



Enhanced fatigue resistance of suppressed hysteresis in perovskite solar cells by an organic crosslinker



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ABSTRACT

With record power conversion efficiencies of hybrid perovskite solar cells now exceeding 20% under laboratory conditions, improvements in stability of the cells under real-world working conditions are now key requirements for their commercial success. Here, we present a novel strategy to reduce penetration of humidity and oxygen into perovskite films via incorporation of a diammonium glycol. The two ammonium groups of this molecule allow it to serve as a crosslinker in the structure, bridging two unit cells within a crystallite or even across a grain boundary. In a planar heterojunction solar cell containing PCBM as an electron transport layer, the power conversion efficiency of the cell with ~0.1% diammonium glycol in the absorber layer was 13.96%, slightly exceeding that of the glycol-free device (13.53%). Most importantly, the glycol-free device exhibited the typical growth in hysteresis with performance degradation, but hysteresis remained suppressed in the device doped with diammonium glycol, even as its overall performance deteriorated. Furthermore, the chemical stability of the unpackaged device under continuous AM1.5 G illumination at ambient conditions was substantially improved relative to the glycol-free device. Formation of PbI₂ was significantly suppressed, which could minimize release of toxic Pb ions.

1. Introduction

Solution processed methylammonium lead halide perovskites have become the most promising new active light harvester for photovoltaic devices over the past few years [1,2]. However, prospects for commercialization of perovskite solar cells (PSC) are still limited by two major challenges: poor stability and hysteresis. Hysteresis is mainly attributable to an imbalance between electron and hole mobilities in the device due to interfacial electronic traps, ionic migration, and unbalanced carrier transport from the perovskite layer [3]. Recently, researchers have successfully suppressed the hysteretic behavior of PSCs by incorporation of a fullerene-based electron-transport material, usually phenyl-C61-butyric acid methyl ester (PCBM), into or upon the perovskite layer [4–6]. This treatment reduces electron trapping and ion migration, and passivates defects at the interface between the electron-transporting layer (ETL) and the perovskite film. The lack of stability of PSCs is largely attributable to the high water solubility of perovskite materials, which leads to degradation at high humidity [7].

Various strategies for improving the stability of the perovskite layer, including replacement of methylammonium with formamidinium [8,9] or Pb with Cs [10,11], introduction of an organic crosslinker [12,13] or a halogen/pseudo halogen (such as thiocyanate (SCN)) anion [14,15], and formation of a 2D hydrophobic interlayer between active 3D perovskite domains [16–18] have shown potential to block diffusion of water into the active layer or to stabilize the cubic phase [19]. However, the crosslinked devices showed hysteretic behavior and the 2D perovskite devices suffered from a loss of efficiency relative to their 3D counterparts. Meanwhile, UV illumination of mesoporous (mp) TiO₂ in bulk heterojunction devices has accelerated oxygen-induced degradation through the conversion of molecular oxygen to a reactive radical [7]. Planar heterojunction structures (without mpTiO₂) are less susceptible to this problem, but exhibit greater hysteresis compared to bulk heterojunction devices [4]. Therefore, a strategy for improving stability and suppressing hysteresis, simultaneously, without a loss of performance, remains a crucial need.

To address this need, here we propose and demonstrate planar

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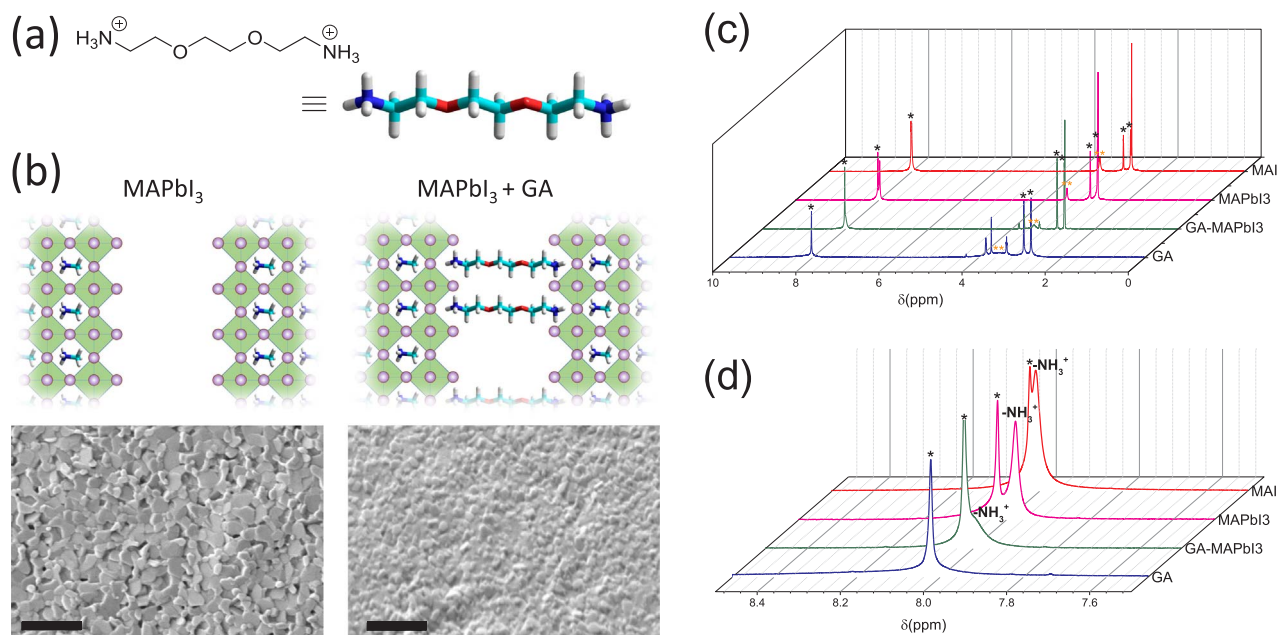


Fig. 1. Structure and surface morphology of methylammonium lead iodide (MAPbI₃) perovskite thin layer with or without 2,2'-(ethylenedioxy)bis(ethylammonium iodide) (GA) (a) Chemical structure of GA. (b) Schematic chemical structures (upper) in grain boundaries of the perovskite film and surface morphologies by SEM (lower). Scale bars are 1 μm . (c) Full and (d) enlarged (at 8 ppm) ¹H NMR spectra of MAI (9.5 mM), MAPbI₃ (9.5 mM of MAI + 10 mM of PbI₂) with or without GA (1 mM), and GA (1 mM) in DMF-d₆ are shown. * and ** represent proton peaks of DMF and water, respectively. The ammonium proton peaks were assigned as -NH₃⁺ in (d).

heterojunction PSC devices that combine a PCBM ETL with a new approach to sealing crystalline grain boundaries of the perovskite layer, using diammonium crosslinkers to improve device performance and stability. Use of PCBM suppresses hysteresis and improves photovoltaic performance, while crosslinking with diammonium glycol molecules seals the grain boundaries to reduce oxygen and water diffusion into the active layer. With this strategy, we achieved improvements not only in the performance and stability, but also in suppression of hysteresis even during degradation of the devices. The improved chemical stability of the diammonium glycol-doped device can prolong device lifetime, while reducing potential leakage of toxic Pb ions.

2. Experimental

2.1. Perovskite precursor preparation

Methylammonium iodide (CH₃NH₃I, MAI) and 2,2'-(Ethylenedioxy) bis(ethylammonium iodide) (GA) were synthesized in our laboratories. Briefly, to prepare MAI and GA, 40 wt% methylamine in water (0.1 mol) and 98% 2,2'-(Ethylenedioxy)bis(ethylamine) (0.05 mol) were each separately dissolved in 20 mL of methanol. 57 wt% HI in water (0.2 mol) was added dropwise to each amine solution at RT with stirring, and the mixtures were stirred at RT for 4 h. The solvent in the resulting mixture was evaporated, and the products were each dissolved in ~10 mL of methanol with mild heating. The product solutions were added dropwise to diethyl ether (200 mL) with stirring to obtain white precipitates. The filtered precipitates were recrystallized from methanol, and the white crystals were dried in a vacuum oven at 90 °C for 24 h. The perovskite precursor solution was prepared by mixing MAI, PbAc₂, and GA in dimethylformamide (DMF) at a 3:1 molar ratio of MAI to PbAc₂ and 0.1 wt% GA to MAI. The resulting concentration of the precursor solution was 40 wt%. This solution was stirred at 60 °C for 0.5–2 h before spin coating. For comparison, GA-free perovskite precursor solution was prepared by the same method.

2.2. TiO₂ precursor preparation

438 μL Ti-isopropoxide was diluted with 3 mL anhydrous IPA, while

83 μL 1 M HCl was diluted with another 3 mL anhydrous IPA. Then the diluted acid solution was added dropwise into the Ti-isopropoxide solution with vigorous stirring. The reaction proceeded at room temperature for 2.5 h. Before spin-coating, the solution was filtered through a PTFE membrane syringe filter with 0.2 μm nominal pore size.

2.3. Device fabrication

The solar cells were fabricated on prepatterned ITO substrates (Thin Film Devices, Inc., 20 Ωsq^{-1}), which were cleaned sequentially with Hellmanex III solution, acetone, methanol, and isopropyl alcohol with 10 min ultrasonication in each solvent, followed by 40 min ozone treatment. The hole blocking compact layer of TiO₂ was deposited on the cleaned substrates by spin-coating at 3000 rpm for 30 s then annealing at 500 °C for 10 min. Substrates were transferred into an inert atmosphere glove box for further fabrication steps. Phenyl-C61-butyric acid methyl ester (PCBM, 20 mg/mL) in chlorobenzene solution was spin-coated on the TiO₂ layer and annealed at 100 °C for 10 min. Then, the perovskite precursor solution was spin-coated at 2000 rpm for 30 s and then annealed at 110 °C for 0.5–1 h to remove residual solvent and fully crystallize the film. During the annealing process, hybrid films changed from light yellow to dark brown. Next, a chlorobenzene solution of poly(3-hexylthiophene-2,5-diyl) (P3HT, 15 mg/mL) was deposited by spin-coating at 2500 rpm for 30 s. The top electrode (Au) was thermally evaporated through a shadow mask to achieve a device area of 0.07 cm². For comparison, PCBM-free devices were made by directly spin-coating the perovskite precursor solution on the TiO₂ layer following the same method.

2.4. Photovoltaic characterization

The current density-voltage (*J-V*) characteristics were determined using a Keithley 2400 source meter to apply an external potential bias to the solar cells. The generated photocurrent under a simulated AM 1.5G spectrum (Oriel solar simulator) was recorded at a 0.03 V/s scan rate. The measurements were carried out under ambient laboratory conditions (Avg. temp.: 25 °C and Avg. relative humidity: 60%). The solar cell devices were masked with an aperture with 0.07065 cm²

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