

Background

Perovskites are materials with chemical formulas of the form ABX_3 , where A and B are cationic and X is an anion. Hybrid lead halide perovskites (where $CH_3NH_3PbI_3$, methylammonium lead iodide) is the most notable member of the family, have been known for decades, but several recent experiments have started a “perovskite fever” thanks to the dramatic increase in perovskite solar conversion efficiency observed over the course of only a few years.

To capitalize on this, we investigated lead halide perovskites with the intention of further improving the already excellent qualities of perovskite solar cells, particularly in the areas of energy absorption, quantum yield, carrier mobility and lifetime, and diffusion length. We aimed to synthesize members of two lead halide perovskite families - $CsPbX_3$ and $CH_3NH_3PbX_3$ - and examine their performance in the areas above given their prominence in the field of solar energy.

Structure

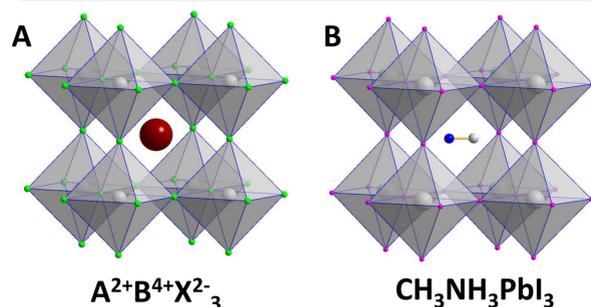


Fig. 1. Crystal structures of (A) generic perovskites such as $CsPbX_3$ and (B) methylammonium lead iodide ($MAPbI_3$, $CH_3NH_3PbI_3$). One cation is at the center of each cube, and another is found at the center of each octahedron. The corners of the octahedra are anions.

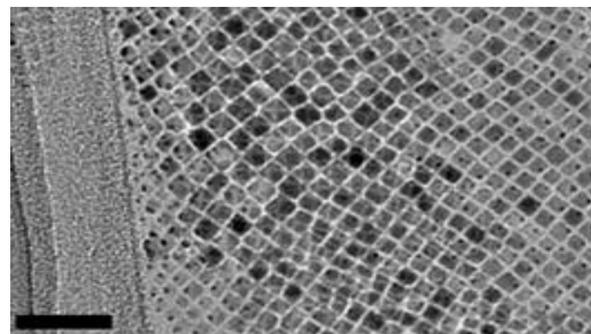


Fig. 2. Transmission electron microscopy image of $CsPbBr_3$ quantum dots. Scale bar is 50nm.

$CsPbX_3$ Nanoparticles

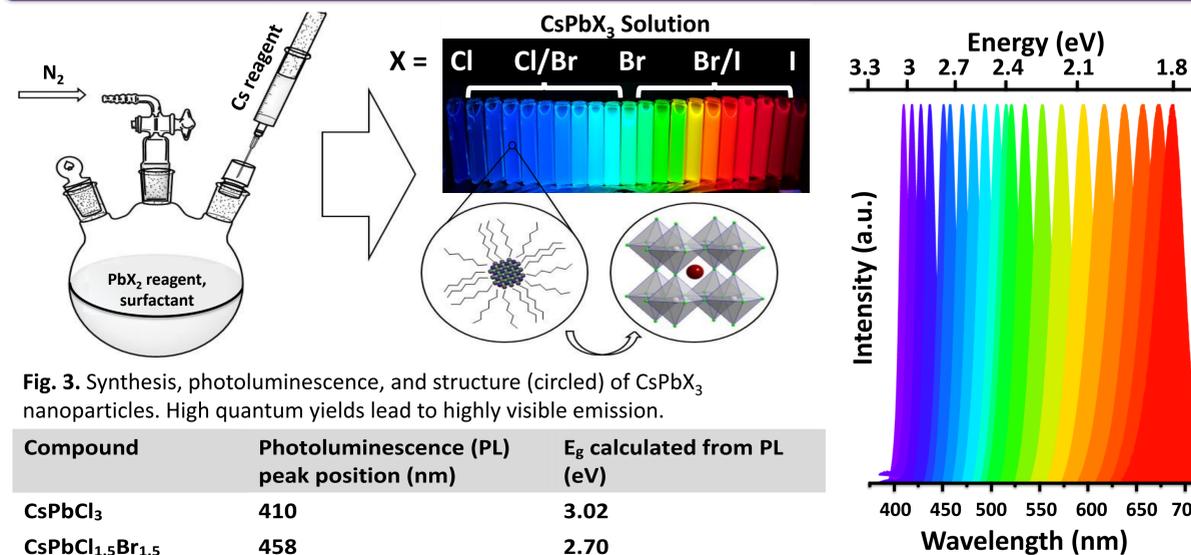


Fig. 3. Synthesis, photoluminescence, and structure (circled) of $CsPbX_3$ nanoparticles. High quantum yields lead to highly visible emission.

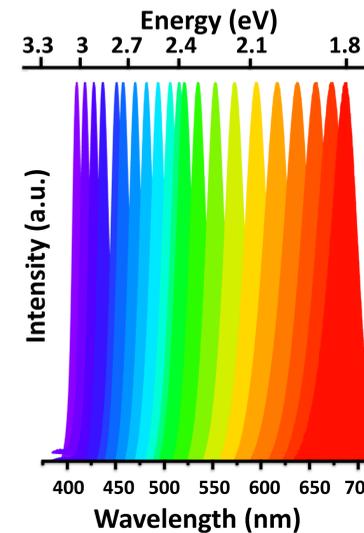


Fig. 4. Fluorimetric measurements of $CsPbX_3$ nanoparticles.

Methods

Synthesis of $CsPbX_3$ nanoparticles: Under an N_2 atmosphere, 15 mL of ODE, 3 mL of oleylamine, 1.5 mL of oleic acid and 0.54 mmol of PbX_2 should be added to a three-neck flask. The mixture should be degassed at $100^\circ C$ for 10 minutes, mixed at $100^\circ C$ for 30 minutes (until PbX_2 dissolves - $150^\circ C$ and 1 mL of trioctylphosphine are needed to dissolve $PbCl_2$) and then brought to desired temperature (typically $170^\circ C$). 0.55 mL of Cs-oleate should be quickly injected into the PbX_2 solution via glass syringe through a septum. After five seconds, the three-neck flask should be cooled down by the ice-water bath. Centrifugation can extract the nanoparticles, (5000 rpm, 5 min) which should then be redissolved in 8 mL of hexane. In the case of $CsPbCl_3$ and $CsPbBr_3$, 10 mL of acetone could be added to facilitate the precipitation.

Crystallization of $CH_3NH_3PbBr_3$: $PbBr_2$ and CH_3NH_3Br (1:1, 0.2 M) should be dissolved in N,N-dimethylformamide. $CH_3NH_3PbBr_3$ single crystals should grow along with the slow diffusion of the vapor of the anti-solvent dichloromethane (DCM) in to the solution.

Crystallization of $CH_3NH_3PbI_3$. The same technique and anti-solvent for crystallizing $CH_3NH_3PbBr_3$ applies. PbI_2 and CH_3NH_3I (1:3 by molar, 0.5 M PbI_2) should be dissolved in gamma-butyrolactone.

$CH_3NH_3PbX_3$ Devices

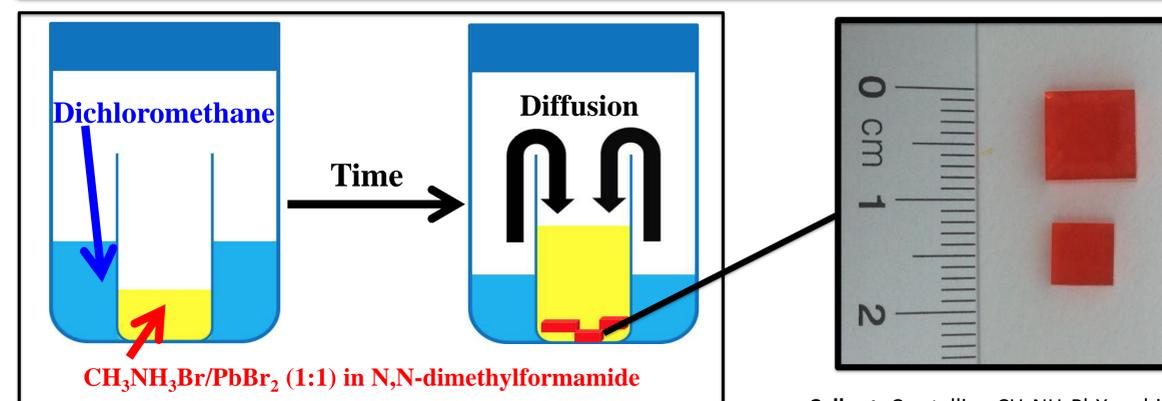


Fig. 5. Synthesis of $CH_3NH_3PbBr_3$ crystals, with callout of large crystals.

Callout: Crystalline $CH_3NH_3PbX_3$ exhibits charge transport efficiency that exceeds that of thin-film materials in mobility, lifetime, and diffusion length.

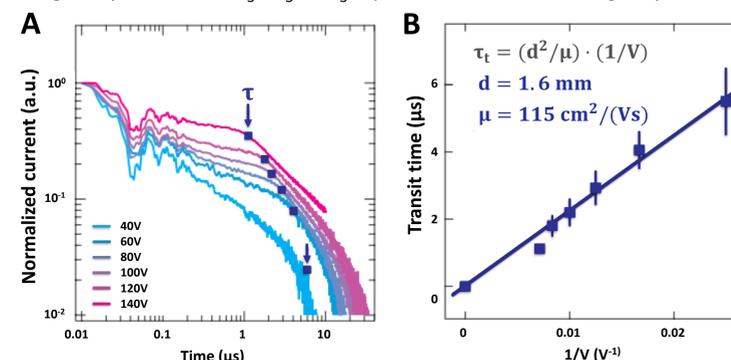


Fig. 6. Charge-carrier lifetime and mobility measurements of $CH_3NH_3PbBr_3$.

Summary

Simply-synthesized $CsPbX_3$ nanoparticles exhibit fluorescent quantum yields up to 90%, and their emission is in visible range of spectrum with a narrow band width. The emission wavelength can be modified by tuning both size and composition of the nanoparticles, which is most easily done through the choice of halide. This, in turn, can be accomplished prior to synthesis through precursor mixture or afterwards through stoichiometric mixture of nanoparticle solutions. This facile yet versatile means of control makes them desirable for absorbing energy in solar cells, as the wide range of wavelengths covered efficiently captures a broad spectrum of solar output.

$CH_3NH_3PbX_3$ perovskites performed exceptionally well, even relative to the highest in the efficiency competition. They exhibited electron mobilities up to 115 cm^2/Vs , a diffusion distance of up to $17\mu m$, and carrier lifetimes approaching $22ns$, which all contribute heavily to greater efficiency.

References

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