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Stability Studies of $MAPbI_3$: Identification of Degradation Pathways and Strategies for Observing the Native Structure of Lead Halide Perovskites

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Methylammonium lead iodide ($MAPbI_3$) is an important new material for solar power generation, with some devices demonstrating >20% conversion efficiency. However, this material is highly unstable, and degrades easily in the presence of humidity, irradiation, and heat [1]. Due to the unstable nature of this material, many questions about its structure- both in single crystalline form and when incorporated into devices- remain open. Additionally, the damage mechanisms of this material themselves are important, as $MAPbI_3$ has been shown to degrade under illumination, potentially limiting its ultimate utility as a solar material [1]. Performing structural studies via TEM is a way to provide important insight into the structure and degradation pathways of $MAPbI_3$. However, imaging and comparing the pristine and damaged microstructures of this material in the electron microscope pose a challenge, as the TEM itself induces significant structural changes. To separate the effects of electron radiation on this material and understand other damage mechanisms that affect device performance, we have performed a systematic study of electron radiation damage on $MAPbI_3$ during TEM imaging. This damage is compared to damage induced by heating, high-energy alpha particle (He^{2+}) irradiation, and illumination to understand the origins of instability in this material.

By imaging sample degradation by electron radiation in-situ, we have observed that electron irradiation induces regions of PbI_2 and loss of material. This is consistent with natural degradation of $MAPbI_3$ in air and even under vacuum [1]. However, here the damage is spatially limited to the illuminated area and does not result in large iodine deficient areas, as is the case with He^{2+} irradiation (Fig. 1c and 1d).

To limit the effects of electron radiation damage, we have employed both cryo-EM imaging and scanning nanodiffraction. Scanning nanodiffraction reveals a sample's microstructure without the need to image at atomic resolution. By rastering a 1 nm probe over the sample and collecting a series of convergent beam electron diffraction patterns, features such as strain and crystalline grain orientation can be mapped. Cooling the sample down to cryogenic temperatures enhances stability, but induces sample vibration and drift, necessitating fast data acquisition and drift correction. Studying single-crystalline pristine $MAPbI_3$ has revealed uniform chemical composition, with small (10nm) slightly misoriented grains (Fig 1a and 1b). In comparison, both He^{2+} and e- irradiated samples exhibit areas of iodine deficiency. Previous studies have observed changed in cathodoluminescence spectra upon irradiation with lower energy (5 kV) electrons [2], indicating that these structural changes are related to device performance.

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By developing new low dose electron microscopy methods, we have imaged pristine $MAPbI_3$ and tracked its degradation under He^{2+} irradiation, heating and illumination. We have identified the type of degradation of this material under various conditions, giving us greater understanding of this exciting material system to inform future design considerations.

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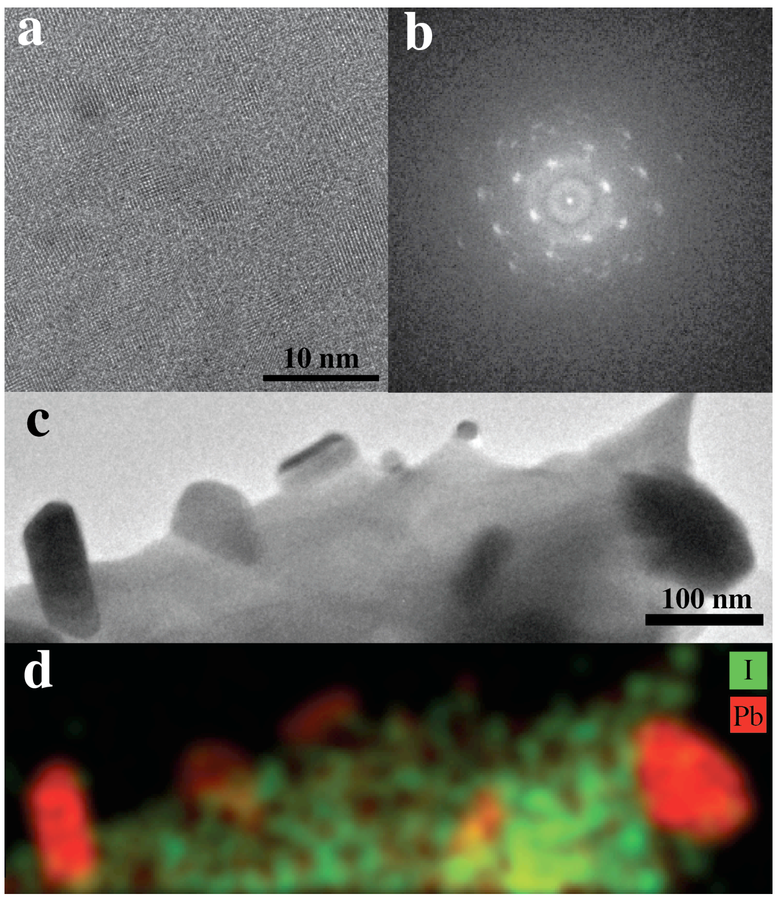

Figure 1: Pristine and irradiated $MAPbI_3$. a) HRTEM image of pristine $MAPbI_3$ oriented along the <100> direction. The sample is nearly single crystal, with small, slightly misoriented grains b) The Fourier transform of (a). c) A lower resolution image of $MAPbI_3$ damaged by He^{2+} radiation. d) EDS elemental map indicating the sample in c) has segregated into lead and iodine rich regions.

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