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Fluorescence spectroscopy-based study of balanced transport of charge carriers in hot-air-annealed perovskites

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ABSTRACT

Using fluorescence spectroscopy, we investigate the transport of charge carriers in (p-i-n) planar perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) solar cells with the structure ITO/PEDOT:PSS/perovskites/PCBM/Ca/Al, in which the perovskite morphology is optimized by moisture pretreatment (MPT) and the hot-air-annealing process (HAAP). After annealing with hot air, the electron transport time of the perovskites is shortened by a factor of 3.6 (from 28.8 to 7.9 ns), eventually leading to balanced transport of electrons and holes (characterized by the fluorescence-decay time constants of 7.9 and 7.6 ns, respectively). These results are in good agreement with the observed increase in the photovoltaic conversion efficiency.

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1. Introduction

Organic-inorganic halide perovskite solar cells (PESCs) have attracted considerable attention, because of their high device performance, low cost, and ease of fabrication. The high performance results from the excellent characteristics of perovskites, such as high absorbance [1,2], ambipolar carrier transport [3,4], small exciton binding energies (~20 meV) [5–7], long electron–hole diffusion lengths (100–1000 nm), and long exciton lifetimes (~100 ns) [8–10]. To fabricate high-performance PESCs, the morphology of perovskites needs to be controlled to realize high crystallinity, high coverage extent, and large grain sizes [11–14]. The presence of nonuniform crystalline networks in the perovskite layer results in a short electron–hole transport distance and high electron–hole charge recombination loss [13], while a poor surface coverage causes the incident photons to pass through the uncovered areas, leading to a low photocurrent [14].

Recently, we have improved the crystallinity and coverage of perovskites by annealing the pristine perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) layer with exposure to moisture and hot air, and have realized enhancement in the photovoltaic conversion efficiency from 9.05% to 15.55% [15]. In this study, with the goal of understanding what currently limits the photovoltaic conversion efficiency in this system, we comparatively investigate the carrier transport dynamics of various PESCs. From analyses of the fluorescence-decay profiles of the conventional, moisture

pretreatment (MPT)- and hot-air-annealing process (HAAP)-perovskite layers coated on or under the carrier transporting layers of PEDOT:PSS and PCBM or sandwiched at their interface, we characterize the time constants for the transport of electrons and holes onto respective transporting layers. From analyses, we find that the efficiency of PESCs is significantly influenced by the carrier transport rates. Notably, the most-efficient cell fabricated by using both processes of MPT and HAAP exhibits short and balanced hole and electron transport times, consistent with enhancements in the short circuit current (J_{sc}), open circuit voltage (V_{oc}), and fill factor of PESCs.

2. Experimental

All reagents purchased from Sigma–Aldrich were used without purification. Methylammonium iodide (MAI) was synthesized according to the literature [16]. Methylamine (24 mL and 33 wt% in absolute ethanol) and HI (10 mL and 57 wt% in water) were reacted in a round bottom flask under N_2 atmosphere at 0 °C for 2 h with stirring. Then, the resulting solution was dried by rotary evaporation at 50 °C to form a white powder of MAI. For the purification of the pristine MAI, the dried MAI powder was dissolved in ethanol followed by sedimentation in diethyl ether by stirring the solution. This process was repeated three times and an MAI powder with high purity was recovered and dried in a vacuum oven for 24 h at 60 °C.

Thin-film perovskite samples were fabricated as follows. A quartz substrate was cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried in an oven at 100 °C.

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PEDOT:PSS (Baytron PH) was spin-casted on quartz at 4500 rpm from an aqueous solution to form a 40 nm thick film. The PEDOT:PSS-coated substrate was dried for 10 min at 140 °C in air and then transferred into a glove box to spin-cast the perovskite layers. A solution containing a mixture of MAI:PbCl₂ with a molar ratio of 3:1 in DMF solvent (40 wt %) was spin-casted at 5000 rpm for 45 s on top of pure or PEDOT:PSS-coated quartz substrate. The precursor perovskite film was dried in the glove box for 30 min at room temperature. The thickness of the perovskite films was ~350 nm. In conventional process, the precursor perovskite film was directly heated on a hot plate in the glove box at 120 °C for 30 min. Meanwhile, in the moisture pretreatment process, the film was placed in a humid atmosphere (relative humidity 60%) for 3 min before the annealing process and subsequently annealed on a hot plate. For hot air annealing, the film was annealed in a hot-air environment in a N₂ filled dry oven at 120 °C for 30 min after the moisture pretreatment. The PC₆₁BM (20 mg/mL in chlorobenzene) was deposited by spin coating at 1000 rpm for 40 s to form a complete film. Further details of fabrication of the perovskite films and PSCs have been reported in a previous paper [15].

The steady-state fluorescence spectra and time-resolved fluorescence-decay profiles are recorded using a Hitachi F-4500 fluorescence spectrophotometer and a time-correlated single photon counting (TCSPC) system, respectively [17,18]. In the fluorescence measurements, we deliberately photoexcite the quartz sides of films of quartz/perovskites, quartz/PEDOT:PSS/perovskites, quartz/perovskites/PCBM, and quartz/PEDOT:PSS/perovskites/PCBM for monitoring carrier transport dynamics under the same condition with sun light irradiation onto PSCs: Intensities of the steady-state fluorescence spectra and profiles of the time-resolved fluorescence-decays are also found to be influenced by the direction of photoexcitation of the films. The decay-time constants for the fluorescence-decay profiles are obtained by first deconvoluting the measured signal from the pump time profile (characterized by a full width at half maximum of ~100 ps) and then fitting to a sum of exponential terms [19]. The chi-square (χ^2) values of the fitting are 1.0–1.5.

3. Results and Discussion

The scanning electron microscope images and time-resolved fluorescence-decay profiles of the conventional, MPT-, and HAAP-perovskite films and corresponding solar cell device characteristics (current–voltage curves) are shown in Fig. 1. After annealing the perovskite film with moisture and hot air, the number of pinholes systematically decreases, while the fluorescence-decay time and device power conversion efficiency (PCE) increase, as characterized by the decay-time constants of 68, 207, and 397 ns and the PCEs of 9.05%, 11.87%, and 15.55%, respectively (Fig. 1). We note that in Fig. 1b, the time-resolved fluorescence-decay profiles of the perovskite samples are consistently fitted by using single exponential-decay functions. These single exponential decays are comparable to those of other small grain-sized perovskites with diameters of a few micrometres [20]. Lie et al., previously demonstrated that these single exponential decays result from trap-assisted carrier recombination rather than free-carrier-assisted carrier recombination characterized by multi-exponential fluorescence-decay profiles of larger grain-sized perovskites [20]. Following these, the elongated fluorescence-decay times after annealing the perovskites are indicative of reduced number of carrier trapping sites, in good agreement with the reduced number of pin holes shown in Fig. 1a. Note that in Fig. 2, the reduced number of carrier trapping sites after annealing the perovskites results in the intensified fluorescence spectra of MPT- and HAAP-perovskites compared to the one of conventional perovskite.

Charge carrier transports of PSCs are investigated by comparing the steady-state fluorescence spectra and time-resolved fluorescence-decay profiles obtained from films of pure perovskites, PEDOT:PSS/perovskites, perovskites/PCBM, and PEDOT:PSS/perovskites/PCBM, fabricated with the conventional, MPT- and HAAP-perovskite layers (Figs. 2 and 3).

When coated on or under the carrier transporting layers of PEDOT:PSS and PCBM, the conventional, MPT- and HAAP-perovskites exhibit differing degrees of fluorescence quenching (Fig. 2). The fluorescence

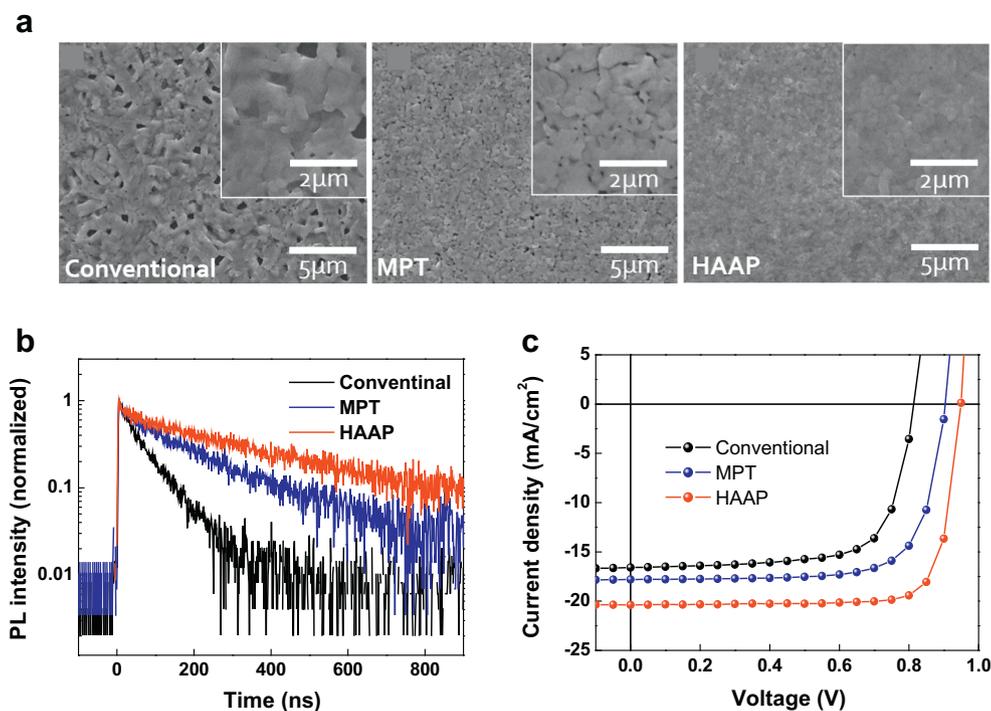


Fig. 1. (a) Scanning electron microscope images, (b) time-resolved fluorescence-decay profiles of the conventional, MPT-, and HAAP-perovskite films, and (c) current density–voltage (J–V) characteristics of corresponding PSCs, adapted from [15]. The excitation wavelength of 470 nm is used for measurement of time-resolved fluorescence-decay profiles. The optimized HAAP cell shows the best device characteristic parameters (PCE, FF, J_{sc} , and V_{oc} of 15.55%, 80.30%, 20.39 mA/cm², and 0.95 V, respectively), compared to the conventional cell (9.05%, 64.43%, 16.34 mA/cm², and 0.67 V, respectively) and the MPT cell (11.87%, 74.07%, 17.80 mA/cm², and 0.90 V, respectively).

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