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Low Dose Methods for Atomic-scale Transmission Electron Microscopy of $Cs_{1-x}FA_xPbI_3$ Quantum Dots: Structure, Defects, and Performance

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Metal halide perovskites, with a common formulation of ABX_3 (as shown in figure 1, where A is an organic cation methylammonium MA, formamidinium FA, or Cs; B is commonly Pb or Sn; X is halide Cl, Br or I), have become promising candidates for the next generation of photovoltaics, light-emitting diodes and lasers due to their excellent power conversion efficiencies and low processing cost. However, challenges remain for application in devices, such as structural degradation and current density-voltage hysteresis.

Tuning size and composition of perovskites are two effective pathways toward stable and high performances photovoltaics and optoelectronics. For example, the mixed organic-inorganic cation perovskites $Cs_{1-x}FA_xPbI_3$ (with x = 0-1) in the format of quantum dots have achieved a record power conversion efficiency of 16.6% with negligible hysteresis [1]. The performance of such perovskite devices is governed by many parameters, such as the nature of the cation mixture and defect structures. By better understanding the defect structures at the atomic scale we can establish correlations between structure and device properties, which can enable further improvement in device properties and efficiency [2]. However, these materials are extremely delicate and can damage with electron doses $<10e/Å^2$ [3, 4].

In this work, we develop and apply low dose transmission electron microscopy techniques to analyze pristine perovskite microstructures. This includes phase contrast high-resolution TEM, selected annular and bright-field STEM and scanning diffraction methods. With the use of direct electron counting detectors, the total electron dose during the TEM experiments is controlled well below the measured damage thresholds [3, 4].

Using these methods, we reveal defect structures in $Cs_{1-x}FA_xPbI_3$ quantum dots and characterize their atomic structure (fig. 2). We next develop a synthetic strategy to control the defect density and measure the corresponding changes in device performance, revealing their impact on device properties.

We also investigate changes in structure and ion migration induced by electron doses just above the damage thresholds and determine structural models for the resulting crystal structures that varies with dose and composition of Cs/FA.

Overall, our results show how advanced low dose TEM, STEM and scanning diffraction can be utilized to obtain atomic-scale insights into extremely beam-sensitive perovskites and how it helps improve device properties and performance [5].

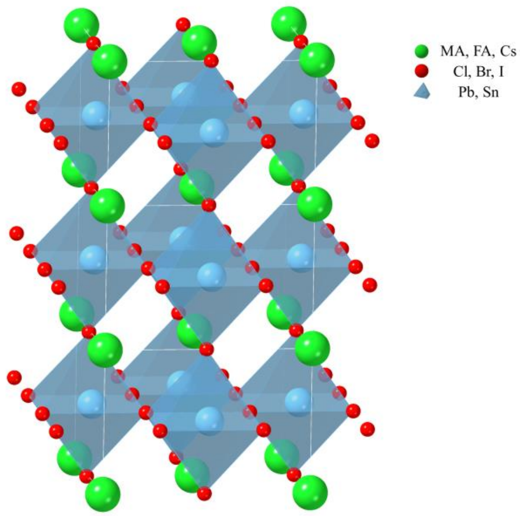

Figure 1. Atomic structure of perovskites with a common formulation ABX_3

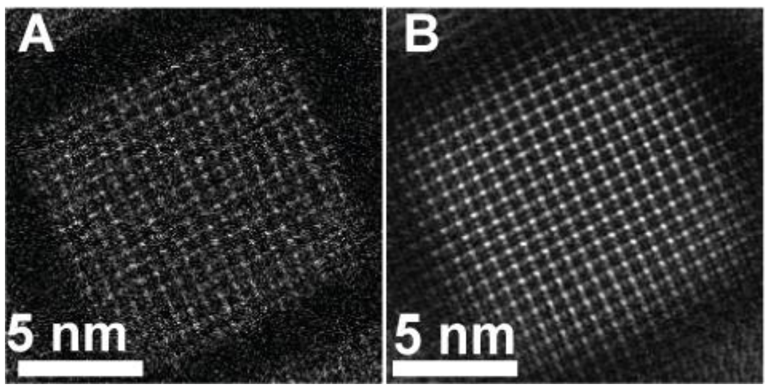

Figure 2. STEM images of $Cs_{1-x}FA_xPbI3$ quantum dots taken with collection angles optimized for sensitivity to chosen features. (B) is a Bragg filtered image of (A).

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