Post-treatment of perovskite film with phenylalkylammonium iodide for hysteresis-less perovskite solar cells

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ABSTRACT

Superb solar-to-electricity conversion property of organic-inorganic halide perovskite has recently received considerable attention. Although the power conversion efficiency (PCE) reaches over 22%, severe current-voltage hysteresis in perovskite solar cells has been issues. To solve the hysteresis, we report here on interfacial engineering via post-treatment of perovskite films with phenylalkylammonium iodide. The 145 °C-annealed $FA_{.9}Cs_{.1}PbI_{2.9}Br_{.1}$ perovskite films are post-treated with series of phenylalkylammonium iodides with chemical formula of $(C_6H_5)C_nH_{2n}(NH_3I)$, where effects of concentration and solvent on photovoltaic performance and hysteresis are systematically investigated. For n = 2 phenylethylammonium iodide (PEAI), hysteresis is reduced by PEAI treatment but there is optimal concentration to minimize the hysteresis. Average PCE, estimated from reverse and forward scanned data, of 15.94% before PEAI treatment is improved to 17.62% after 4 mM PEAI treatment mainly due to increase in average FF from 0.696 to 0.751. At higher concentration of 10 mM, average PCE is declined again to 15.60% due to the large difference in FF between reverse and forward scan. Post-treatment with PEAI increases carrier life time from 500 ns (pristine) to 795 ns, which is responsible for the reduced hysteresis. Longer alkyl chain such as PEAI (n = 2) is found to be better to reduce the hysteresis than shorter one like PAI (n = 0) because of longer carrier life time, which indicates that dipole moment of phenylalkylammonium iodide is involved in time-dependent charge extraction.

1. Introduction

Since the report on the ca. 10% and 500-h stable solid-state perovskite solar cells in 2012 [1,2] following the perovskite-sensitized liquid junction solar cells reported in 2009 [3] and 2011 [4], a considerable attention has been paid to the organic-inorganic halide perovskite solar cells (PSCs) because of superb efficiency, low cost and facile fabrication process. Power conversion efficiency (PCE) as high as 22.1% was recently certified [5]. Such a high PCE value resulted mostly from developments of perovskite film coating process and highly crystalline perovskite grains [6–11]. Defect and interfacial engineering of perovskite layer was also found to be equally important in enhancing PCE [12–14]. Surface defects of perovskite grains can trap charges, which leads to low photovoltaic performance and current-voltage hysteresis [15,16]. As one of methods, interfacial engineering has been proposed to passivate the surface defects [17–21]. Especially Phenylethylammonium iodide (PEAI) is located and the PEA^+ interact with PbI_2 at grain boundary, which leads to improve open-circuit voltage when methylammonium lead iodide ($MAPbI_3$, MA = CH_3NH_3) or formamidinium lead iodide ($FAPbI_3$, FA = $HC(NH_2)_2$) film was post-

treated with PEAI [21–23], while effect of PEAI on hysteresis could not be observed because hysteresis-less inverted structure was used. As compared to inverted structure, normal structure with mesoporous TiO_2 has usually demonstrated better photovoltaic performance [24]. Thus, we have been interested in investigating effect of PEAI on the hysteresis in the normal mesoporous structure. Moreover, we are also interested in photovoltaic performance and hysteresis depending on carbon chain length between phenyl and ammonium such as phenylalkylammonium iodide $(C_6H_5)C_nH_{2n}(NH_3I)$ (n = 0,1 and 2).

Here we report on surface passivation of $FA_{.9}Cs_{.1}PbI_{2.9}Br_{.1}$ perovskite films with phenylalkylammonium iodides (phenylammonium iodide (PAI), phenylmethylammonium iodide (PMAI) and phenylethylammonium iodide (PEAI)) and its effect on photovoltaic performance and hysteresis of perovskite solar cells with normal structure employing blocking TiO_2 layer, mesoporous TiO_2 layer and spiroMeOTAD hole transporting layer. The composition of perovskite $FA_{.9}Cs_{.1}PbI_{2.9}Br_{.1}$ was selected because this composition is more stable than pure α-$FAPbI_3$ due to Cs incorporation [25]. When the perovskite films were post-treated with phenylalkylammonium iodides, effects of solution concentration, kind of solvent and temperature on performance and

hysteresis are systematically investigated. In this work, we found that hysteresis tends to be reduced as carbon chain length between phenyl and ammonium functional group increases.

2. Material and methods

2.1. Synthesis of materials

HC(NH$_2$)$_2$I (FAI) was synthesized according to the method described elsewhere [1,4]. 30 ml of hydroiodic acid (57 wt% in water, Sigma-Aldrich) was reacted with 15 g of formamidinium acetate (99%, Aldrich) in ice bath. After stirring for 1 h, dark yellow precipitate was obtained by evaporating the solvent at 60 °C using rotary evaporator. The solid was washed with diethyl ether and recrystallized from anhydrous ethanol. Resulting white precipitate was dried under vacuum for 24 h at 60 °C and stored under Ar atmosphere. Phenylalkylammonium iodides (C$_6$H$_5$)C$_n$H$_{2n}$(NH$_3$I) (phenylammonium iodide (PAI) for C = 0, phenylmethylammonium iodide (= benzylammonium iodide) (PMAI) for C = 1 and phenylethylammonium iodide (PEAI) for C = 2) were synthesized by reacting aniline (≥ 99.5%, Sigma-Aldrich) or benzylamine (98 + %, Alfa-Aesar) or phenethylamine (≥ 99%, Aldrich) with excess ([HI]/[phenylalkylamime] = 1.2) of hydroiodic acid (57 wt% in water, Sigma-Aldrich) in ice bath. After stirring for 1 h, dark yellow precipitate was obtained by evaporating the solvent at 60 °C using rotary evaporator. The solid was washed with diethyl ether and recrystallized from anhydrous ethanol. Resulting white precipitate was dried under vacuum for 24 h at 60 °C and stored under Ar atmosphere.

2.2. Solar cell fabrication

FTO glasses (Pilkington, TEC-8, 8 Ω/sq) were first cleaned with detergent and ethanol, which was followed by further cleaning with ultraviolet-ozone (UVO) for 20 min to remove organic contaminants. The compact blocking TiO$_2$ layer (cp-TiO$_2$) was deposited on the cleaned FTO glass by immersed 20 mM aqueous TiCl$_4$ (99.9%, Sigma-Aldrich) solution at 70 °C for 20 min. The TiCl$_4$-treated film was cleaned with deionized water and annealed at 500 °C for 30 min. After cooling down to room temperature, the film was exposed to UVO for 20 min before coating mesoporous TiO$_2$ layer. Mesoporous TiO$_2$ (mp-TiO$_2$) layer was deposited on top of the cp-TiO$_2$ layer by spin-coating a diluted TiO$_2$ paste (40 nm sized TiO$_2$ nanoparticles, terpineol, ethylcellulose and lauric acid with a nominal composition of 1.25: 6.0: 0.9: 0.1 in wt%) in 1-butanol (0.11 g/ml) at 2000 rpm for 20 s. The film was annealed at 550 °C for 1 h, which was post-treated with 20 mM aqueous TiCl$_4$ solution at 70 °C for 10 min and then annealed again at 500 °C. For FA$_{.9}$Cs$_{.1}$PbI$_{2.9}$Br$_{.1}$ perovskite film, a coating solution was prepared by mixing 0.1547 g of FAI, 0.0213 g of CsI (99.999%, Aldrich) and 0.461 g of PbI$_2$ (99.9985%, Alfa-Aesar) in a mixed solvent of 0.5 ml of N,N-dimethylformamide (DMF) (anhydrous, 99.8%, Sigma-Aldrich) and 0.075 ml N,N-dimethylsulfoxide (DMSO) (> 99.5%, Sigma-Aldrich), which was stirred at room temperature for 2 h before use. The 25 μl of precursor solution was spin-coated on the top of the substrate at 4000 rpm for 20 s, where 0.35 ml of diethyl ether (≥ 99.7%, anhydrous, Sigma-Aldrich) was dropped while spinning to induce intermediate adduct film. The perovskite layers were formed by annealing at 145 °C for 40 min. The 145 °C-annealed perovskite films were post-treated with phenylalkylammonium iodide solution using spin-coating method, where solution concentration was varied from 2 mM to 10 mM in different solvents of methanol (99.9%, Alfa-Aesar), ethanol (99.5%, anhydrous, Sigma-Aldrich) and isopropanol (IPA, ≥ 99.5%, anhydrous, Sigma-Aldrich). The post-treated perovskite films were dried at 100 °C for 10 min to remove residual solvent (we have tested at different temperature ranging from 65 °C to 100 °C and 100 °C was found to be optimal drying condition). Spiro-MeOTAD [2,2′,7,7′-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9′-spirobifluorene] hole transporting layer was deposited on top of the perovskite film by spin-coating the 20 μl of spiroMeOTAD solution, consisted of 72.3 mg of spiroMeOTAD, 28.8 μl of 4-tert-butyl pyridine and 17.5 μl of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) solution stock solution was prepared by dissolving 520 mg of LiTSFI in 1 ml of acetonitrile (99.8%, Sigma-Aldrich) in 1 ml of chlorobenzene, at 3000 rpm for 30 s. Finally, Au electrode was deposited by thermal evaporation at a constant evaporation rate of 0.3 Å/s for 80 min.

2.3. Characterizations

Photocurrent density (J)–voltage (V) curves were measured by 4-point probe technique with a solar simulator (Oriel Sol 3A class AAA) equipped with a 450 W Xenon lamp (Newport 6279NS) and a Keithley 2400 source meter. The light intensity was adjusted with the NREL calibrated Si solar cell having a KG-2 filter for approximating one sun light intensity (100 mW/cm^2). The active area was covered with a metal aperture mask (0.125 cm^2) during the measurement. External quantum efficiency (EQE) was measured using an EQE apparatus (PV measurement). The monochromatic beam was generated from a 75 W xenon lamp (USHIO). EQE data were collected in the DC mode [26]. Steady-state and time-resolved photoluminescence (PL) were measured by a Quantaurus-Tau compact fluorescence lifetime spectrometer (Quantaurus-Tau C11367-12, Hamamatsu). The film samples were excited with 464 nm laser (PLP-10, model M12488-33, peak power of 231 mW and pulse duration of 53 ps, Hamamatsu) pulsed at repetition frequency of 10 MHz for time-integrated and 500 kHz for time-resolved PL. Absorbance was measured using a UV/vis spectrometer (Lamda35, PerkinElmer). X-ray diffraction patterns were collected by using a PW 1050 diffractometer (Philips) under graphite-monochromated Cu-K$_\alpha$ radiation (λ = 1.54184 Å). Surface morphology was investigated using scanning electron microscope (SEM, JSM-7600F, JEOL).

3. Results and discussion

In Fig. 1, procedure for the post-treatment of perovskite film with phenylalkylammonium iodides is schematically illustrated, along with chemical structure of PAI, PMAI and PEAI. Spin-coating of perovskite precursor solution leads to adduct of perovskite composition with DMSO [27], which results in perovskite grains after eliminating DMSO at 145 °C. According to the previous report [28], small amount of PEAI was admixed with FAI in isopropyl alcohol, which was spin-coated on PbI$_2$ film. However, the location of PEAI is hard to determine because PEAI can form 2-dimensional (PEA)$_2$PbI$_4$ [29] that could be mixed with 3-dimensional FAPbI$_3$. Our method is aiming at surface passivation, which should be performed by post-treatment. Phenylalkylammonium iodide solution is spin-coated on the 145 °C-annealed perovskite film, which is followed by drying at 100 °C to remove the residual solvent on
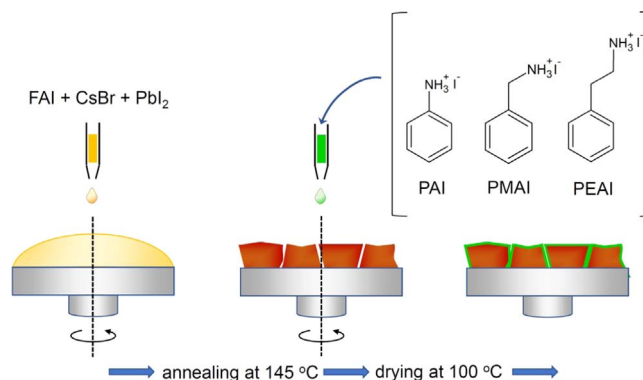

Fig. 1. Schematic illustration of coating of FA$_{.9}$Cs$_{.1}$PbI$_{2.9}$Br$_{.1}$ perovskite film and post-treatment with phenylalkylammonium iodides with different alkyl chain between phenyl and ammonium. Perovskite film was annealed at 145 °C and the poste-treated phenylalkylammonium iodide was dried at 100 °C.