Direct formation of I_3^- ions in organic cation solution for efficient perovskite solar cells

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ABSTRACT

This work presents an easy and controllable method for introducing I_3^- ions into organic cation dripping solution via chemical reaction of $I^- + I_2 \rightarrow I_3^-$ to effectively decrease the concentration of defects in organic-inorganic lead halide perovskite films. The perovskite solar cells based on additional I_3^- ions exhibited better photovoltaic performance, with a maximum power conversion efficiency of 18.7%, being about 15% higher than that of the control device. The elucidation of defects and its suppression by employing additional I_3^- ions provide an important direction for defects elimination and future enhancement of perovskite solar cells efficiency.

1. Introduction

To date, organic-inorganic lead halide perovskite solar cells (PSCs) have developed rapidly with the highest certification power conversion efficiency (PCE) of 22.7% [1]. Such a great success of organic-inorganic lead halide perovskite can be mainly attributed to its superior optoelectronic properties, like direct band-gap, small exciton binding energy, and long carrier recombination lifetime [2–4], which are ideal for photovoltaic applications. In view of high efficiency, low-cost fabrication methods, PSCs have become one of the most promising candidates for next generation solar cells [4].

Uniformly high-quality organic-inorganic lead halide perovskite films are critical for achieving high-performance PSC devices. In this regard, the nucleation and growth process of perovskite crystal films during low temperature, solution-processed preparation determines the device performance [5,6]. Several investigations have pointed out that defects like vacancies, interstitials and cation substitutions, are unavoidably introduced into polycrystalline perovskite films during low temperature, solution-processing perovskite film preparation process [3,7–9]. This naturally results in a relatively high defect density. Taking $CH_3NH_3PbI_3$ ($MAPbI_3$) as an example, the defect density in a polycrystalline film is in the range of 10^{16}–10^{17} cm^{-3}, being 6–7 orders higher than its single crystal [10,11]. Though organic-inorganic lead halide perovskite is proposed to be defect tolerance for most defects create only shallow trap states near the band edges [12], we have been aware of the negative effects from defects like Pb-interstitials and Pb-I anti-sites which create deep-level defect states [3,13]. These defects could induce a high-rate non-radiative charge recombination, and thus decrease open-circuit voltage (V_{OC}) of PSC devices [14,15]. Therefore,

reducing defect density has become essential for processing high-quality organic-inorganic lead halide perovskite films aiming for highly efficient PSC devices. To achieve this goal, for example we have investigated the role of synthesis parameters on quality of perovskite films and demonstrated that larger perovskite precursor concentration with higher spinning speed enable the fabrication of perovskite films with larger grain size and less defects [16].

During the annealing process of $MAPbI_3$ perovskite films, iodine is easily vaporized from the perovskite lattices due to its weak binding strength with Pb atoms [17]. The loss of iodine creates iodine vacancy-site defects, as well as unsaturated Pb, which is correlated with deep-level defects including Pb interstitials and Pb-I anti-sites [3,13]. X-ray photoelectron spectroscopy (XPS) characterization has clearly verified the presence of Pb^0 with a binding energy at 136.8 eV and 141.7 eV [18–20]. Very recently, Seok et al. introduced additional tri-iodide ions (I_3^-) into the organic cation dripping solution, achieving efficient organic-inorganic lead halide PSC devices [3]. The additional I_3^- ions in organic cation solution reduce the concentration of vacancies of iodine, as well as deep-level defects in the perovskite films. However, the process of producing I_3^- ions by reacting iodine with isopropyl alcohol (IPA) is time-consumable (about 7 days) and easily influenced by experimental conditions.

Herein, this study presents a direct and easy method for introducing I_3^- ions in organic cation dripping solution through chemical reaction $I^- + I_2 \rightarrow I_3^-$. Considering the extremely high equilibrium constant for the reaction of $I^- + I_2 \rightarrow I_3^-$ ($pK = 10^7$ $L\,mol^{-1}$), I_3^- ions can be spontaneously formed in a solution that containing I_2 and I^- ions [21,22]. The advantage of our method can be foreseen that the concentration of I_3^- ions can be precisely controlled. Various characterizations, including

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X-ray photoelectron spectroscopy (XPS), nanosecond transient absorption spectroscopy (n-TAS), transient photo-voltage decay (TPVD) and electronic impedance spectroscopy (EIS) measurements reveal that the introduction of additional I_3^- ions in organic cation solution can significantly compensate the loss of iodine during perovskite film annealing process, as well as decrease the concentration of defects in resulting perovskite films. Thus, highly efficient organic-inorganic lead halide PSC devices with PCE of 18.7% can be achieved under standard testing condition.

2. Experimental section

2.1. Materials

PbI$_2$ (99%), SnCl$_2$·2H$_2$O (98%), anhydrous N, N-dimethylformamide (DMF), anhydrous dimethylsulphoxide (DMSO), isopropyl alcohol (IPA), anhydrous chlorobenzene (CB), lithium bis-(triuoromethylsulfonyl) imide (Li-TFSI) and 4-tert-butylpyridine (t-BP) were purchased from Sigma-Aldrich. Spiro-OMeTAD was purchased from Lum-Tec. Anhydrous ethanol, methylamine (40% in methanol) and hydroiodic acid (57% in water) were purchased from Aladdin reagent. All reagents were used as received without any further purification.

2.2. Synthesis of CH₃NH₃I (MAI) and CH₃NH₃Cl (MACl)

In brief, MAI was synthesized by adding 15 mL methylamine (40% in methanol) and 16.15 mL hydroiodic acid (57% in water) into a flask at 0 °C and stirring for 2 h. To precipitate MAI, rotary evaporation was used to remove the solvents and the products were washed several times with diethyl ether. White MAI crystals were obtained after drying the products in vacuum for 3 days. MACl was synthesized using the same method, only changed the hydroiodic acid to hydrochloric acid.

2.3. Introduction of I₃⁻ ions in organic cation solution

Additional I_3^- ions were introduced into MAI/MACl dripping solutions (50 mg MAI and 5 mg MACl in 1 mL IPA). Firstly, solid-state iodine particles were dissolved in isopropyl alcohol (IPA) to form a 0.1 M (mol L^{-1}) iodine IPA solution. Then, different amount of the 0.1 M iodine IPA solution was added into the three MAI/MACl solutions to produce MAI/MACl solutions with different concentration (0.1 mM, 0.4 mM, 1 mM) of I_3^- ions through chemical reaction $I^- + I_2 \rightarrow I_3^-$. Since equilibrium constant for the reaction $I^- + I_2 \rightarrow I_3^-$ is 10^7 L mol^{-1}, the concentration of I$^-$ and I$_2$ is only 1% of the concentration of I_3^- for a solution that contains a total of 1 mM I_3^- [21]. Therefore, the amount of I_3^- ions in the MAI/MACl solutions can be generally considered as the same to added iodine.

2.4. Device fabrication

Patterned ITO glass substrates were ultrasonically cleaned with detergent water, deionized water, acetone and ethanol for 20 min respectively. After dried with clean dry air, the substrates were treated with UV-O$_3$ for 15 min. Compact SnO$_2$ layer was fabricated by spin-coating SnCl$_2$·2H$_2$O precursor solution (11.5 mg mL^{-1}) with 4000 rpm twice onto the ITO glass substrates, followed by annealing at 150 °C for 30 min and 180 °C for 60 min, respectively. After cooling to room temperature, the glass/ITO/SnO$_2$ substrates were again treated with UV-O$_3$ for 15 min and then transferred into the argon filled glove box. CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite films were prepared via a two-step sequential deposition method. 520 mg mL^{-1} PbI$_2$ solution in DMF and DMSO (9:1, v/v) was spun onto the glass/ITO/SnO$_2$ substrates at 3000 rpm for 30 s, then, the substrates were annealed on a 70 °C hot plate for 15 min. After cooling to room temperature, the PbI$_2$ substrates were dripped with MAI/MACl solution (50 mg MAI and 5 mg MACl in 1 mL IPA) with/without additional I_3^- ions at 3000 rpm for 30 s. After

that, the substrates were transferred onto a 135 °C hot plate for 20 min to form the perovskite layers. Hole transport material (HTM) was prepared by dissolving 72.3 mg of spiro-OMeTAD, 28.8 mL of t-BP and 17.5 mL of a stock solution of 520 mg mL^{-1} Li-TFSI in acetonitrile in 1 mL of CB, then spin-coated at 4000 rpm for 30 s on to the perovskite layer. Finally, 80 nm gold electrode was thermal evaporated on to the PSC devices in a vacuum chamber.

2.5. Characterization

X-ray diffraction (XRD) experiments were conducted using a Philips X-ray diffractometer with Cu Kα radiation. UV–visible absorption spectra were observed with a PE950 spectrophotometer at 25 °C. Top view and cross section SEM images of the sample were obtained with a field-emission scanning electron microscope, FEI Nova NanoSEM 450. Tapping mode atomic force microscopy (AFM) was performed using a Veeco multimode instrument to identify surface roughness of perovskite films. The steady-state photoluminescence (PL) spectrum was measured using Horiba Jobin Yvon system with an excitation laser beam at 450 nm from the air side. Time-resolved photoluminescence decays were was measured at 760 nm with a 500 nm light pulse as excitation by Delta Flex Fluorescence Lifetime System (Horiba Scientific Com., Japan). For the nanosecond transient absorption spectroscopy, about 50 μJ of pulse energy as the fundamental output from a Ti: Sapphire femtosecond regenerative amplifier (800 nm, 35 fs FWHM, 1 kHz, Newport Spectra-Physics) was used to generate pump and probe beams. By introducing the fundamental beams into an optical parametric amplifier (Light Conversion Ltd), we could select a certain wavelength from the tunable output as the pump pulses, whereas light continuum probe pulses were obtained by focusing the fundamental beams onto a sapphire plate (contained in LP920, Edinburgh Instruments). The transmitted probe light from the samples was collected and focused on the broadband VIS-NIR detector for recording the time-resolved excitation induced difference spectrum (ΔOD). A xenon light source solar simulator (450 W, Oriel, model 9119) with an AM 1.5 G filter (Oriel, model 91192) was used to give an irradiance of 100 mW cm^{-2} at the surface of the solar cells. The photocurrent density-voltage (*J-V*) characteristics of the perovskite solar cell devices were measured by recording the current through Keithley 2400 digital source meter. A xenon light source solar simulator (450 W, Oriel, model 9119) with AM 1.5 G filter (Oriel, model 91192) was used to give an irradiance of 100 mW cm^{-2} at the surface of solar cells. A white-light bias (10% sunlight intensity) was applied onto the sample during the EQE measurements with the alternating current (AC) model (130 Hz). The electronic impedance measurements were performed using the PGSTAT302N frequency analyzer from Autolab (The Netherlands) together with the Frequency Response Analyzer to give voltage modulation under the giving range of frequency. The electronic impedance spectra (EIS) of the devices were recorded at potentials varying from $-1.2 – 0$ V at frequencies ranging from 1 Hz to 4 MHz, the oscillation potential amplitudes being adjusted to 10 mV. The Z-view software (v2.8b) was use to analyze the impedance data.

3. Results and discussion

Additional I_3^- ions were introduced into MAI/MACl dripping solutions (50 mg MAI and 5 mg MACl in 1 mL IPA) to decrease the concentration of defects in resulting perovskite films. The MAI/MACl solutions with different concentration (0.1 mM, 0.4 mM, 1 mM) of I_3^- ions were produced through chemical reaction $I^- + I_2 \rightarrow I_3^-$. Comparing to the method of producing I_3^- ions through complicated chemical process by reacting iodine with IPA, the advantage of our method is easily foreseen: the concentration of I_3^- ions can be precisely under control. Fig. 1a compares the UV–visible absorption spectra of IPA, MAI/MACl solution, and MAI/MACl solutions with different concentration (0.1 mM, 0.4 mM, 1 mM) of I_3^- ions. Two peaks at 361 nm and 291 nm