

Low Dose TEM on the Degradation of the MAPbI₃ Perovskite

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The MAPbI₃ perovskite is very sensitive to electron beams, particularly to transmission electron microscopy making it a challenge for characterization [1]. Here we present a unique set of results that are associated merely to the sunlight and atmosphere natural degradation of the perovskite rather than the interaction of the electron beam and its respective damage. The low dose/atomic resolution transmission electron microscopy imaging was carried in the TEAM 0.5 microscope with aberration correction operated at 80 kV. The experimental images were taken with a spherical aberration coefficient of -0.015 mm with a focus spread of ~10 Å and in conditions of low dose using ~20 e⁻/Å²s. The images were collected using 40 focal series to reconstruct the exit wave (EWR) in the software MacTempas®. The total dose in a focal series reaches approximately 800 e⁻/Å² that is sufficient for imaging and prevents most damage. Therefore the degrading PbI₂ is purely attributed to the natural degradation of the perovskite rather than the electron damage.

The PbI₂ is known as the final degrading product of the MAPbI₃ [2]. Here we present the presence of both products in a sequence of degrading samples for up to 30 days under environmental conditions (air and sunlight). The main finding is the observation of MAPbI₃ nanocrystals embedded in PbI₂ matrix in naturally degraded MAPbI₃. Yet the reported degradation mechanisms, as proposed by FTIR, mainly consists on the environmental effects on methylammonium that escapes from the perovskite [2]. As of today there is no true evidence of those and other finding; except for the interpretation of highly sophisticated methods such as FTIR, Raman, XRD, etc. Yet, our present work elucidates this phenomena in detail and shows potential mechanisms purely related to structure transformation from the highly ordered perovskite to its quasi-amorphous state. The fresh sample is presented in Figure 1. Where one can see some early precipitation of PbI₂ along the edge of the perovskite. Presumably, this is the region in direct contact with air and sunlight. In Figure 2 we present a case where the perovskite degraded for 14 days (under same conditions). Here is observable that the PbI₂ is not only along the edges of the particle but it is also embedded within the perovskite. Presumably, the methylammonium moved away leaving behind the main product of degradation, namely PbI₂. Figure 3 show a perovskite degraded for 30 days, where there is a clear evidence of the degraded perovskite and the presence of a “substrate” that is presumably PbI₂. However in this case it is already amorphous. Yet, at those advanced stages of degradation there is evident of crystallinity in the perovskite and the planes belong to the principal planes of this type of MAPbI₃. Despite a low percentage in the PbI₂ matrix, MAPbI₃ nanocrystals exhibit a strong photoluminescence due to enhanced electron-hole interaction and excellent surface passivation by PbI₂. The optical characterization indicates that MAPbI₃ and PbI₂ have a type-I rather than type-II band alignment [3].

References:

[1] C. Xiao et al., *The Journal of Physical Chemistry C* **119** (2015), p. 26904.

[2] G. Abdelmageed et al., *Applied Physics Letters* **109** (2016), p. 233905.

[3] Z. Zhu et al., *Chemistry of Materials* **28** (2016), p. 7385.

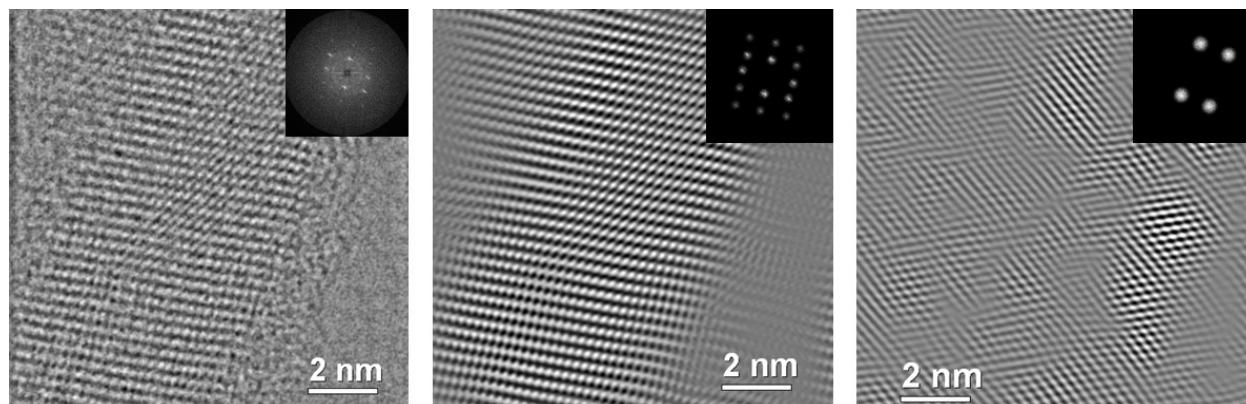


Figure 1. Atomic Resolution TEM images of fresh perovskite (a) exit wave reconstruction, (b) FFT (inset) and IFFT of the perovskite and (c) FFT (inset) and IFFT of PbI_2 .

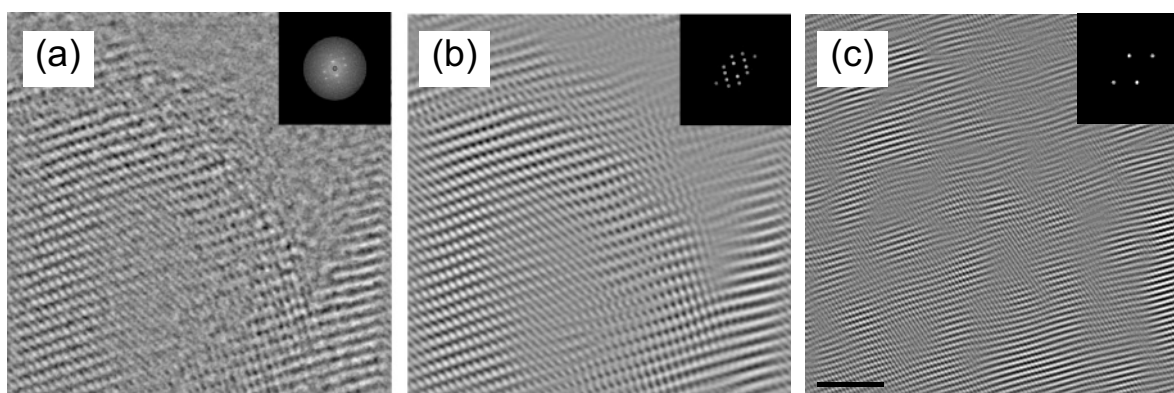


Figure 2. Atomic Resolution TEM images of the perovskite degraded for 14 days (a) exit wave reconstruction, (b) FFT (inset) and IFFT of the perovskite and (c) FFT (inset) and IFFT of PbI_2 .

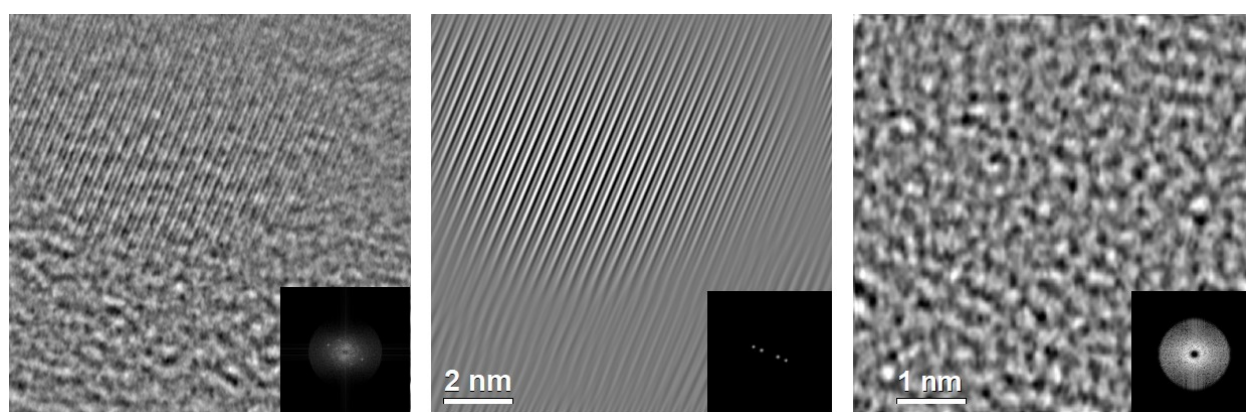


Figure 3. Atomic Resolution TEM images of perovskite degraded for 30 days (a) exit wave reconstruction, (b) FFT (inset) and IFFT of the perovskite and (c) FFT (inset) and IFFT of the amorphous region.