New insights on halide perovskites from nanoparticle transformations, and hybrid quantum dot-perovskite solar cells

Dan Oron

Dept. of Physics of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel. dan.oron@weizmann.ac.il

The study of colloidal halide perovskites nanoparticles and their formation and transformation processes grants us with new insights about the stability and phase diagram of these materials. It also highlights the tremendous possibilities in the use of nano crystals in halide perovskites solar cells. Here we present results on the formation and growth mechanism of cesium lead halide (CsPbX₃) nanocrystals which highlights the tremendous effects of surface passivation on their growth and crystal habit. Futhermore, we study the reversible transformation (in solution) between CsPbX₃ and Cs₄PbX₆, driven by small modifications of the acid-base ratio in solution. These results reveal, on one hand, the rapid structural transformations these particles can undergo, and on the other point at routes to stabilize either phase. Finally, a new solar cell design using tin sulfide quantum dots to template a halide perovskites, somewhat analogous to bulk heterojunction cells, will be presented.

 $CsPbX_3$ nanoparticles can serve as an excellent testbed to understand underlying phenomena in the broader class of either organic or inorganic lead halide perovskites. These particles are relatively easy to synthesize. Moreover, in contrast with bulk crystals where the transition from one crystalline phase to another requires a change in either the temperature or the pressure, nanoparticles can be formed in several desired phases at room temperture simply by controlling their ligand shell (thus favoring a particular phase). Together with the ability to control their shapes, sizes and even (as shown here) to induce dynamic changes in the crystalline lattice in solution, they serve as a microscopic "lab" for the study of the materials properties under readily accesible conditions.

Here we begin by considering the nucleation and growth dynamics of isolated $CsPbX_3$ nanoparticles in solution [1]. We show that particles nucleate in solution through growth of the perovskite onto a preexisting metallic lead seed. Surprisingly, the initial growth process does not seem to strongly depend on the seed properties. Growth then typically proceeds by self-assembly via an oriented attachment mechanism. This holds yet another surprising result, since the metallic seeds should, in principle, impede the selfassembly process. As it turns out, likely since the seeds do not have good epitaxy with the rest of the particle, they are loosely bound and are lost to the solution during this process, leading to the formation of high quality particles. This finding alone can have some implications on the growth of absorber layers for solar cells, which sould potentially be seeded by inorganic nanoparticles introduced before crystallization.

We then show that in solution, $CsPbX_3$ nanocrystals can undergo a transformation to particles of a different chemical composition Cs_4PbX_6 by relatively small changes to the composition of ligands (in particular, the amine-to-acid ratio), and try to elucidate the mechanism by which this transformation occurs [2]. Briefly, this is driven by the very different chamical nature of the surfaces of the two crystals which are charged for $CsPbX_3$ and closer to neutral for Cs_4PbX_6 . In particular, we show that the transformation from $CsPbX_3$ to Cs_4PbX_6 proceeds through an amorphous phase, while the reverse transformation likely proceeds via exfoliation of 2D layers, giving rise to thin $CsPbX_3$ nanoplatelet intermediates. TEM images of the two types of particles along with XRD and optical spectra during and following the transformations are shown in Fig. 1.



Figure 1. Ligand control of the dynamic reversibility between CsPbBr₃ and Cs₄PbBr₆. (a) Transmission electron microscopy images of cubic CsPbBr₃ to Cs₄PbBr₆ NCs (from left to right, respectively) by means of addition of an excess of oleic acid/oleylamine for the forward reaction and the addition of oleic acid for the backward reaction. (b) Changes in the absorption spectra during the progress of the forward reaction from CsPbBr₃ to Cs₄PbBr₆ and conversion back to CsPbBr₃. (c) X-ray diffraction (XRD) of the conversion of CsPbBr₃ (red) to Cs₄PbBr₆ NCs (blue) and back along with the intermediates (green). Bulk XRD spectra for cubic CsPbBr₃ and Cs₄PbBr₆ are given as a bar plot. (d) Two complete CsPbBr₃–Cs₄PbBr₆ NC cycles as followed by UV–vis spectroscopy. Plotted is the wavelength of the first excitonic absorption peak.

Finally, a new design for a perovksite solar cell, based on a hybrid SnS-MAPI absorber layer will be presented [3]. Surprisingly, the photovoltaic performance of the hybrid device exceeds that of an equivalent device based on pure MAPI. The performance improvement (nearly 17% vs. about 13.5%) is mostly due to enhanced current collection (probably due to the improved crystallinity of the MAPI in the device) and to some extent due to the enhanced absorption at the red edge due to absorption in the SnS (whoic has a slightly lower band gap). This new design may help in tuning the band edge of perovskite solar cells without resorting to the use of complex stochiometries of either the organic anion or the halide in the absorber.

References:

[1] T. Udayabhaskararao, M. Kazes, L. Houben, H. Lin, D. Oron, "Nucleation, growth and structural transformations of perovskite nanocrystals", *Chem. Mater.* 29, 1302 (2017).

[2] T. Udaybhaskararao, L. Houben, H. Cohen, M. Menahem, I. Pinkas, L. Avram, T. Wolf, A. Teitelboim, M. Leskes, O. Yaffe, D. Oron, M. Kazes "A mechanistic study of phase change in perovskites NCs driven by ligand passivation", *Chem Mater.* 30, 84 (2018).

[3] J. Han, X. Yin, H. Nan, Y. Zhou, Z. Yao, J. Li, D. Oron, H. Lin, "Enhancing the performance of perovskite solar cells by hybridizing SnS quantum dots with CH₃NH₃PbI₃", *Small* 13, 1700953 (2017).