

## Structural modulation and defect passivation in perovskite solar cells via lithium doping.

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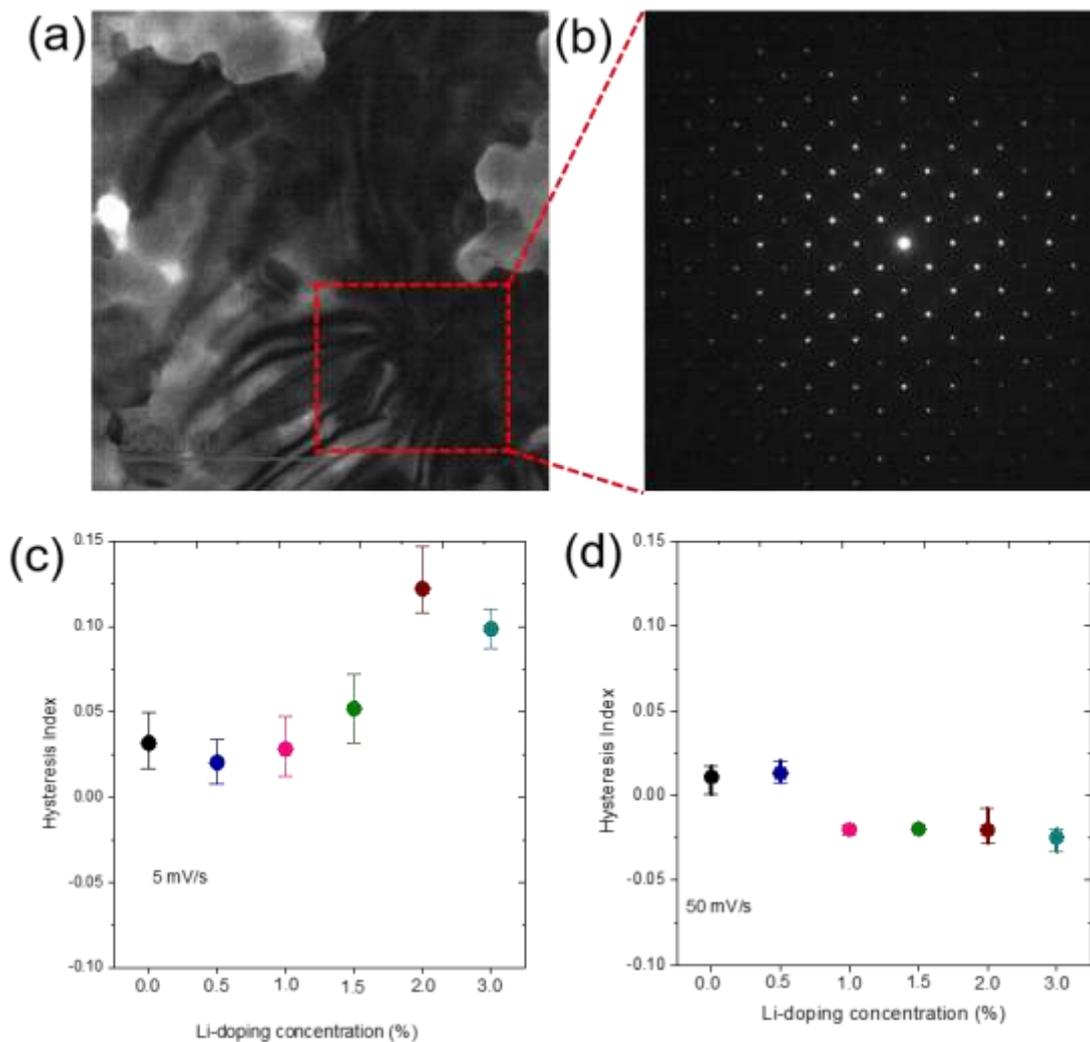
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Halide perovskites are comprehensively studied photovoltaic materials, owing to their high charge separation and carrier transport abilities. Introducing alkali metals such as lithium into perovskite absorbers has been shown to enhance charge extraction, modulate the interface energy band alignment and increase device efficiency. However, the detailed mechanism of lithium inclusion into the perovskite absorber is poorly understood.

In this report, we demonstrate Li-doped perovskite solar cells with efficiencies up to 21.5% and combine a range of material and electrical characterisation techniques to probe the structural and optoelectronic changes induced by the addition of LiI to the perovskite precursor. Transmission electron microscopy (TEM) is used to investigate the crystallographic orientation of pristine and lithium-doped triple cation perovskite (Figure 1a,b), while depth profile analysis from time-of-flight secondary ion mass spectrometry (TOF-SIMS) reveals a highly nonuniform distribution of the Li within the perovskite film. The small size and mobility of Li<sup>+</sup> ions allows them to readily diffuse into the charge transport layers after aging and may also explain the observed changes in the current-voltage hysteresis response of Li-doped cells. Inverted hysteresis is observed at fast (500 mV/s) and moderate (50 mV/s) scan rates, in contrast to slow (5 mV/s) scan rates, which exhibit normal hysteretic behaviour. Interestingly, normal hysteresis behaviour is exhibited from devices with low doping concentration (< 1.0 mol%) irrespective of the scan rates (Figure 1c,d).

Lower trap density and reduced charge recombination values extracted from space-charge-limited current (SCLC) and impedance spectroscopy (IS) measurements at optimal doping concentration are consistent with improved photovoltaic performance compared to pristine and highly doped perovskite devices. Our work demonstrates the benefits of judicious use of lithium dopant in the perovskite absorber to tune the structural order, suppress charge recombination and minimize trap defects, resulting in enhanced power conversion efficiency.



**Figure 1.** (a) Bright-Field TEM image of triple cation perovskite with 0.5 mol% Lil, and (b) corresponding [001] selected area electron diffraction (SAED) patterns. Hysteresis behaviour of different lithium concentration at (c) 5 mV/s and (d) 50 mV/s scan rates.

## References

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