PEROVSKITE ENVIRONMENTAL STABILITY: EFFECTS OF ION TUNING

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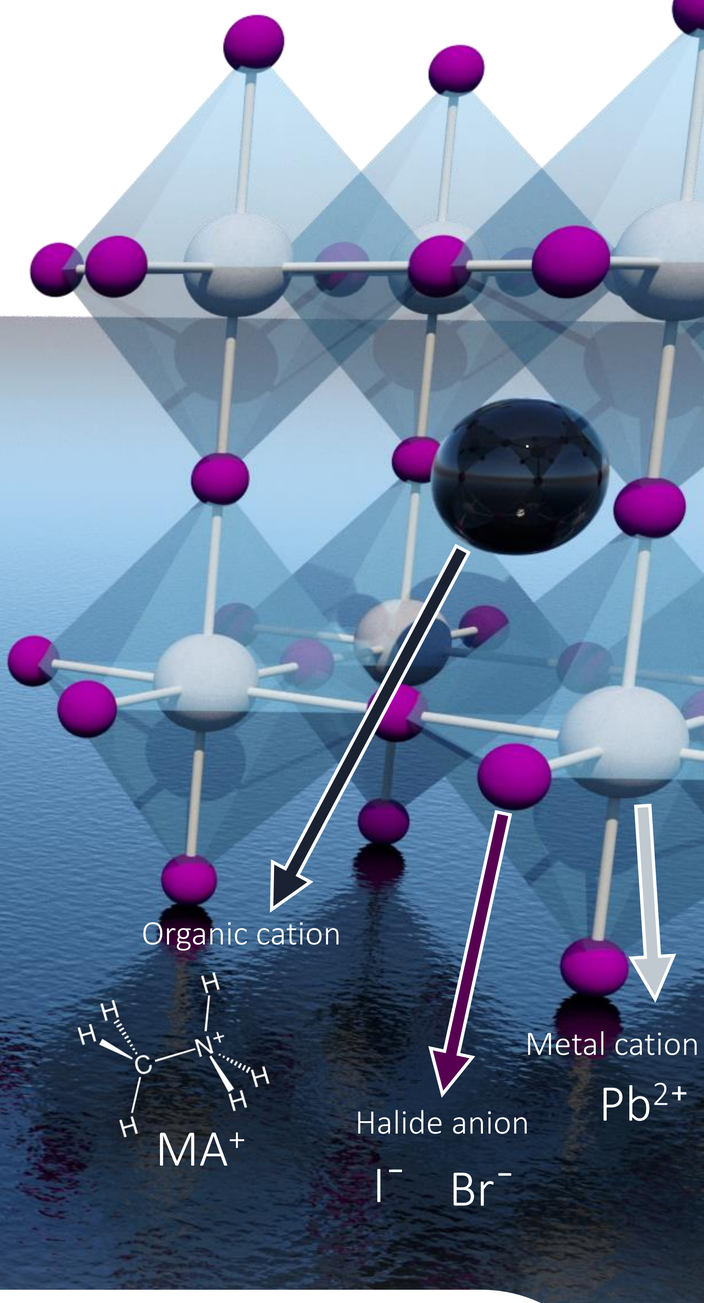


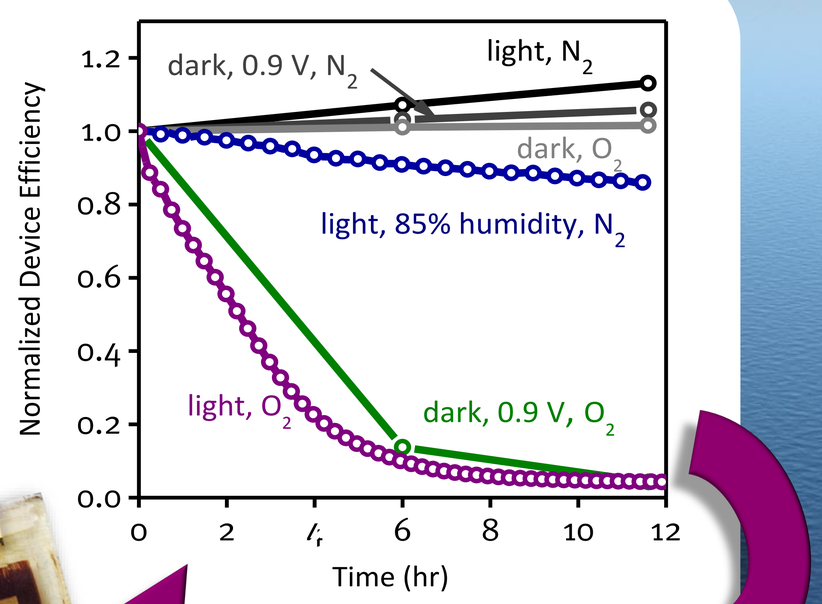
INTRODUCTION

Perovskite commercialisation challenges:

- High power conversion efficiency > 22% solar
- Low raw material and processing costs
- Long term stability > 25 years

Moderate environmental stability is likely required for long term applications due to imperfect encapsulation. Previously we've shown Light + O_2 degrades MAPI rapidly, compared to all other environmental conditions (right).[1,2]

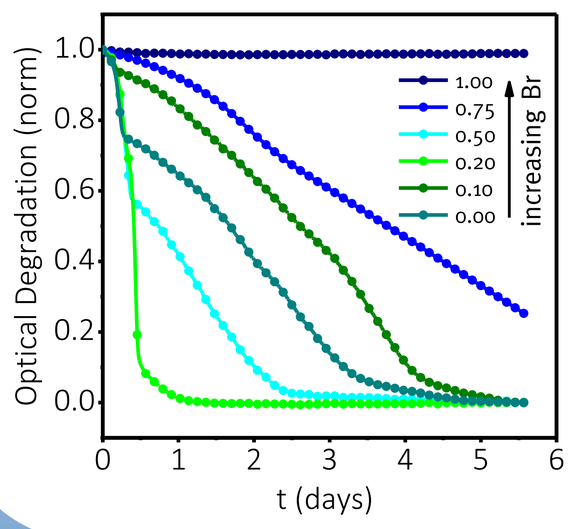
Here we ask can we improve light + O_2 stability by tuning perovskite ions?[3]

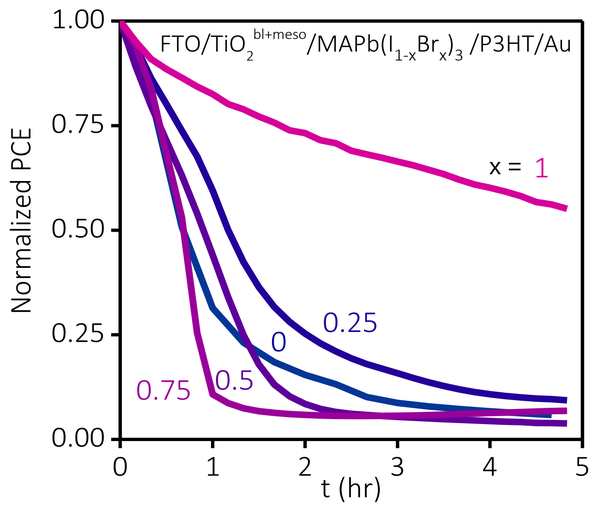


$$O_2 + e^- \rightarrow O_2^- \rightarrow degradation$$

$MAP(I_{1-x}Br_X)_3$ - O_2 + LIGHT STABILITY

- Optical degradation of $MAP(I_{1-x}Br_X)_3$ in dry air + light, monitored with a CCD camera (below left), shows instability for all ratios excepts $MAPBr_3$.
- Two-phase of degradation seen for $x \leq 0.5$, suggesting separate degradation of Br^- and I^- rich regions.
- The $MAPBr_3$ device has improved stability however, $x \leq 0.75$ devices have similar stability (below right). Photo-bleaching of the P3HT in the degraded $MAPBr_3$ device suggests the HTL is limiting stability, not the perovskite.

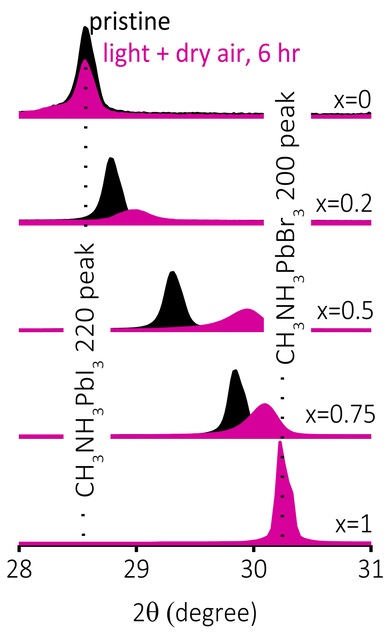


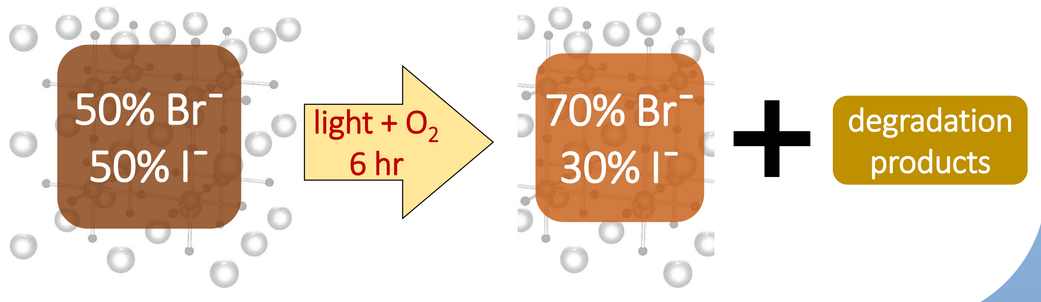


X-Ray Diffraction

- Pristine films show the clear trend of tetragonal (220) to cubic (200) peaks.
- After degradation 3 major results:
  1. Peak height reduce for $x < 1$ – crystal degrading.
  2. Peak angle increases for mixed halide films.
  3. **MAPBr XRD stable in light and O_2.**

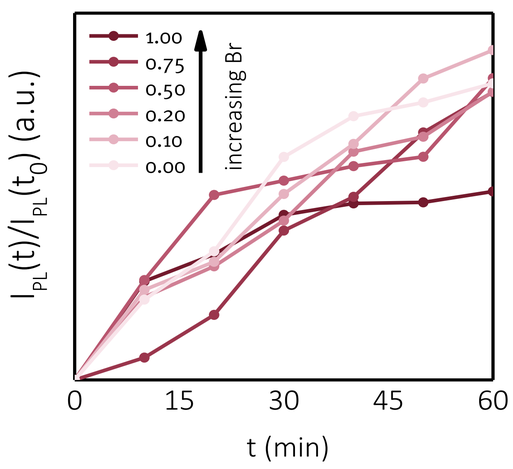
XRD agrees with optical results. Schematic describes reaction mechanism of mixed halide in hv + O_2:





SUPEROXIDE GENERATION

- **Superoxide generation rate independent of halide ratio.**
- Increased thermodynamic stability of MAPBr inhibits superoxide degradation
- Transient absorption spectroscopy (TAS) shows oxygen quench long lived charges in MAPBr corroborate the result of the superoxide



$$MAP(I_{1-x}Br_x)_3 + h\nu + O_2 \rightarrow O_2^- \rightarrow unstable$$

$$MAPBr_3 + h\nu + O_2 \rightarrow O_2^- \rightarrow stable$$

CONCLUSIONS

- Tuning halides & organic cation is not effect at inhibiting light + oxygen instability.
- Superoxide generation is independent of halide ratio but greater thermodynamic stability of MAPBr inhibits superoxide degradation.
- MAPBr shows great potential for environmentally stable high voltage perovskite devices or for use in four terminal tandem solar cells.

Financial support from Solvay and EPSRC is gratefully acknowledged.

[1] Aristidou N, et al. Angew Chemie Int Ed. 2015;54(28):8208–12.
[2] Bryant D, et al. Energy Environ Sci. 2016;9(5):1655–60.
[3] Pont S, et al. J Mater Chem A. 2017;5(20):9553–60.

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