Synthesis of Lead Iodide Perovskites for Solar Cell Application

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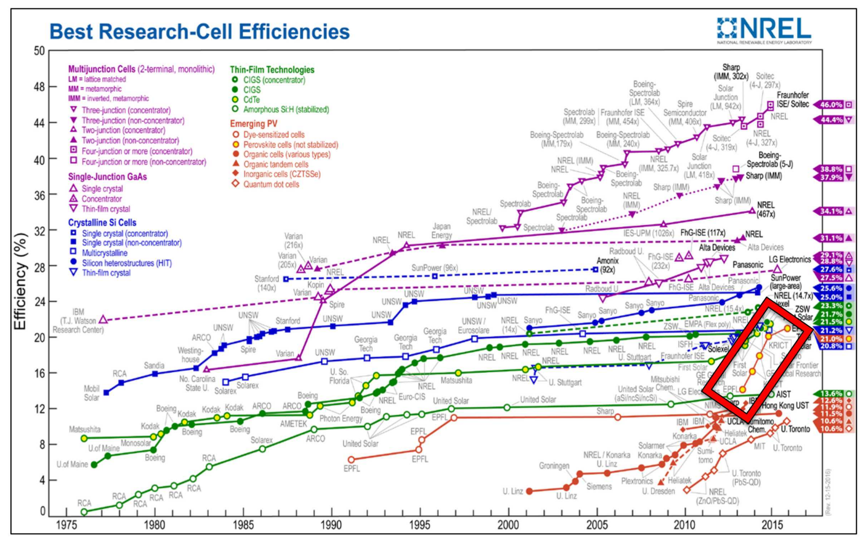
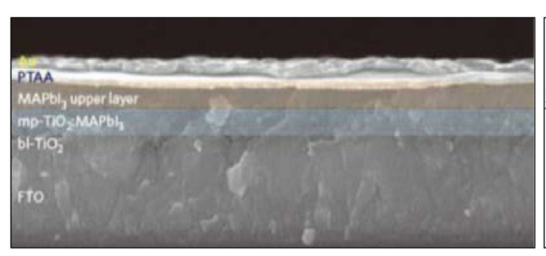
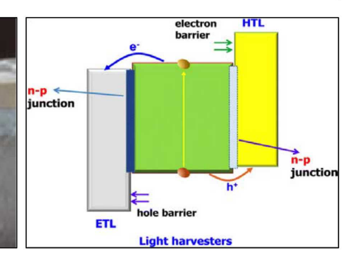
Background

- Perovskite solar cells exhibit efficiencies as high as 21 %
- Suitable photovoltaic band gap: 1.5-1.4 eV
- High absorption coefficient: 10^5-10^4 cm^{-1}
- Low exciton binding energy <50 meV
- Long charge carrier diffusion length: ~175µm







Seo J., Et al. *Accounts of Chemical Research* 2016 *49* (3), 562-572, *NREL: Home Page.* National Renewable Energy Laboratories, 29 June 2016

Current Lead Iodide Perovskite Nanocrystal Synthesis

Step 1: Synthesis of lead iodide nanocrystal precursor

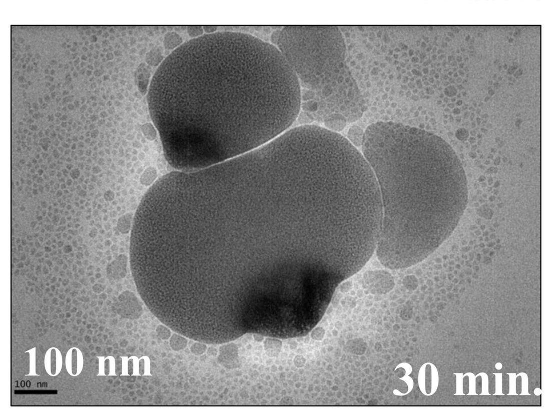
$(CH_3CH_2CH_2CH_2)_4N(I)$ —(1-Octadecene, Oleylamine)→ $(CH_3CH_2CH_2CH_2)_3N + CH_3CH_2CH_2CH_2NH_2(CH_2)_9CH_3(I)$

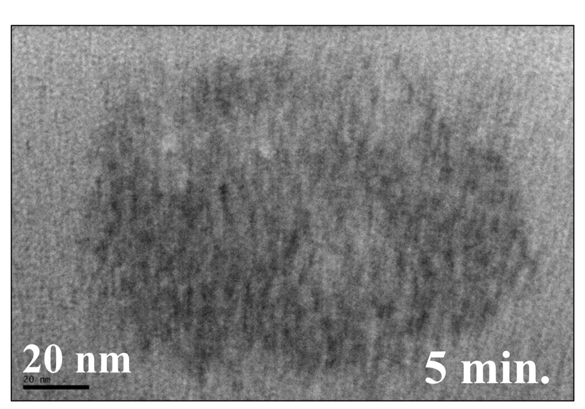
+

PbO —(Oleic Acid, 1-Octadecene)→ $(C_{17}H_{31}COOH)_2Pb$

↓ 5-30 minutes

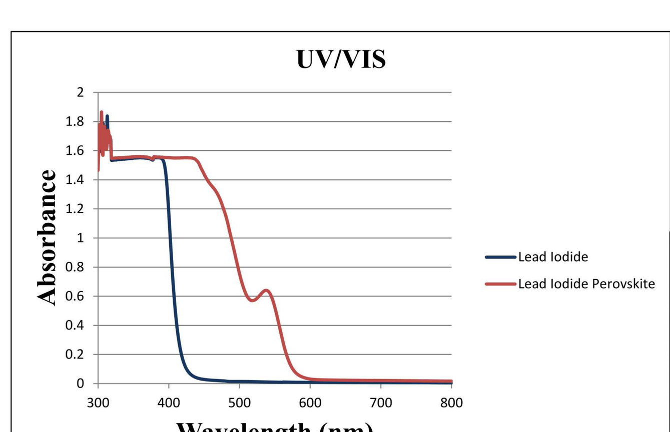
PbI_2

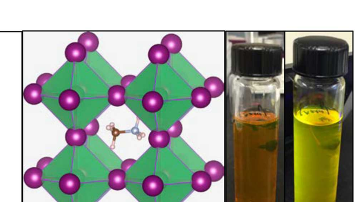


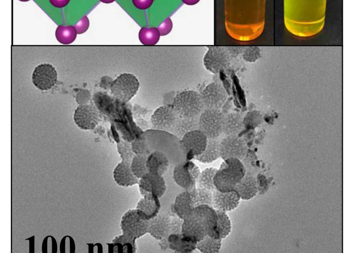


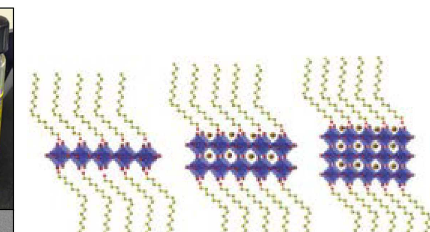
Step 2: Synthesis of two dimensional lead iodide perovskite using the methylammonium cation

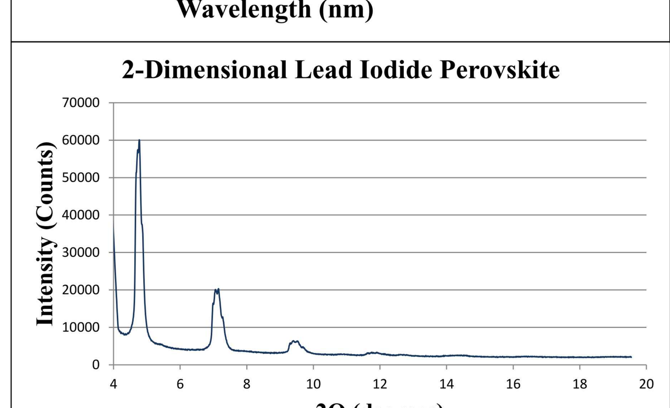
$PbI_2 + CH_3NH_3I \xrightarrow{\text{Octylammonium iodide}} R_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$











- Synthesized the n=2 lead iodide perovskite structure
- All washing methods resulted in degradation of the product
- Removal of excess ligand is necessary for solar cell fabrication

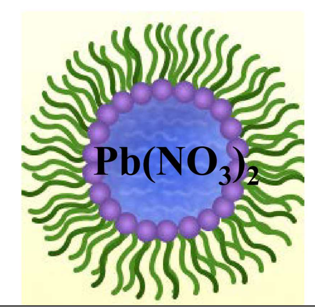
Hassan Y., et al. *Adv. Mater. Advanced Materials* 28.3 (2015): 566-3. Web.
Christopher E, Et al. *Nature Communications Nat Comms* 6, 2015., Hassan Y., et al. *Adv. Mater. Advanced Materials* 28.3 (2015): 566-73. Web

Purpose

Particle uniformity is essential for consistent electrical properties and increased efficiency in perovskite based solar cells. Our goal is to synthesize and control uniform lead iodide perovskite crystals and assemble them into highly ordered crystalline thin films for use in heterojunction solar cells.

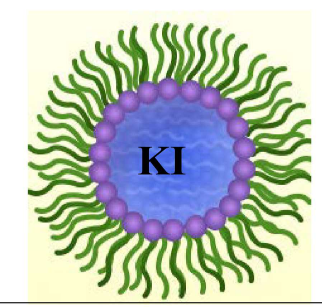
Improved Lead Iodide Perovskite Nanocrystal Syntheses and Results

Step 1: Synthesis of washable uniform lead iodide nanocrystal precursor



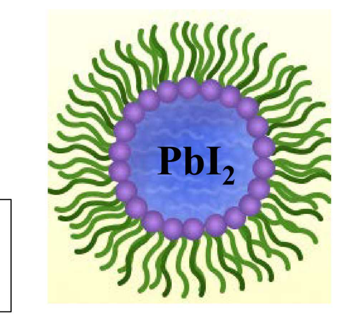
36.6 mM $Pb(NO_3)_2$ methanol solution at 53 °C

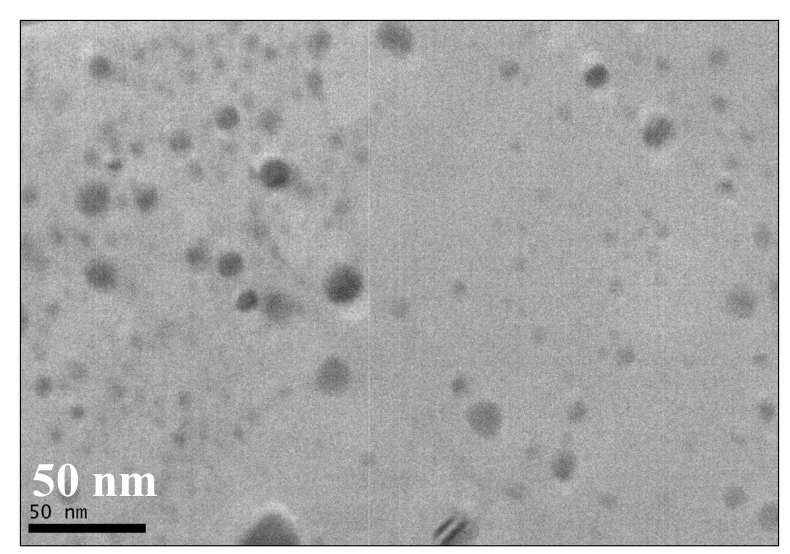
+

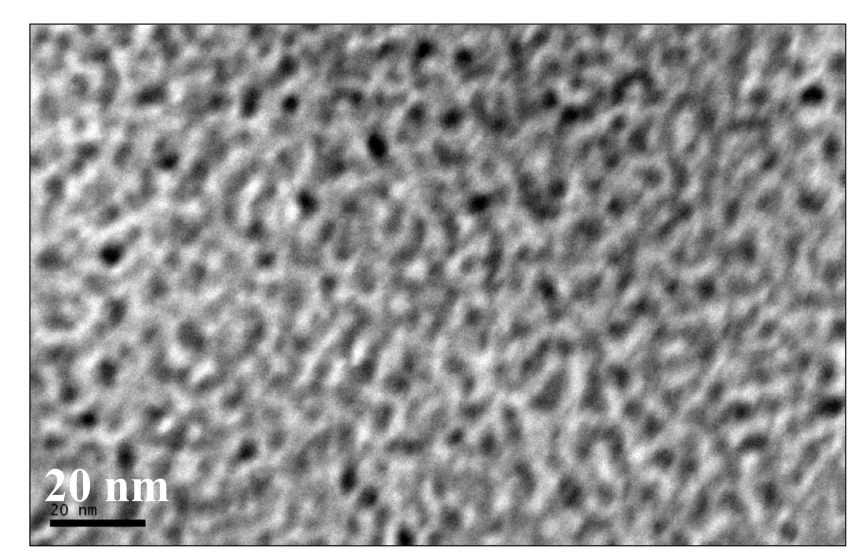


63.3 mM KI ethanol solution at 72 °C

→ 5 µM Tween 20 heptane solution



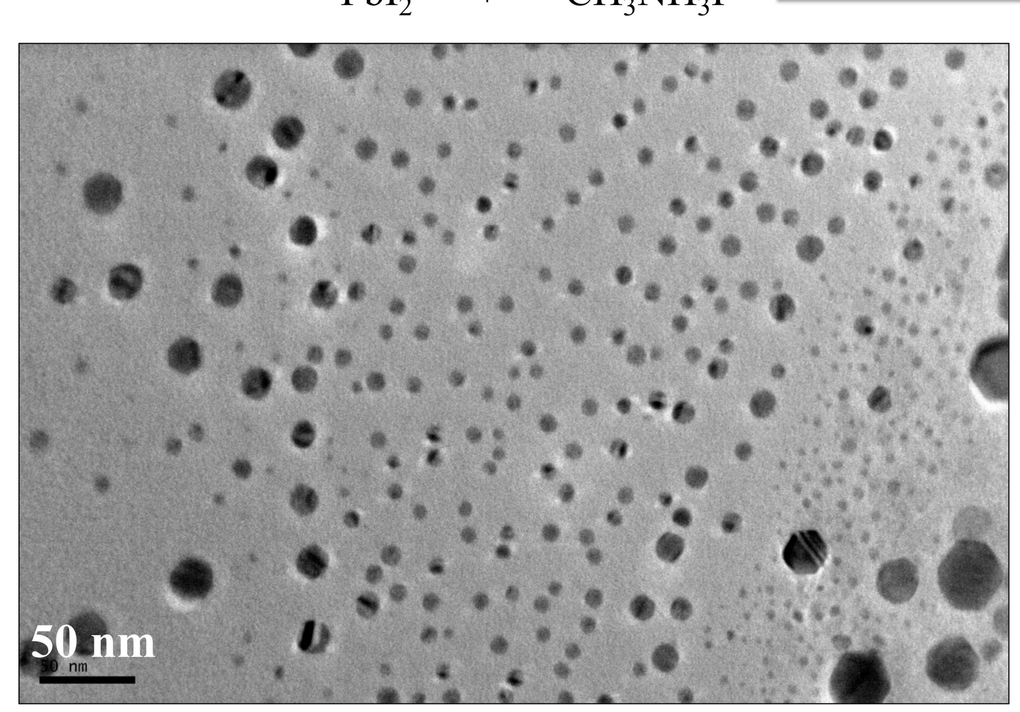




- Lead nitrate and potassium iodide were injected into the heptane solution consecutively with ten minutes in between each injection
- After injections and stirring the solution was heated to 90 °C to remove excess solvent
- Products were washed three times in water to remove excess Tween 20

Step 2: Synthesis of washable lead iodide perovskite nanocrystals using a methylammonium cation

$PbI_2 + CH_3NH_3I \xrightarrow{\text{Isopropyl Alcohol, 50°C}} CH_3NH_3PbI_3$



- The lead iodide precursor was injected into a solution of isopropyl alcohol and methylammonium iodide stirring in an inert atmosphere at 50°C
- The nanocrystals are free of high boiling point solvents and are easily separated from solution
- Size distribution = 13.6 ± 5.3 nm
- Current perovskite solar cell absorber layers utilize perovskite crystals from 50-500 nm.

Remaining Problems: The synthesized crystals are degraded when exposed to humidity. Secondly, they have a phase change around 50-60 °C rendering them thermally unstable

Step 3: Synthesis of thermally stable lead iodide perovskite using a formamidinium cation, lead iodide DMSO complex precursor, and sonication

0.1 M PbI_2(DMSO) in IPA

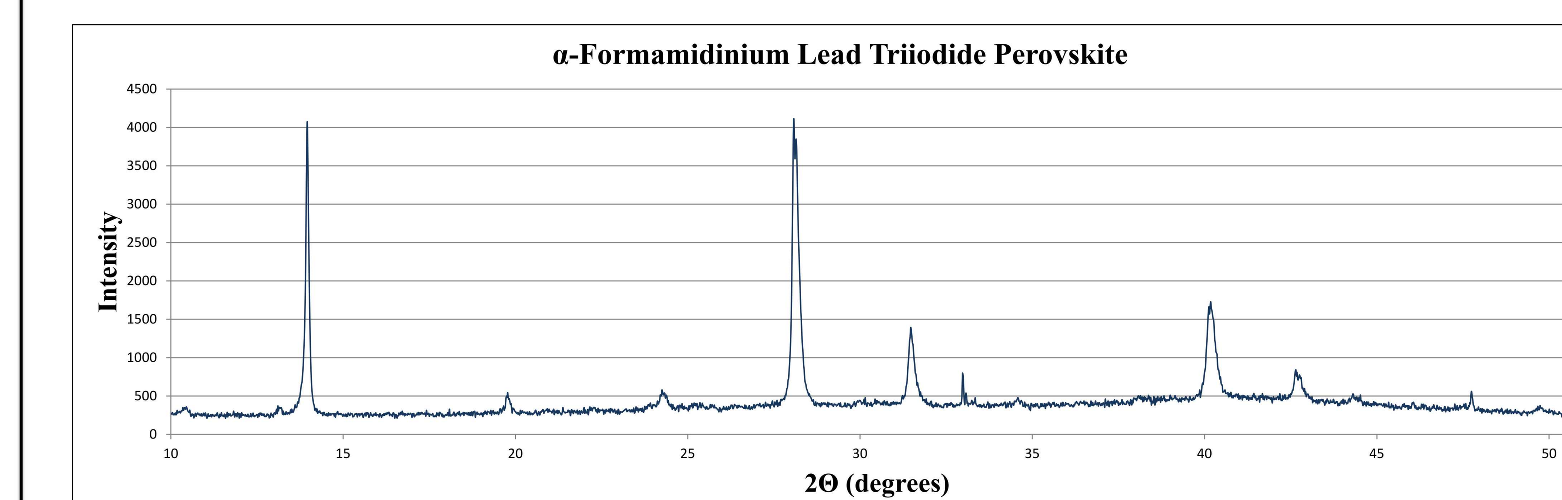
+

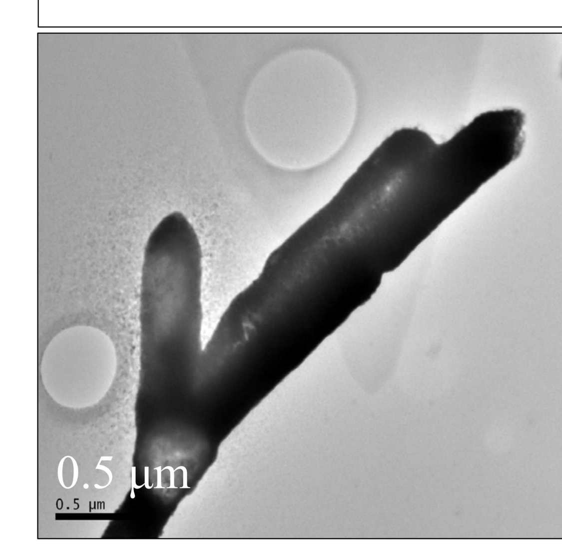
0.1 M FAI in IPA

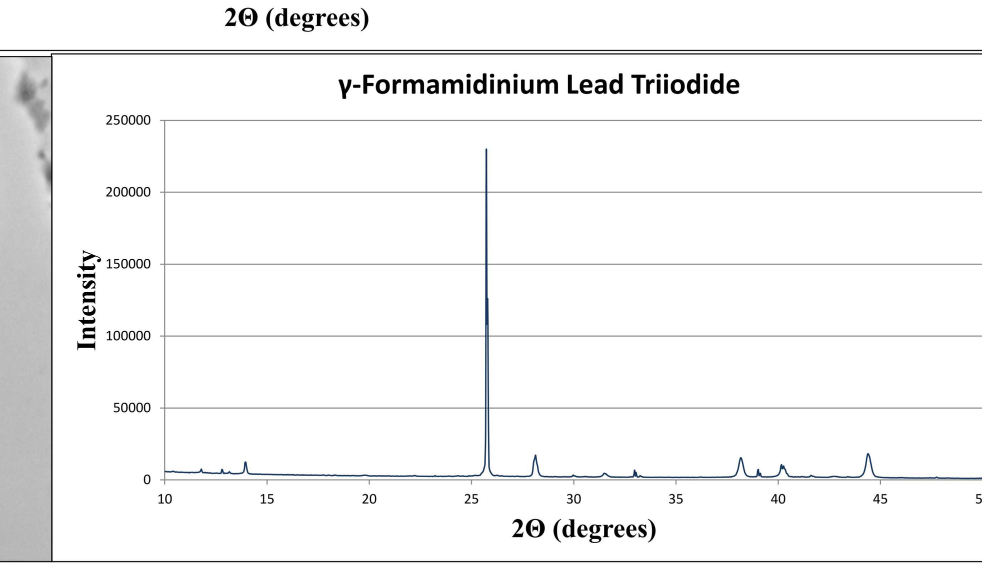
→ Sonication, 20 minutes

$FAIPbI_3$ in IPA

- Only the α-phase of the final product has a perovskite structure and is generally exhibited at temperatures above 150 °C
- The α-phase was synthesized directly after sonication, but returned to γ-phase
- α-phase exhibited again after annealing at 150 °C
- Use of pure PbI_2 precursor will not display complete phase conversion
- The formamidinium cation increases thermal stability and decreases the band gap of the final product







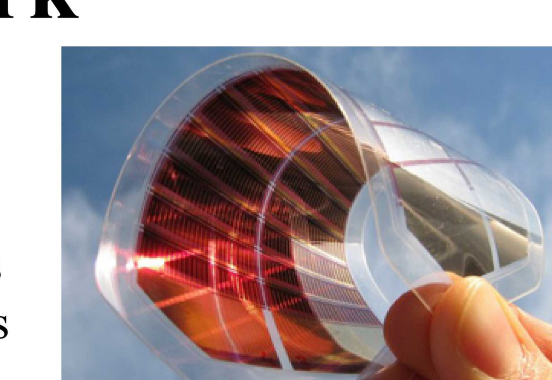
Han, Q., et al. (2016), Single Crystal Formamidinium Lead Iodide (FAPbI3): Insight into the Structural, Optical, and Electrical Properties. Adv. Mater., 28: 2253–2258.

Conclusions

We successfully developed a size tunable lead iodide nanocrystal synthesis, a uniform clean perovskite nanocrystal, and a sonochemical synthesis of formamidinium lead iodide perovskite. The control of the size and uniformity of the lead iodide perovskite nanocrystals is essential for the synthesis of uniform perovskite absorber layers. Also, the formamidinium lead iodide perovskite provides a band gap closer to the ideal 1.35 eV for a solar cell absorber layer. Better control over the size, assembly, and phase of lead iodide perovskite will lead to consistently efficient perovskite solar cells.

Future Work

Perovskite thin films are unstable in atmospheric conditions due to humidity. To improve this various surfactants and new cations must be explored. Our work will focus on stabilization and new deposition techniques for the described perovskite syntheses.



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