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STEM-EELS Exploration of Beam-Sensitive Perovskite Nanocrystals

Brittany Ford[1], David W. McComb[1, 2], Michael Brennan[3] and Tod Grusenmeyer[3]

[1.] Department of Materials Science & Engineering, The Ohio State University, Columbus, OH, United States.
[2.] Center for Electron Microscopy and Analysis, The Ohio State University, Columbus, OH, United States.
[3.] Air Force Research Laboratory, WPAFB, OH, United States.
*Corresponding author: ford.1027@osu.edu

Cesium lead halide perovskites are of interest for photovoltaic and light emitting diode (LED) devices because of their potential for power conversion efficiency, affordable cost of production, and tunable band gaps [1, 2, 3]. While they show a promising high efficiency, are easier to process and source than current photovoltaic options, they are sensitive to environmental conditions and often degrade rapidly under electron beam illumination. In this work we will explore the reduction of electron doses combined with cryogenic conditions, to enable electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) to be used to correlate structure and properties in perovskite superlattices.

The $CsPbX_3$ (X=Br, I or Cl) perovskite samples consist of nanocrystals that self-assemble into superlattice structures with spacing dictated by organic ligands that are responsible for holding the lattice together [1]. Nanocrystals suspended in toluene were drop casted onto sample grids and tested for beam sensitivity. The ligands in the sample can degrade and cause hydrocarbon contamination over the course of a STEM scan making the sample too thick for analysis, and this is what is displayed in Figure 1. Cleaning trials proved that these samples were difficult to remove excess ligands without changing the sample entirely. Therefore, all STEM-EELS data will be collected using a cryogenic specimen holder to reduce both damage and diffusion during analysis.

We are particularly interested in using the low loss region of the energy-loss spectrum to probe band gap and electronic structure in the superlattices, and correlate these properties to the corresponding chemical composition seen in core loss studies. Our experiments will be performed using an FEI Titan 30-300 microscope at the Center for Electron Microscopy and Analysis (CEMAS) operated at 300 kV in monochromated mode. Mapping of the plasmon peaks in the low loss spectrum will be done to compare properties of individual nanocrystals with the bulk of a superlattice region. A reference spectrum will first be established, by taking a low loss spectrum over a large area of assembled nanocrystals. Next, an isolated nanocrystal (by 20-30nm distance) will be analyzed for comparison. In order to limit noise in the band gap area of the spectrum, the low loss spectrum will be taken as a dual spectrum [4]. The first selected energy range needs to include the zero loss peak (ZLP), since it is required for data analysis. The second energy range will be moved just enough to exclude the ZLP. These two spectra can be spliced together using the Gatan Microscopy Suite (GMS) software and should allow for resolving finer details in the low loss region, such as band gap, that can be hard to resolve next to the strong signal of the ZLP.

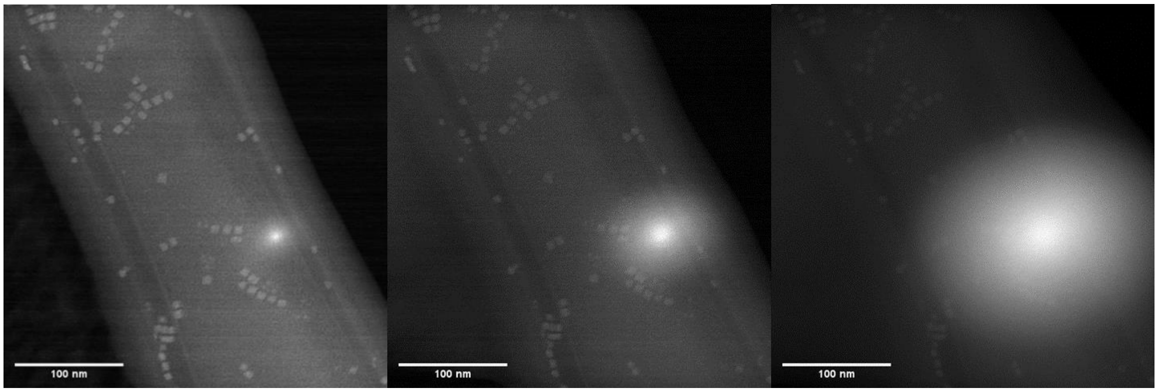

Figure 1. Series of STEM images of the $CsPbBr_3$ sample displaying carbon buildup increasing sample thickness with each subsequent STEM scan.

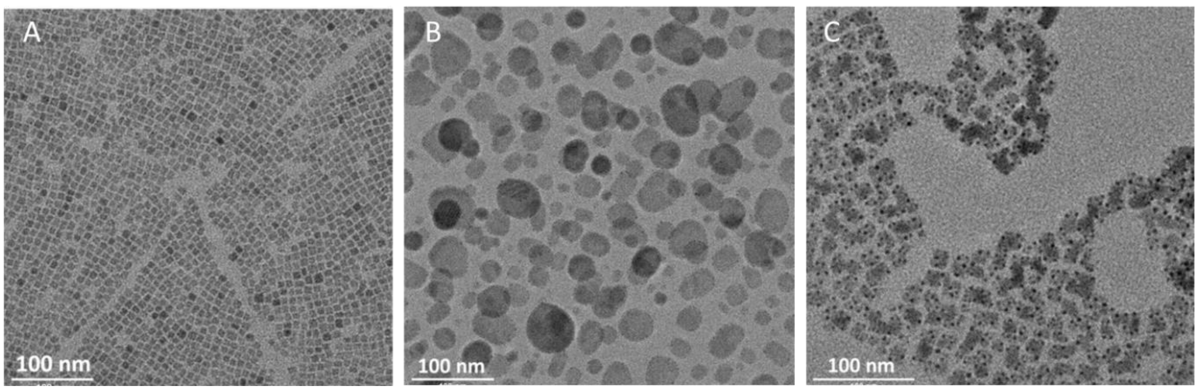

Figure 2. (A) Bright Field image of $CsPbBr_3$ nanocrystals without any damage. (B) $CsPbBr_3$ sample showing degradation after gentle heating and (C) 5 minutes of ozone exposure.

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