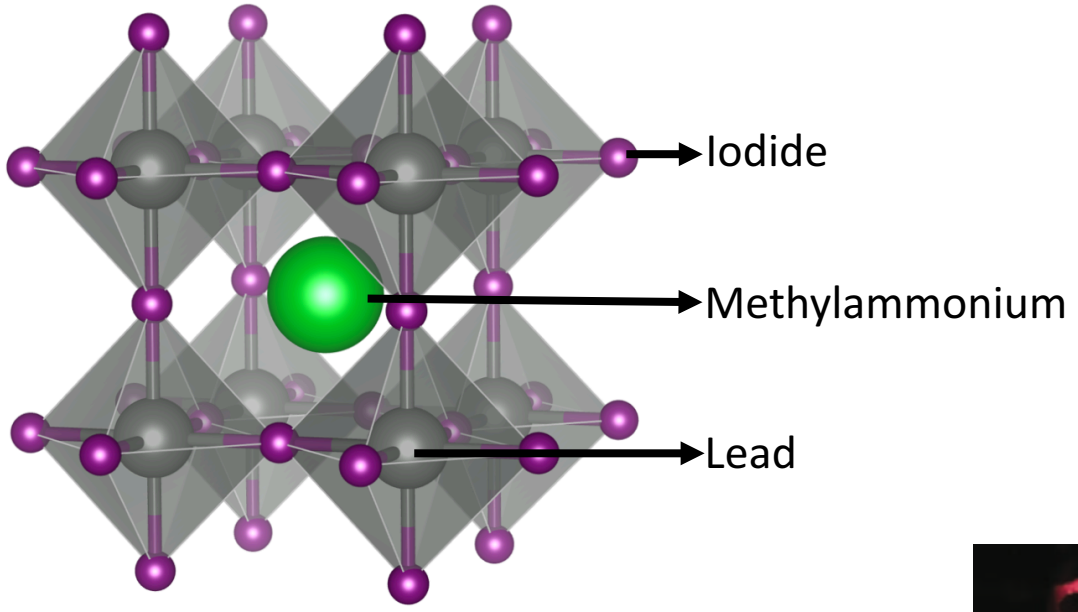
THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

Outline

- **Introduction**
  - Structure and properties of methylammonium lead iodide ($CH_3NH_3PbI_3$) perovskite
- **Objective**
- **Methodology**
  - Chemical vapor deposition (CVD)
- **Results**
  - Scanning electron microscope (SEM)
  - Atomic force microscope (AFM)
  - Photoluminescence (PL)
- **Summary**

What is $CH_3NH_3PbI_3$ Perovskite?

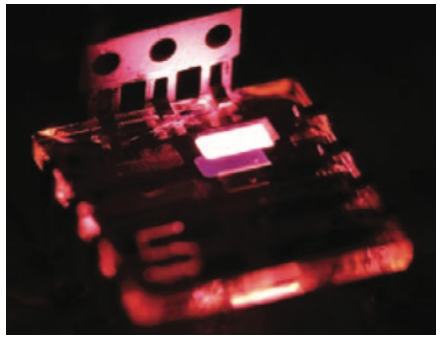
Structure



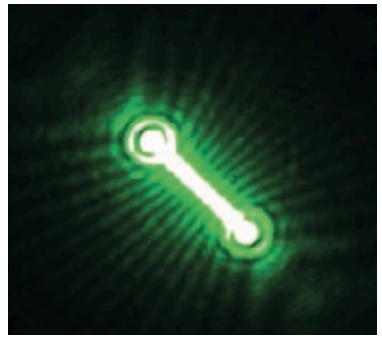
Perovskite possess the same crystal structure as $CaTiO_3$, known as the perovskite structure ABX_3.

Properties

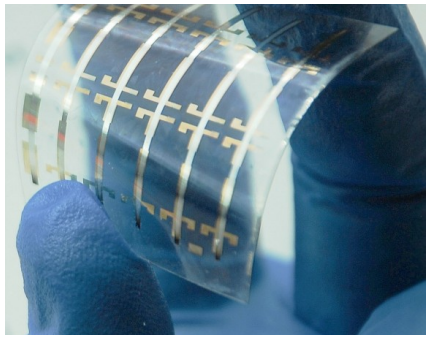
- tunable bandgap
- high optical absorption coefficient
- high charge carrier mobility
- long charge diffusion lengths



LEDs



nanolasers



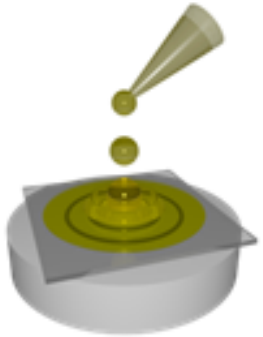
field-effect transistors

(5) Sutherland, B. R. & Sargent, E. H. Perovskite photonic sources. *Nat. Photonics* **10,** 295–302 (2016).

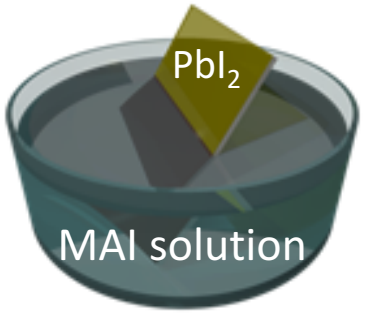
(6) Tan, Z.-K. *et al.* Bright light-emitting diodes based on organometal halide perovskite. *Nature Nanotech.* **9,** 687–692 (2014).

Two-step Synthesis

Solution-based synthesis



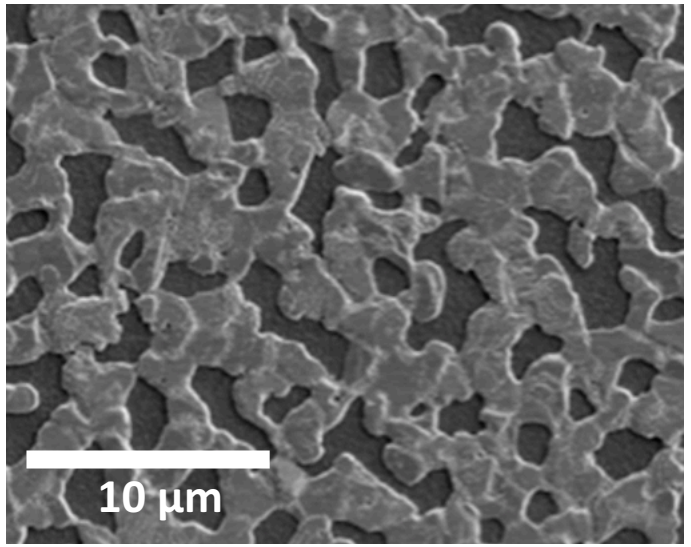
PbI_2 film on a substrate



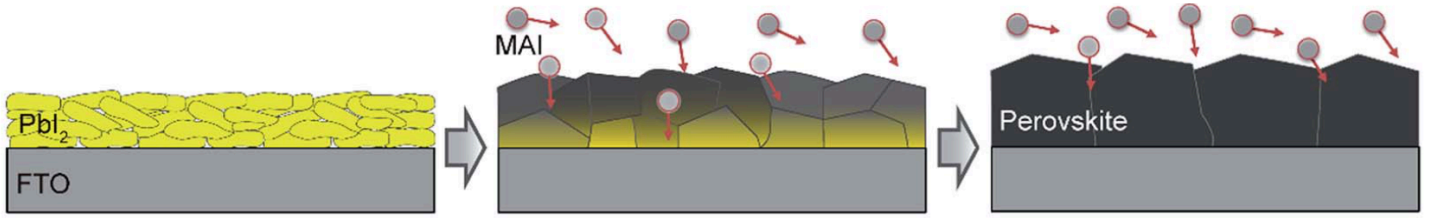
Submerge film in a solution of MAI

Annealing and formation of perovskite

Problem:



Chemical vapor deposition (CVD)



PbI_2 substrate

Vapor-solid reaction with MAI

Formation of perovskite

Advantages:

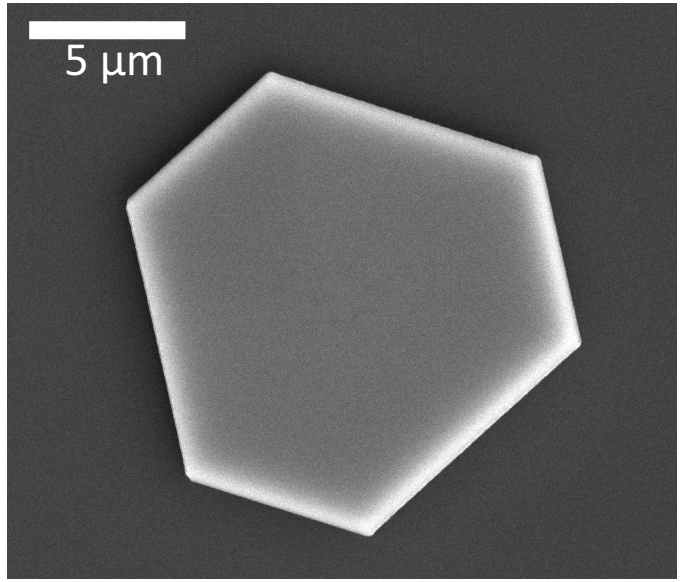
- High level of controllability
- Repeatability

(7) Luo, P. *et al.* Chemical Vapor Deposition of Perovskites for Photovoltaic Application. *Adv. Mater. Interfaces* **4.** (2017).

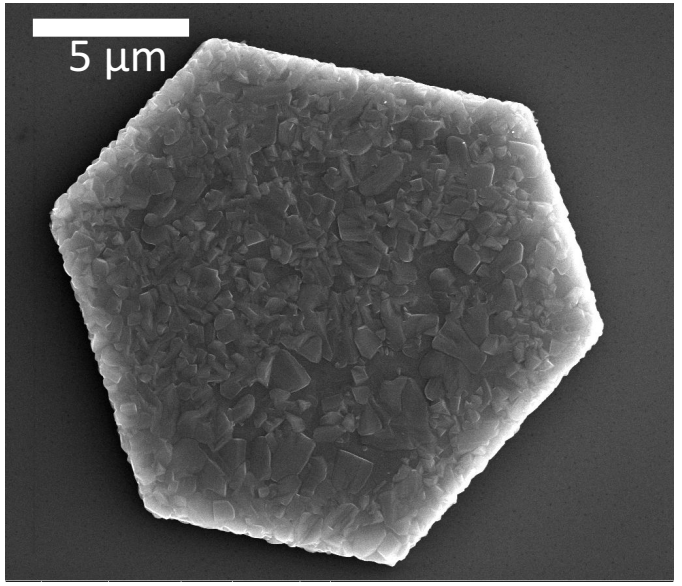
Objective

- Study the structural changes in the perovskite surface morphology by changing;
  - reaction temperature
  - reaction time
  - carrier gas flow rate

PbI_2

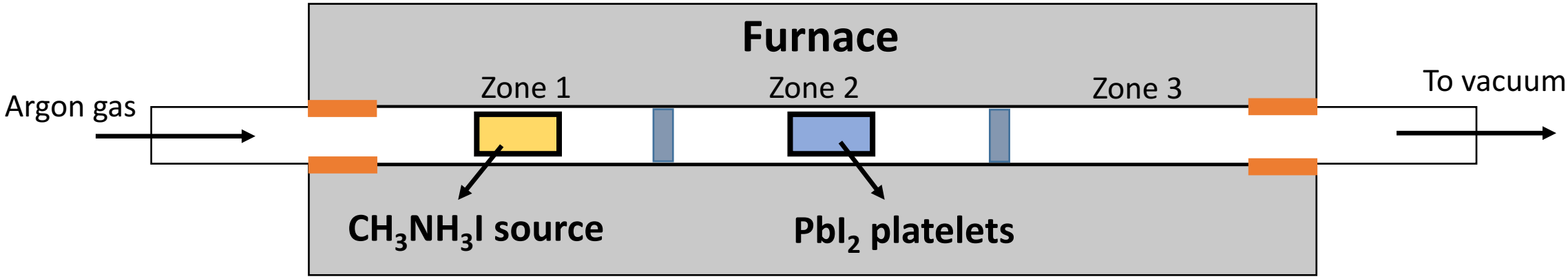


$CH_3NH_3PbI_3$



Methodology

Chemical vapor deposition system

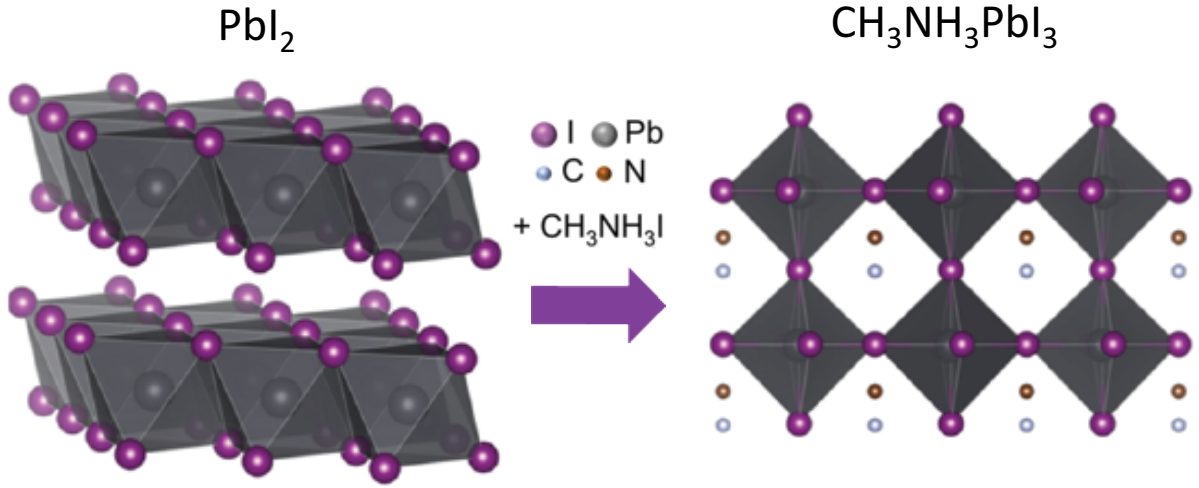


The reaction mechanism:

1) Generation of MAI vapor;

2) transport of MAI vapor to the substrate surface containing PbI_2 microplates;

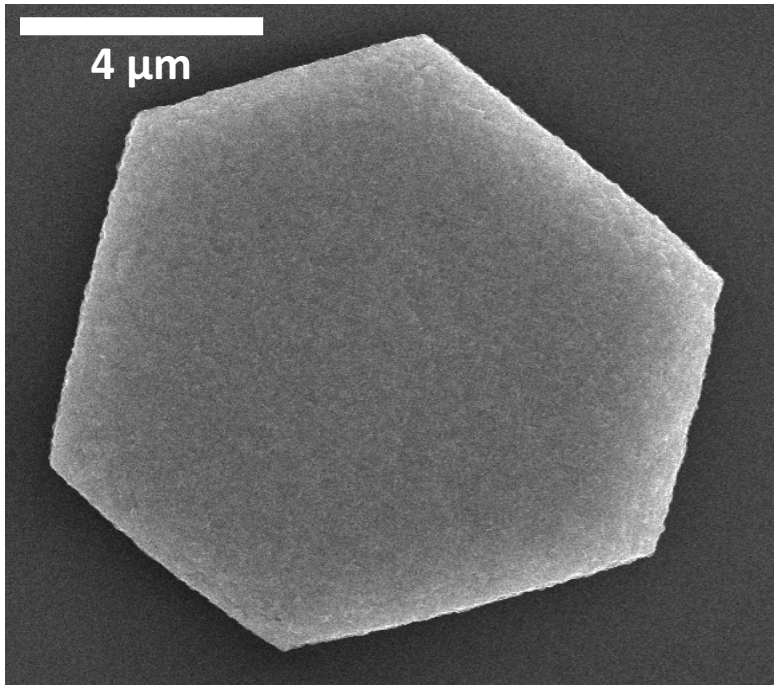
3) Intercalation, surface diffusion, and nucleation resulting in the formation of $CH_3NH_3PbI_3$ perovskite.



Brenner, T. M. *et al.* Conversion of Single Crystalline PbI2 to CH3NH3PbI3: Structural Relations and Transformation Dynamics. *Chem. Mater.* **28,** 6501–6510 (2016).

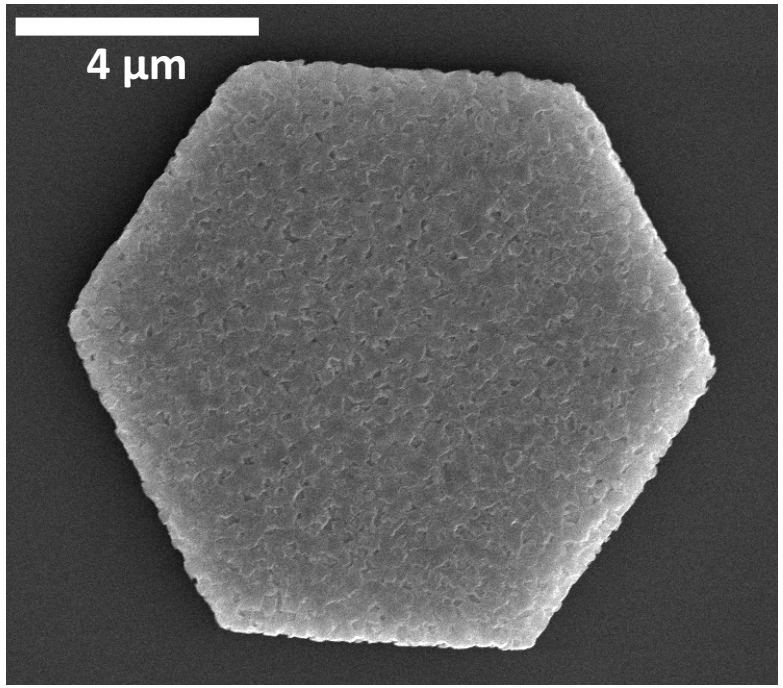
Effect of temperature

90 °C



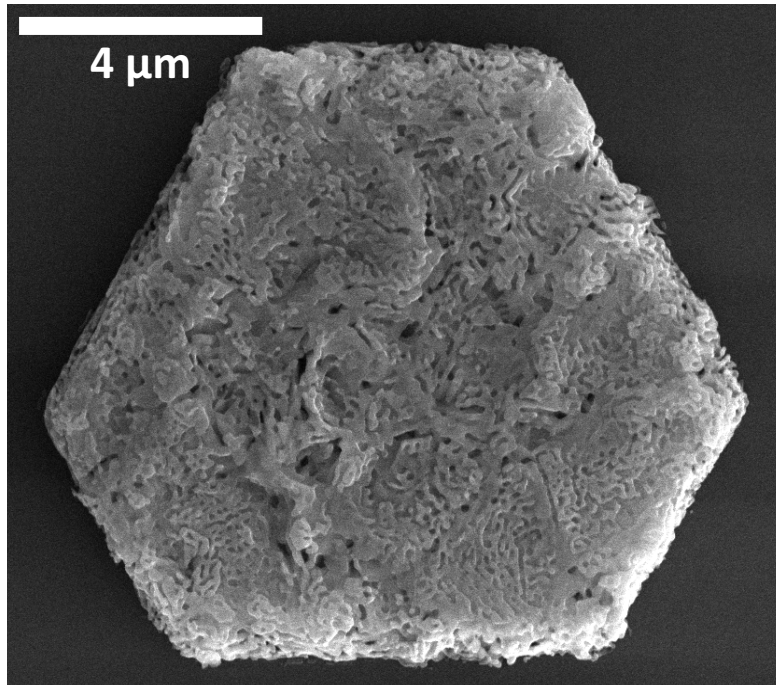
Smooth surface

120 °C



Small grains

160 °C

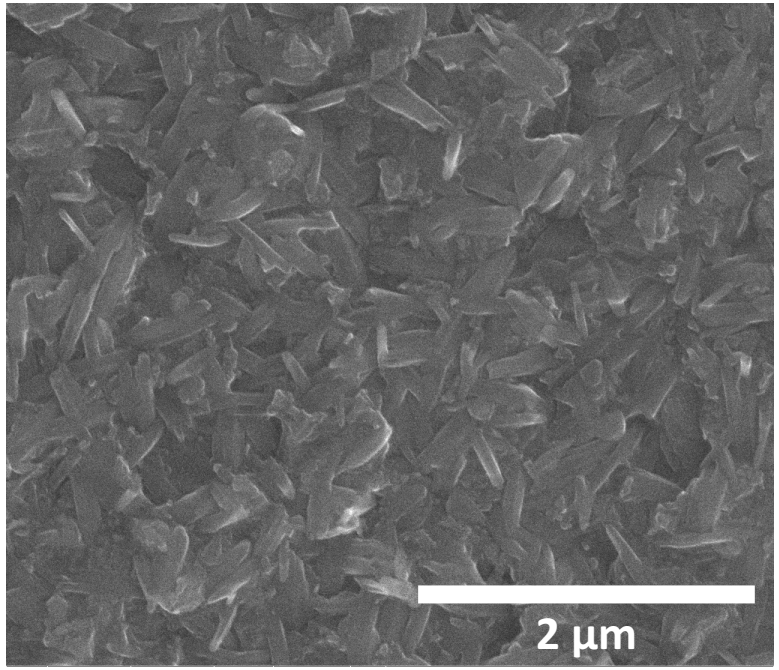
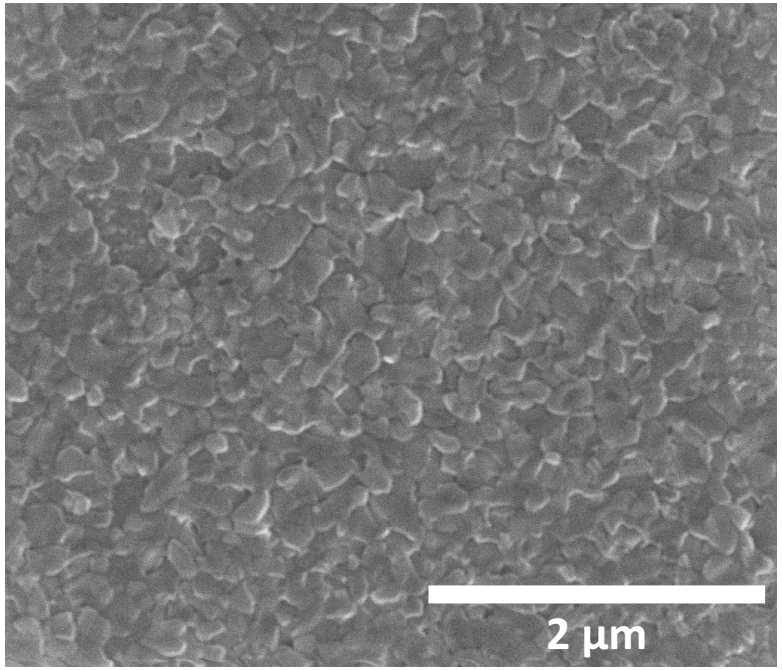
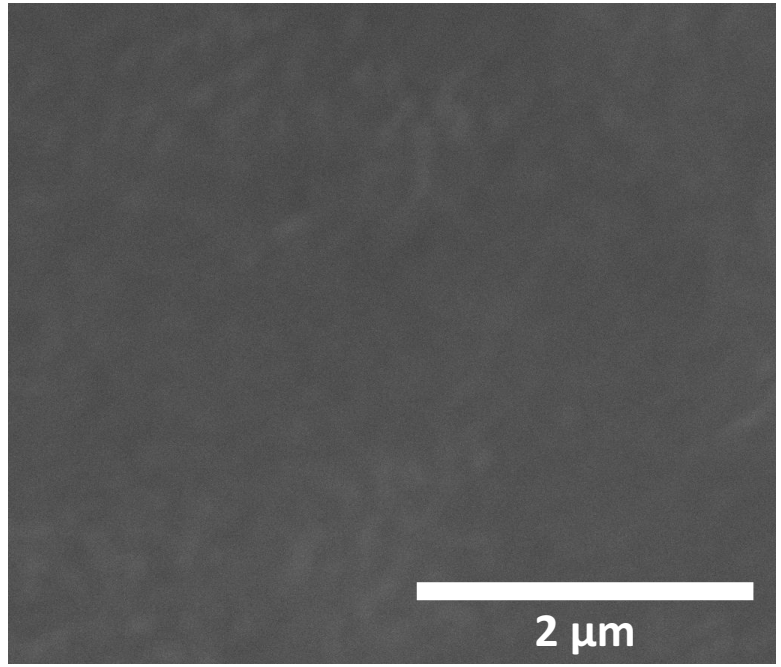


Irregularly shaped grains

Changes in surface morphology

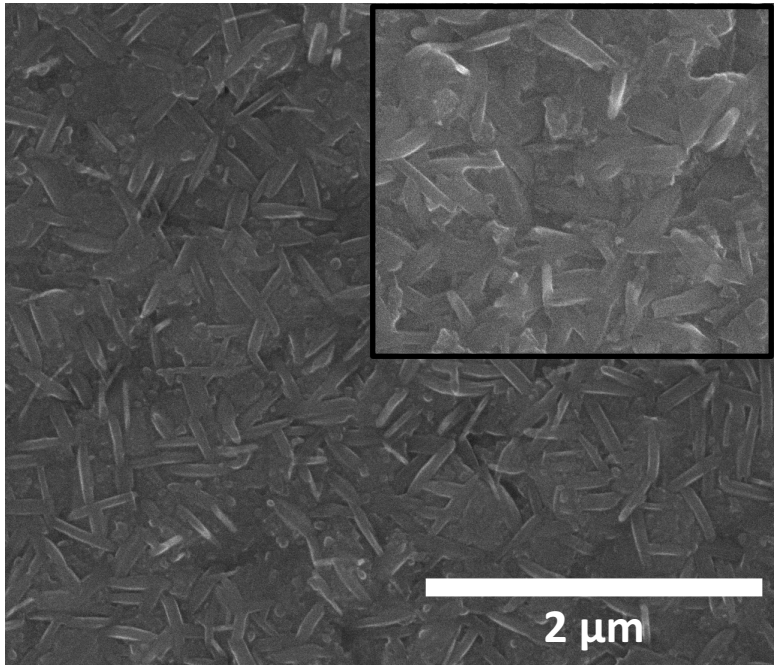
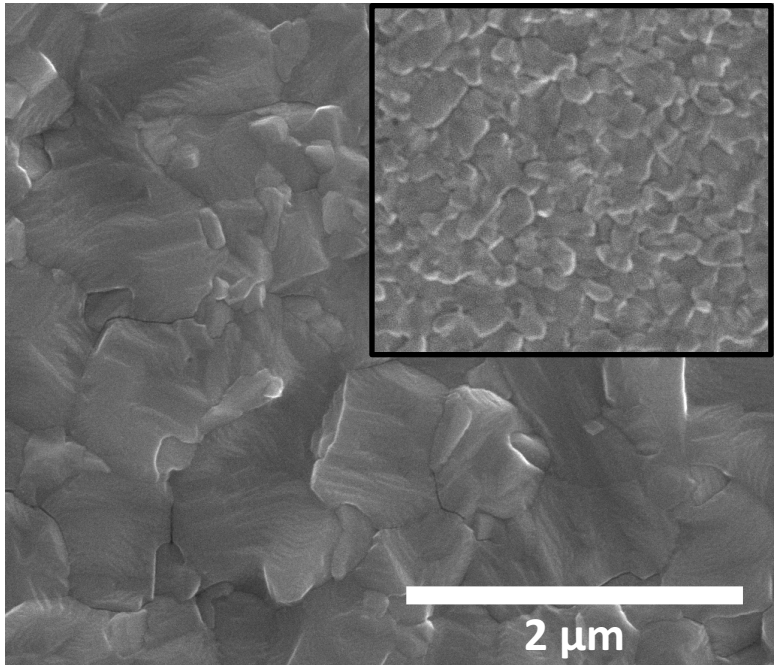
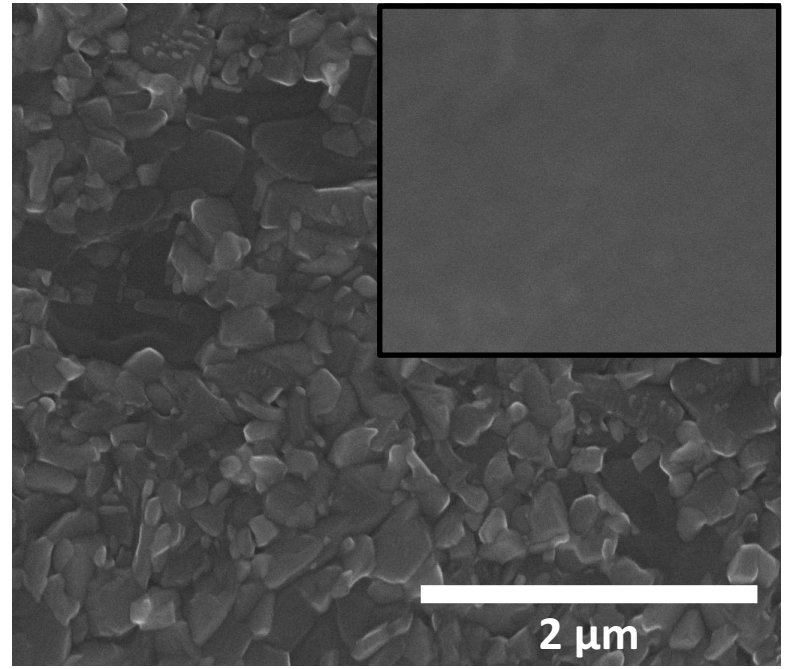
Effect of carrier gas flow and reaction time

15 minutes reaction at 120 °C

30 sccm	100 sccm	180 sccm
		
Pb:I 1 : 2.75	1 : 2.33	1 : 2.05
Ribbon-shaped grains	**Small grains**	**Absence of grains**

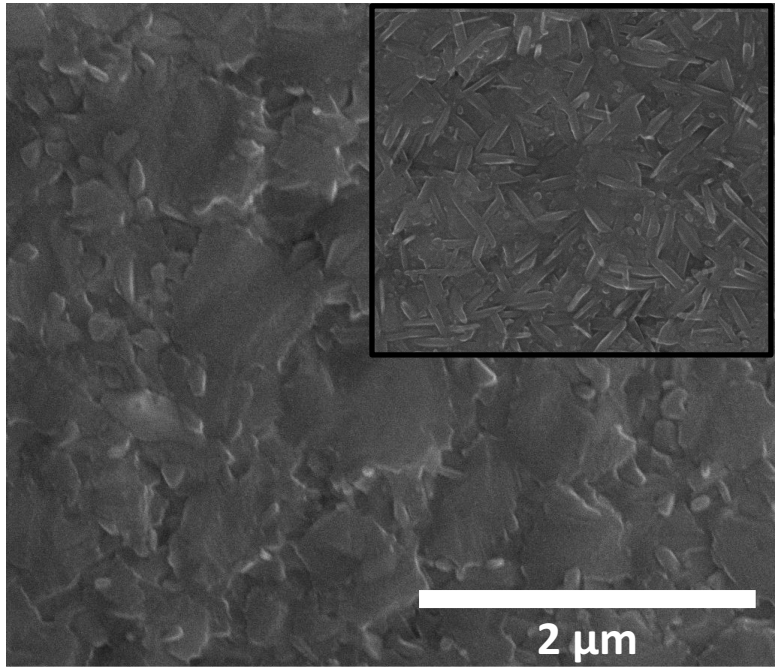
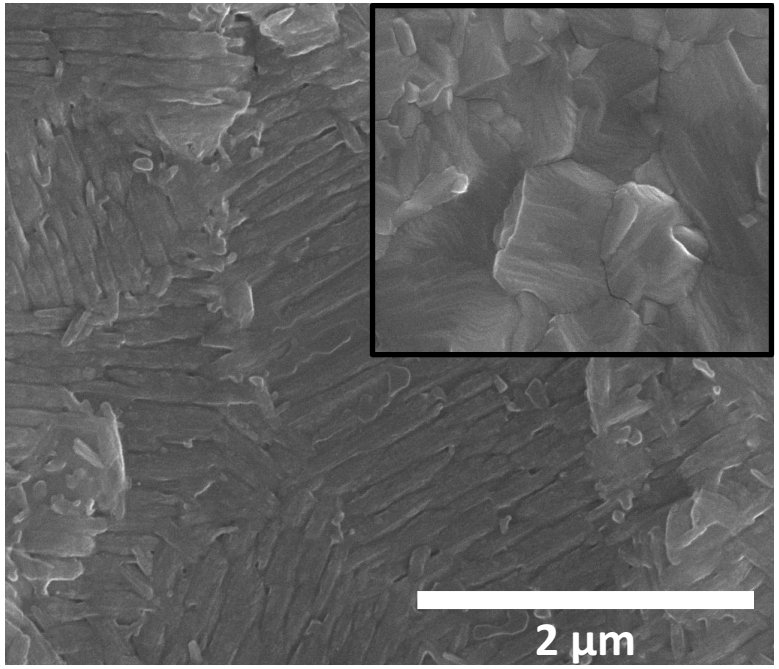
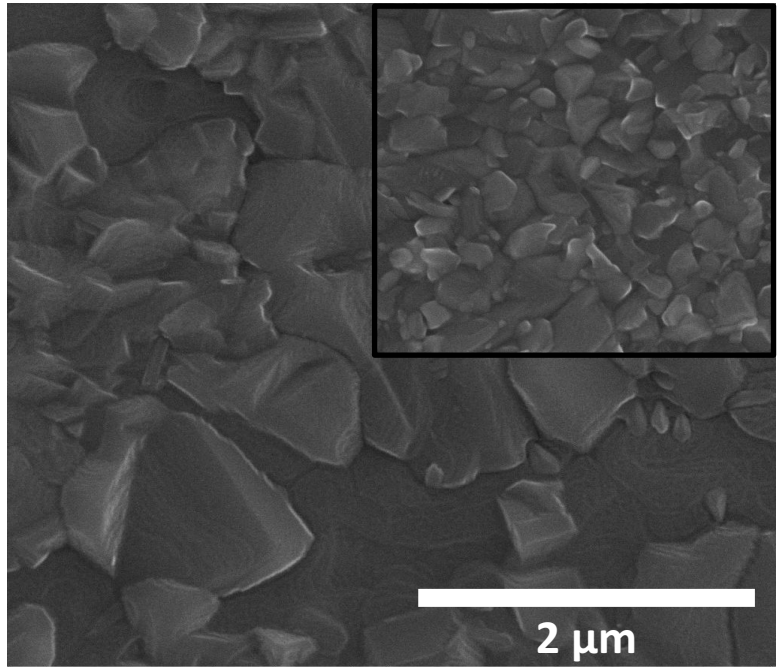
Effect of carrier gas flow and reaction time

45 minutes reaction at 120 °C

30 sccm	100 sccm	180 sccm
		
Pb:I 1 : 3.00	1 : 2.73	1 : 2.50
Ribbon-shaped grains	**Large and crystalline grains**	**Small grains and voids**

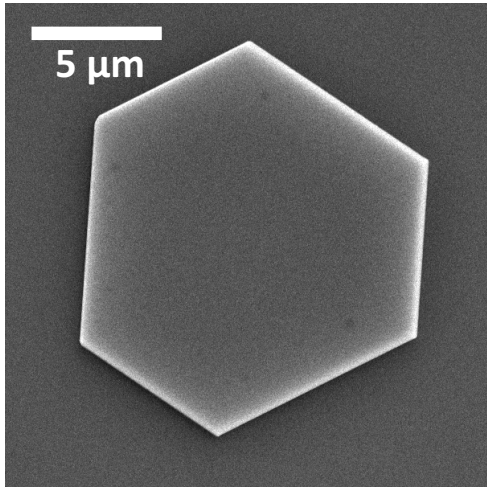
Effect of carrier gas flow and reaction time

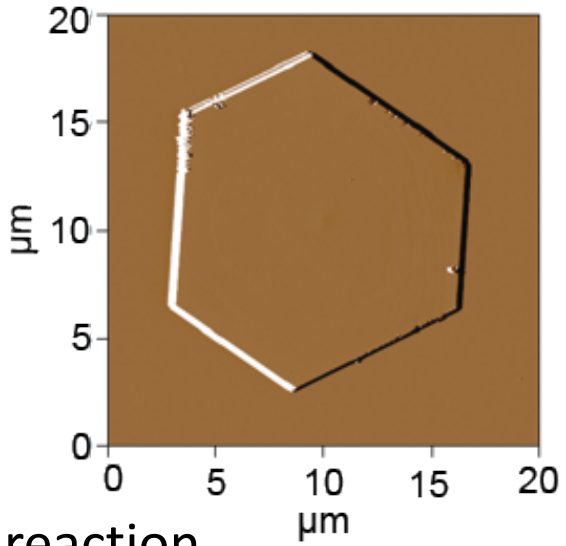
120 minutes reaction at 120 °C

	30 sccm	100 sccm	180 sccm
			
Pb:I	1 : 3.05	1 : 3.11	1 : 2.60
	Large grains	**Aligned ribbon-shaped grains**	**Large grains and voids**

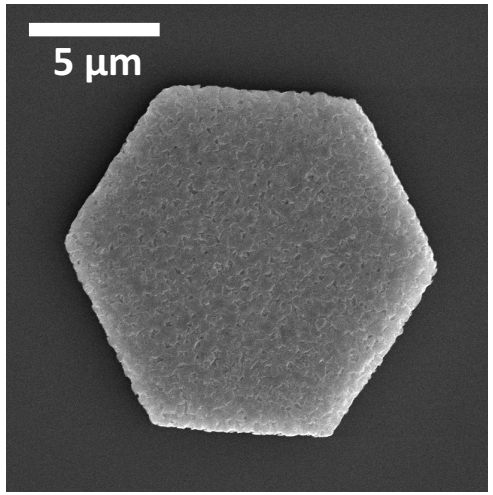
Atomic force microscopy Imaging

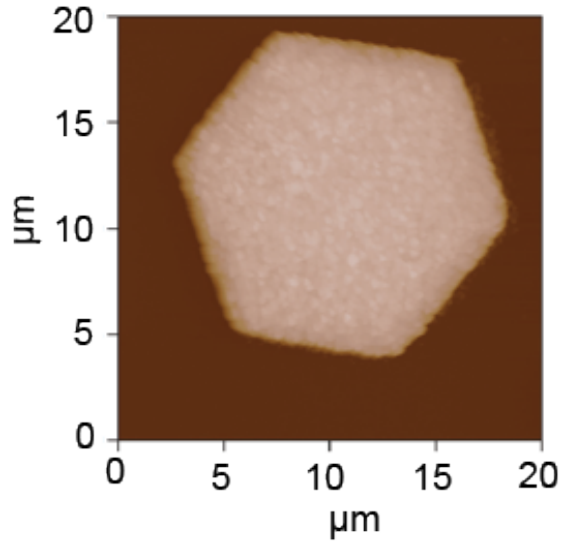
Before reaction



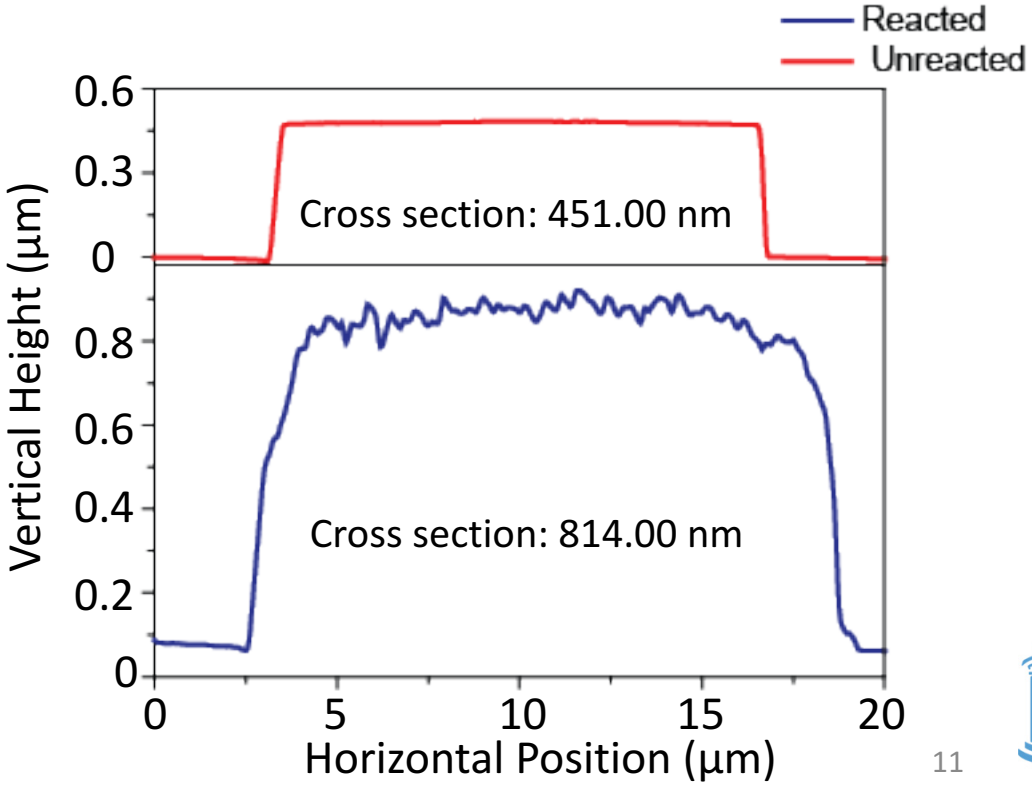


After reaction

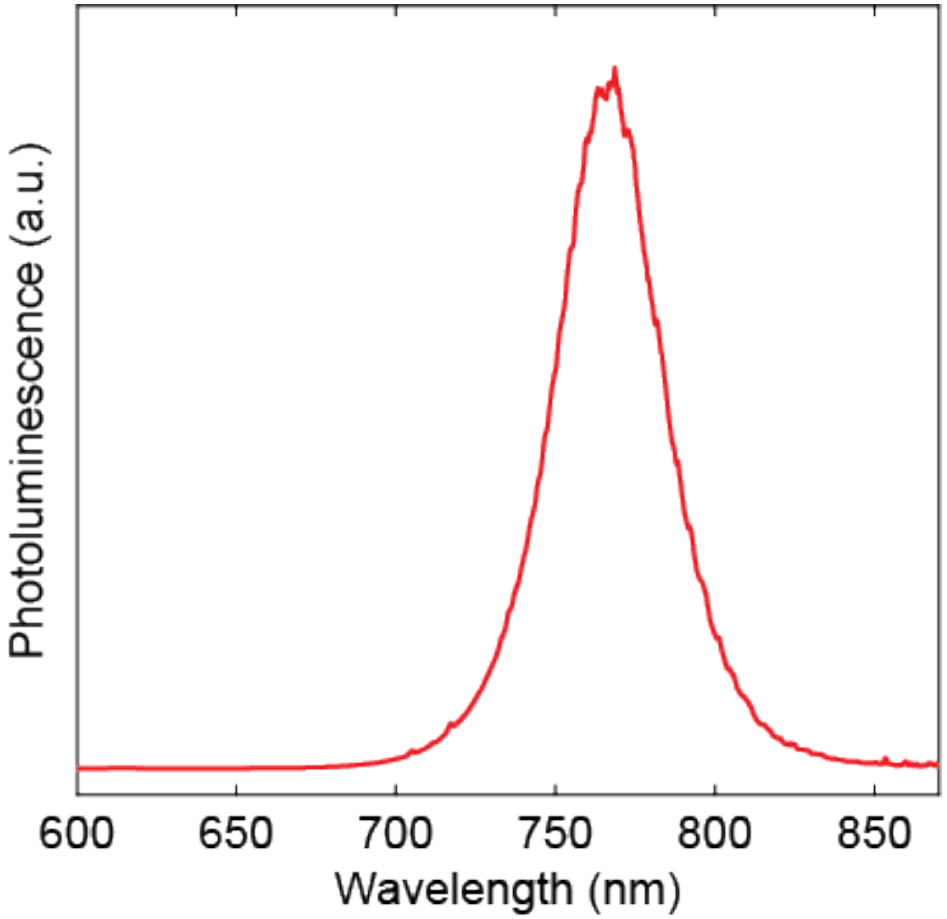


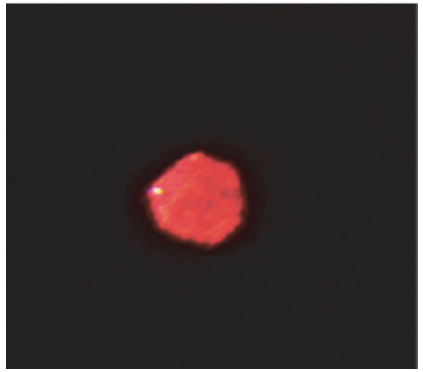


Morphological changes of PbI_2 crystallites upon reaction with MAI vapor to form $CH_3NH_3PbI_3$.

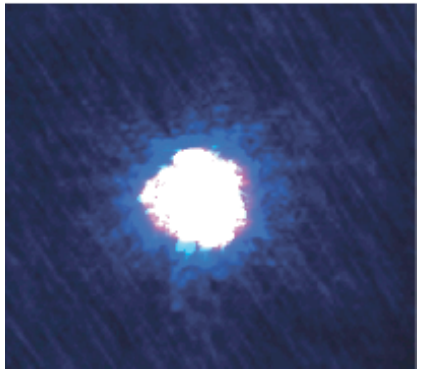


Photoluminescence Imaging

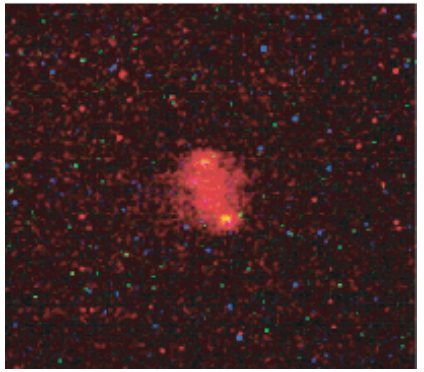




Optical image of a hexagonal platelet



480 nm excitation laser on the platelet



Photoluminescence

Photoluminescence emission spectrum exhibiting strong emission centered at 770 nm

Summary

- We have studied the impact of reaction conditions on the final surface morphology of perovskite using a chemical vapor deposition method.
- SEM and AFM analysis allow for direct imaging in the changes of surface morphology.
- Photoluminescence measurements allow for determination of emission properties of perovskite.

Acknowledgements

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Prof. James Cahoon
Jonathan Meyers
David J. Hill
Seokhyoung Kim
Cahoon Research Group

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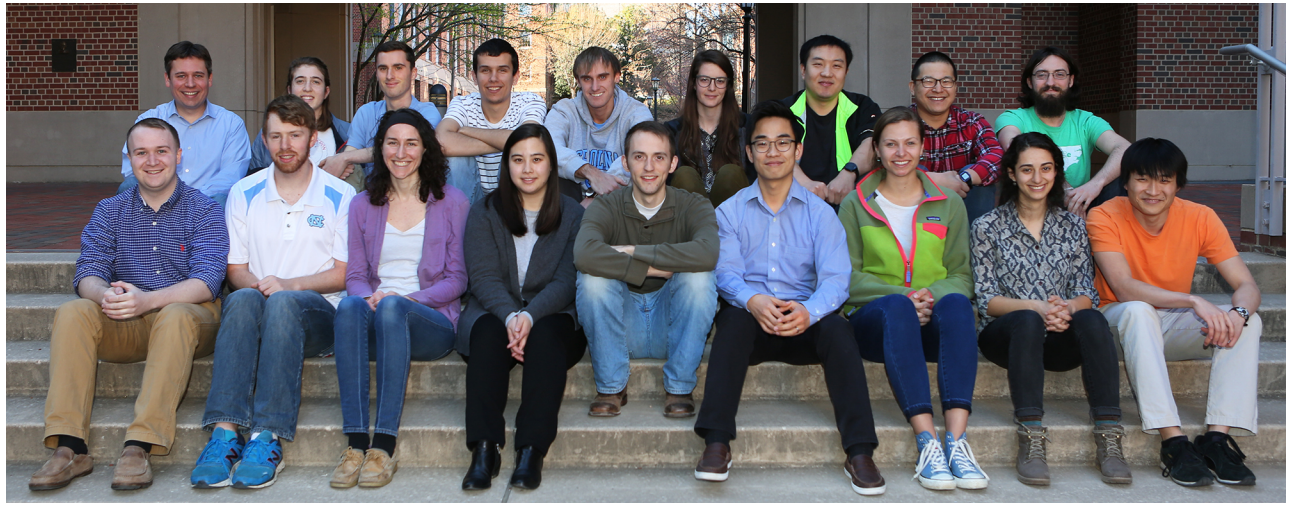
Research Triangle Nanotechnology Network (RTNN) Fellowship



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