
Weilun Li1, Mengmeng Hao2,3, Lianzhou Wang2,3, Qimu Yuan4, Jay B. Patel4, Michael B. Johnston4, Joanne Etheridge1,5

1 Department of Materials Science and Engineering, 5 Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia,
2 Nanomaterials Centre, Australian Institute for Bioengineering and Nanotechnology, 3 School of Chemical Engineering, The University of Queensland, St Lucia, Queensland, Australia
4 Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, United Kingdom

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Metal halide perovskite semiconductors, with are commonly formulated as ABX3 (Figure 1, where A = organic cation, such as methylammonium (MA+), formamidinium (FA+) or inorganic Cs+; B = Pb2+, Sn2+, Ge2+; and X = halogen), have emerged as promising materials for the next generation of photovoltaics (PVs), light-emitting diodes (LEDs) and lasers due to their excellent power conversion efficiencies, defect tolerance and low processing cost. However, several critical questions still need to be answered, including structural stability, ion migration, current-density voltage hysteresis and defects. To address these questions and develop perovskite solar cells with increased efficiency and stability for device applications, a better understanding of their atomic structures is required.

Figure 1. Schematics of perovskite solar cell structure

Transmission electron microscopy (TEM) is a powerful technique for examining the local atomic structure of materials. However, when it comes to perovskite solar cells, the pristine structure can be readily modified by the electron beam, even under a low dose of 10 e/Å2 [1-3]. This poses a significant challenge for TEM characterisations and results in the literature have been controversial. Nonetheless, it is possible to obtain TEM data from pristine structures with careful protocols for TEM specimen preparation, transfer, experiment, and image interpretation.

In this study, we have developed and utilized low-dose TEM techniques (< 5-50 e/Å2), including atomic-resolution phase contrast imaging, 4D-STEM, scanning diffraction and CBED, to investigate pristine microstructures of two technologically important perovskite solar cells: Cs1-xFAXbxPbI3 quantum dots [4] and CsPb(I1-xBrx)3 films [5]. The total electron dose was carefully controlled well below the measured damage thresholds using direct electron counting detectors. Through these techniques, we provided direct observations of the pristine perovskite structure and intrinsic defects and correlate them to device performance. Furthermore, with extended electron dose applied to perovskite films similar to those used in solar cells, we further observed the vacancy formation, migration, ordering and octahedral tilt, thereby establishing a degradation pathway of perovskite solar cells.


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