Lead Halide Perovskites: from Nanoparticles to Devices

Jacob D. Teeter, Takashi Komesu, Mikhail Shekhirev, Xin Huang, Tula R. Paudel, John Goza, Alexey Lipatov, Makhsud Saidaminov, Osman M. Bakr, Evgeny Y. Tsymbal, Axel Enders, Peter A. Dowben, Alexander Sinitskii

Background

Perovskites are materials with a chemical formula of the form ABX_3, where A and B are cationic and X is anionic. Hybrid lead halide perovskites, where $CH_3NH_3PbI_3$ (methylammonium lead iodide, $MAPbI_3$) is the most notable member of the family, have been known for decades, but several recent experiments started a "perovskite fever", thanks to the dramatic increases in perovskite solar conversion efficiency seen in only a few years.

To capitalize on this, we investigate 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

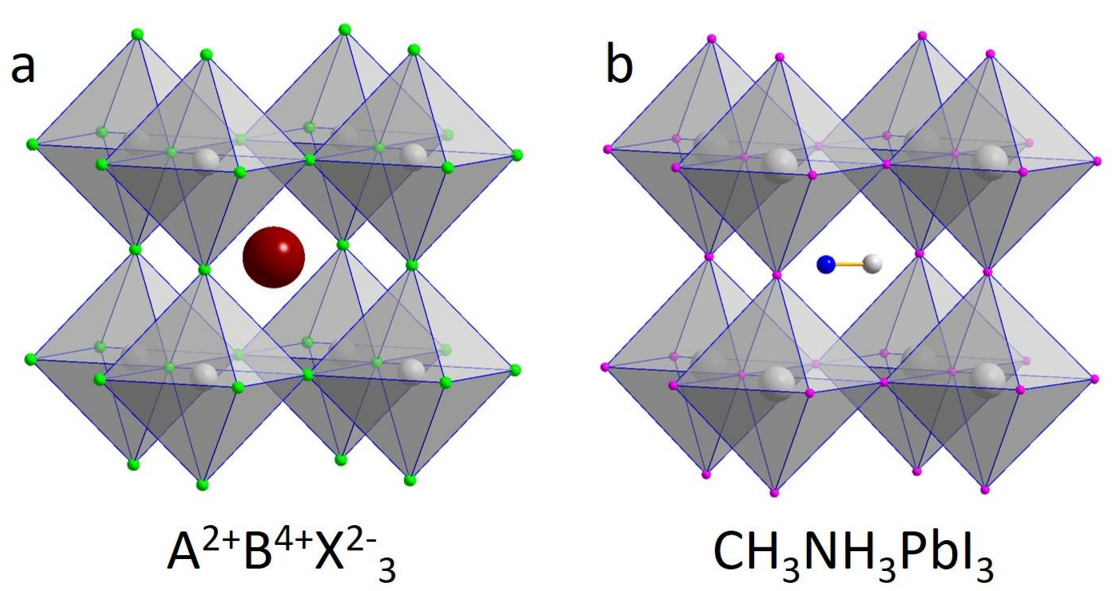

Fig. 1. Crystal structures of (A) generic perovskites such as $CsPbX_3$ and (B) $MAPbI_3$.

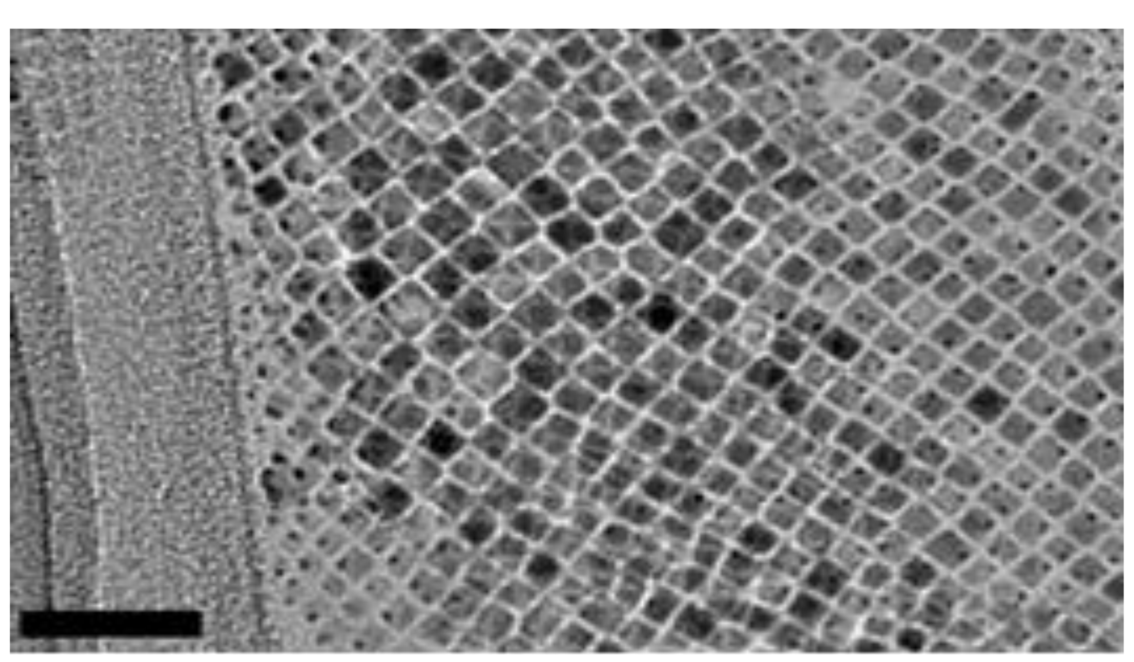

Fig. 2. Transmission electron microscopy image of $CsPbBr_3$ quantum dots. Scale bar is 50nm.

$CsPbX_3$ Nanoparticles

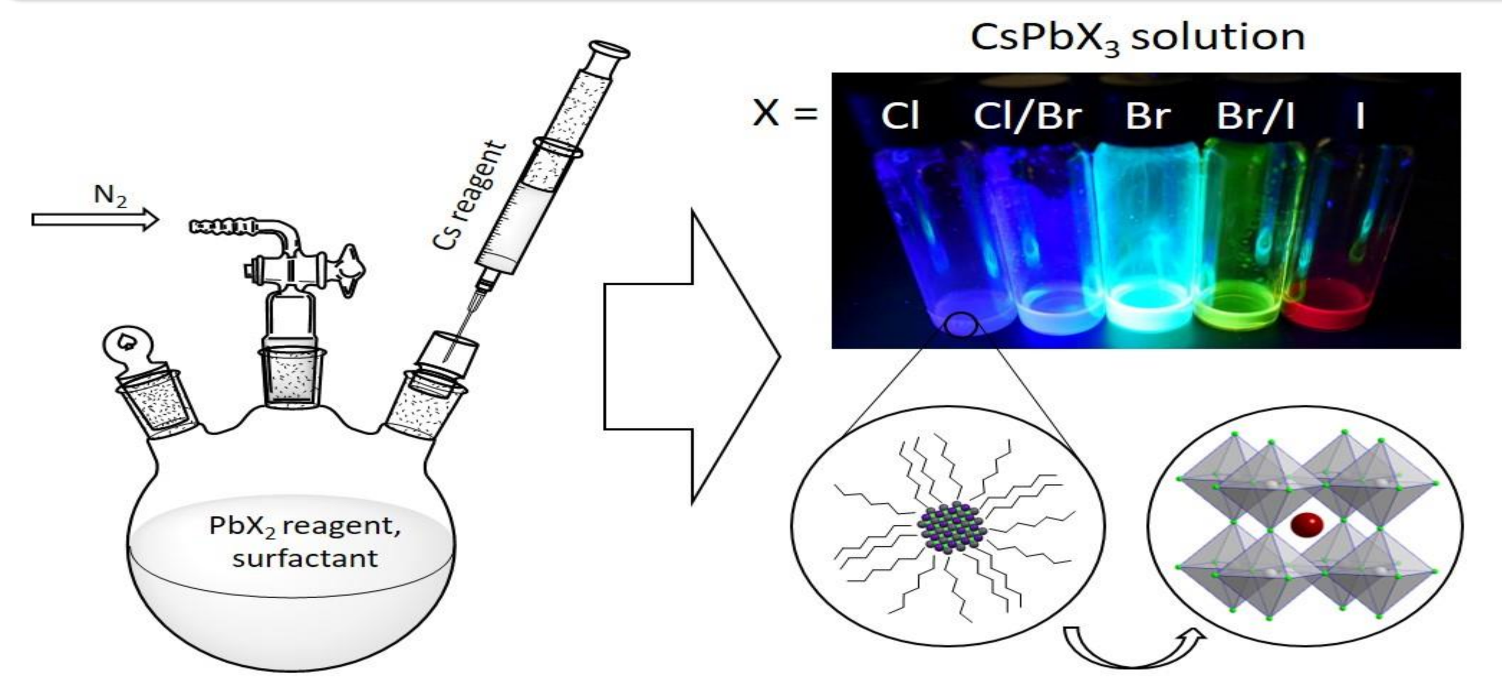

Fig. 3. Synthesis, photoluminescence, and structure (circled) of $CsPbX_3$ nanoparticles.

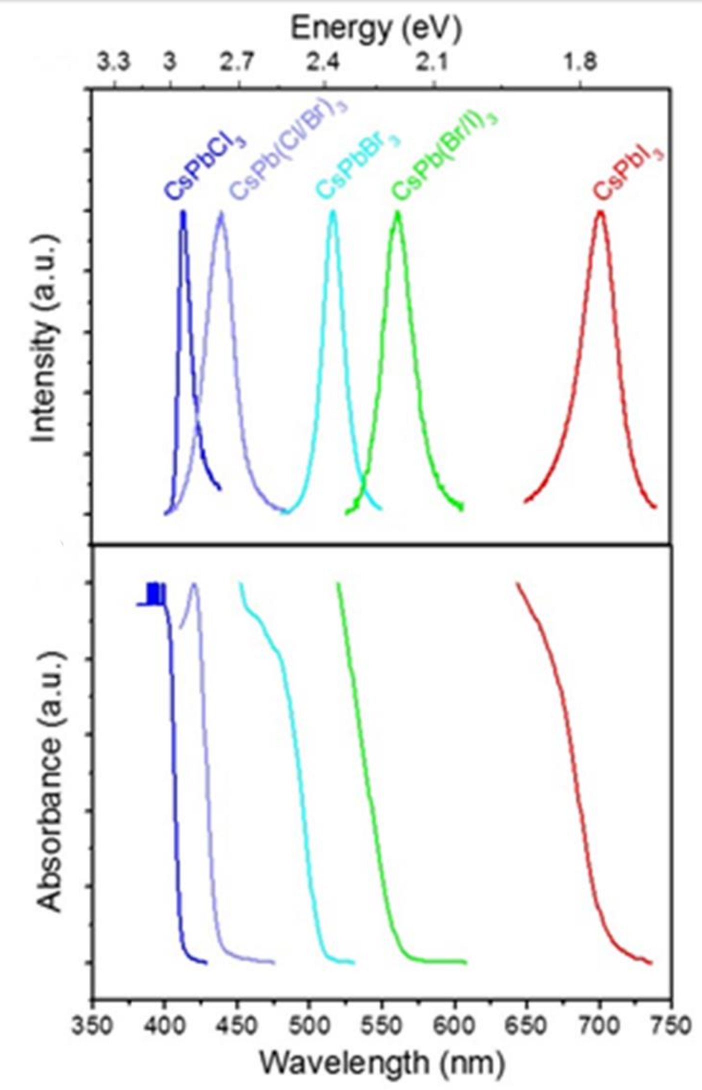

Fig. 4. Photoluminescence and ultraviolet-visible absorbance measurements of $CsPbX_3$ nanoparticles.

Band gap values calculated from photoluminescence and ultraviolet-visible spectra

Compound	Absorption onset from UV-vis (nm)	Photoluminescence peak position (nm)	E_g calculated from UV-vis (eV)	E_g calculated from PL (eV)
$CsPbCl_3$	410	414	3.02	2.99
$CsPb(Cl/Br)_3$	433	440	2.86	2.82
$CsPbBr_3$	507	517	2.45	2.40
$CsPb(Br/I)_3$	558	561	2.22	2.21
$CsPbI_3$	701	701	1.77	1.77

$CH_3NH_3PbX_3$ Devices

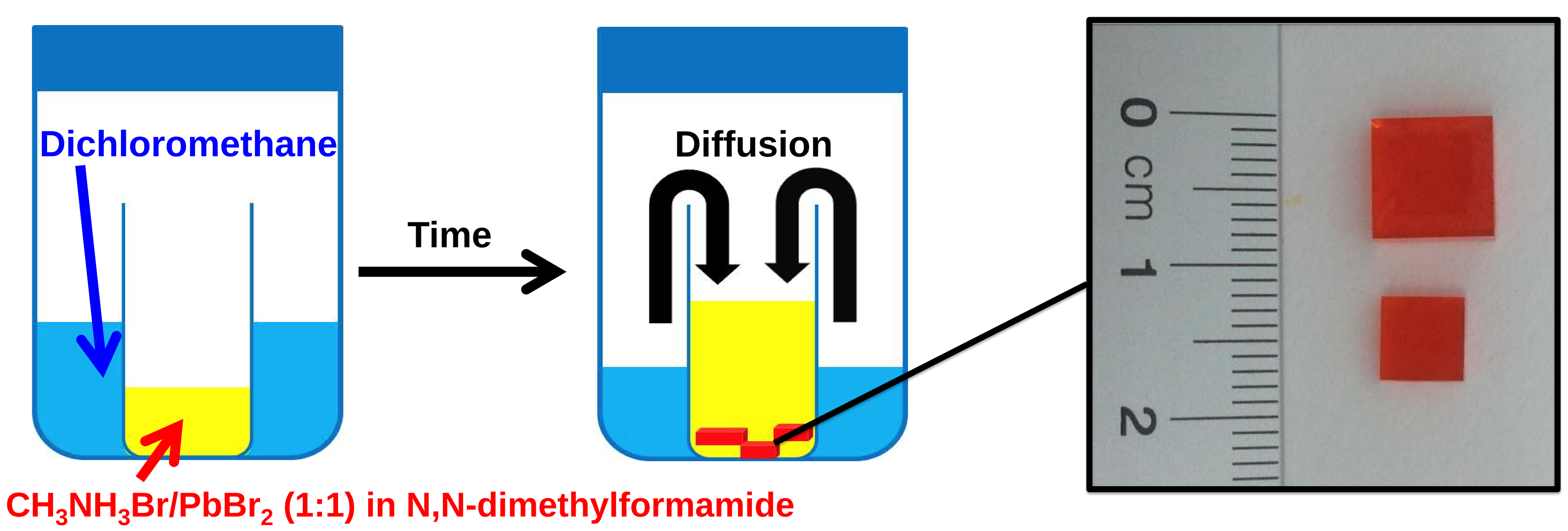

Fig. 5. Synthesis of $CH_3NH_3PbBr_3$ crystals, with callout of large crystals.

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

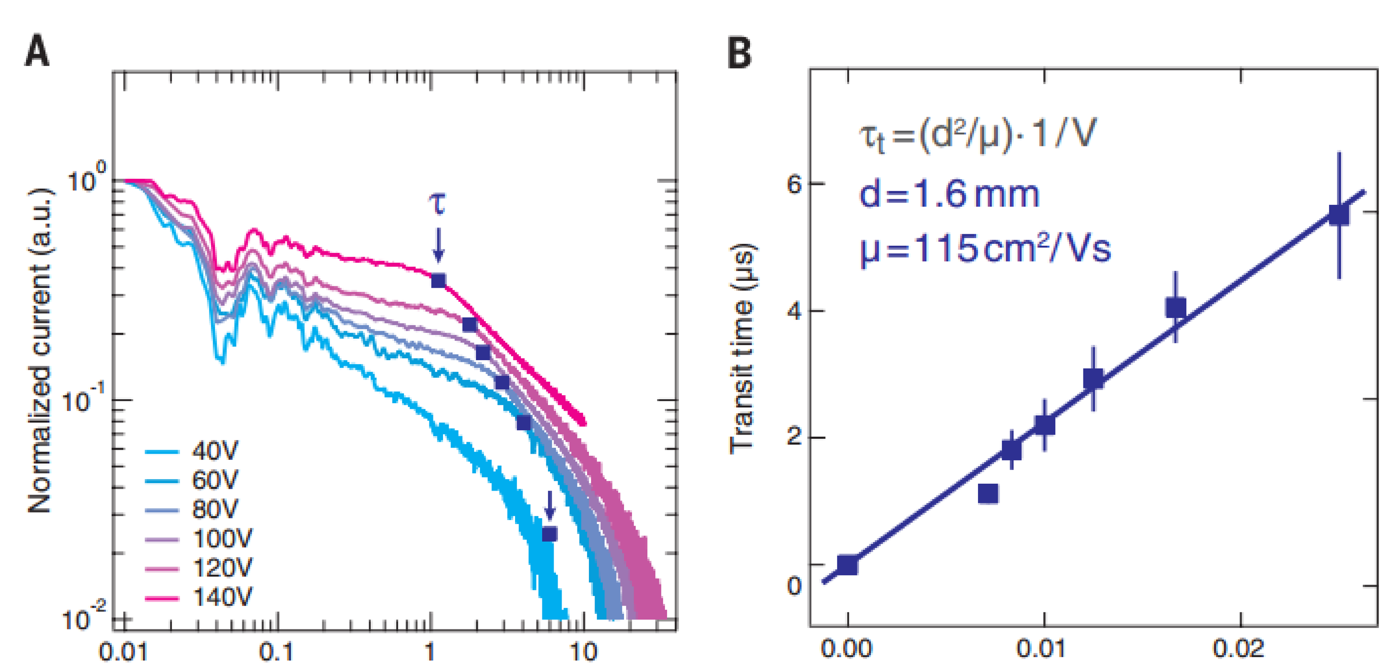

Fig. 6. (A) Charge-carrier lifetime and (B) mobility measurements of $CH_3NH_3PbBr_3$.

Methods

Synthesis of $CsPbX_3$ nanoparticles: Under a 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 ° C for 10 minutes, mixed at 100 ° C for 30 minutes (until PbX_2 dissolves, 150 ° C and 1 mL of trioctylphosphine are needed to dissolve $PbCl_2$) and then brought to desired temperature (typically 170 ° 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 $CH_3NH_3PbBr_3$: $PbBr_3$ 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) into the solution.

Crystallization of CH_3NH_3PbI3. The same technique and anti-solvent for crystallizing CH_3NH_3PbBr3 applies. PbI_2 and CH_3NH_3I (1:3 by molar, 0.5 M PbI_2) should be dissolved in gamma-butyrolactone.

Summary

Simply-synthesized $CsPbX_3$ nanoparticles can exhibit fluorescent quantum yields up to 90%, and their emission is in the 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 makes them highly 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 also performed exceptionally well, even relative to the highest performers in the efficiency competition. They exhibited electron mobilities up to 115 cm^2/Vs, diffusion lengths of up to 17μm, and carrier lifetimes approaching 1μs, all of which contribute greatly to pushing the boundaries of efficiency.

References

1) Shekhirev, M.; Goza, J.; Teeter, J.D.; Lipatov, A.; Sinitskii, A. Synthesis of cesium lead halide perovskite quantum dots. *J. Chem. Ed.,* submitted for publication, 2017.
2) Komesu, T.; Huang, X.; Paudel, T.R.; Losovyj, Y.B.; Zhang, X.; Schwier, E.F.; Kojima, Y.; Zheng, M.; Iwasawa, H.; Shimada, K.; Saidaminov, M.I.; Shi, D.; Abdelhady, A.L.; Bakr, O.M.; Dong, S.; Tsymbal, E.Y.; Dowben, P.A. Surface electronic structure of hybrid organo lead bromide perovskite single crystals. *J. Phys. Chem. C.* **2016**, *120*, 21710–21715
3) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P.A.; Mohammed, O.F.; Sargent, E.H.; Bakr, O.M. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **2015** *347*, 519-522 (6221).