Light-current-induced acceleration of degradation of methylammonium lead iodide perovskite solar cells

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HIGHLIGHTS

- Light-current can induce the acceleration of perovskite solar cells degradation.
- The moisture and iodine play a significant role in the accelerated degradation.
- A degradation hypothesis is proposed to explain the accelerated degradation.

GRAPHICAL ABSTRACT
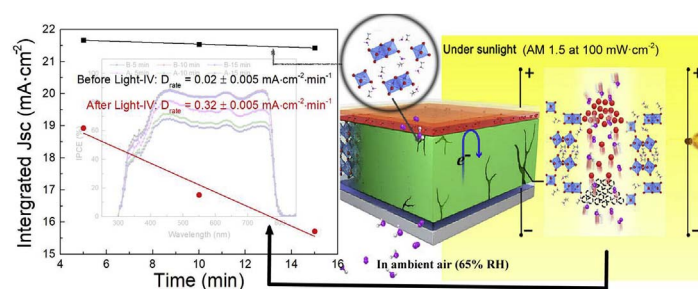
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ABSTRACT

The photo-conversion efficiency of perovskite solar cells (PSCs) has been improved considerably in recent years, but the poor stability of PSCs still prevents their commercialization. In this report, we use the rate of the integrated short-circuit current change (D_{rate}) to investigate the performance degradation kinetics and identify the degradation of PSCs that is accelerated by the light current. The value of D_{rate} increases by an order of magnitude from about 0.02 to $0.35\,\mathrm{mA\,cm^{-2}\cdot min^{-1}}$ after light-IV testing. The accelerated degradation progress is proven to be dominated by the hydration process and the migration of the iodine ions of the light current. The migration of the iodine ions enhances the hydration process through a chain reaction, enabling the formation of fast diffusion channels for both H_2O and O_2, which induce the rapid decomposition of the perovskite film and increase the density of the trap state. The X-ray photoelectron spectroscopy measurement data also indicate that the super oxygen may be formed due to the PCBM damage caused by the migration iodine ions. An understanding of the degradation acceleration mechanism would provide an insight into the effect of ion migration on the stability of PSCs.

1. Introduction

Lead halide perovskite materials have attracted considerable attention in the photovoltaic field in recent years due to their excellent photo-electrical properties. Furthermore, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has rapidly risen from 3.8% [1] to 22.1% [2], as a result of improvements in the fabrication process [3,4], intermediate engineering [5,6], interface engineering [7], and so on [8,9].

However, the poor stability of PSCs has become the main issue preventing their commercialization, and therefore this issue has been addressed by many studies. Many factors are regarded as playing a role in the degradation of PSCs: moisture [10] and oxygen [11] from the air, electric fields [12], light illumination [13], and even iodine-vapor [14]. Moisture and oxygen are the chief factors leading to the decomposition of perovskite films (into PbI_2, CH_3NH_2 and HI) as a result of hydration and redox with superoxide oxygen (O_2^-), respectively [11,15,16]. The

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molecular oxygen can react with the photo-generated electron from the perovskite layer to form O_2^- [11,17]. Exposure to light is assumed to lead to the ultraviolet-assisted decomposition of the perovskite [13] as well as the formation of deep-level trap states which induce the slow and recoverable degradation of the photocurrent [18,19]. The electric field can induce the decomposition of perovskite films accompanied by the migration of ions [20], but the significant decline in the performance can only be observed at voltages higher than the open-circuit voltage (V_{oc}) [21]. Most previous works, however, focused on the identification of the degradation factors, while paying little attention to the dynamic process of performance decline, an understanding of which could provide the insights needed to improve the long-term stability. The moisture-induced degradation is not a simple hydrolysis reaction [15], rather, a four-stage process associated with reactions in the PbI_2-CH_3NH_3I-H_2O system is found to dominate the degradation and proceeds over the course of a minute [22].

In this work, we used the rate of change of the integrated short-circuit current (J_{sc}) to investigate the performance degradation kinetic as D_{rate}. A light-current-induced degradation acceleration of PSCs was observed and investigated from both physical and chemical perspectives. We found that D_{rate} increased by an order of magnitude, from about 0.02 to approximately 0.35 mA cm^{-2}·min^{-1}, after a light-IV test. To further analyze the mechanism of this sudden increase in the rate of degradation, we performed electrochemical impedance measurements (EIS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and focused ion beam assisted scanning electron microscope (FIB-SEM). Based on the experimental data, we attributed the degradation acceleration to the reaction of the moisture and migration iodine ions with the perovskite layer.

2. Experimental

2.1. Device fabrication

The hole transport layer (HTL) was formed through the spin-coating of Clevios PVP AI 4083 poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, Heraeus) on ozone-treated indium tin oxide glass ($< 15 \Omega$/sq) at 6000 rpm for 30 s and subsequently heating to 120 °C for 15 min. For the active layer ($CH_3NH_3PbI_3$ film) fabrication, PbI_2 and MAI were dissolved at a molar ratio of 1:1.1 in a mixture of n,n-dimethylformamide (DMF, Sigma-Aldrich) and dimethyl sulfoxide (DMSO, Sigma-Aldrich) as precursor solutions with a nominal concentration of PbI_2 at 2M, while *sec*-butyl alcohol was used to induce the crystallization deposition, the details of which can be found in the literature [23,24]. The precursor solution was spin-coated on the HTL at 6000 rpm for 20 s after heating to 70 °C for 10 min, and 200 μl of *sec*-butyl alcohol was dripped onto the surface over 7 s during the spin-coating. After a short annealing at 100 °C for 10 s, the films underwent a three-step annealing to improve the crystallization and photo-electric properties of the perovskite films. The films were first solvent-annealed with 200 μl of *sec*-butyl alcohol for 12 s, then were subjected to thermal annealing at 100 °C in ambient air (65% RH) for 15 min and subsequently in a DMSO atmosphere for another 15 min. Finally, a 100-nm Al layer was thermally evaporated onto the top of the device with an interfacial buffer layer. The interfacial buffer layer was spun on the ETL at 6000 rpm for 20 s using diphenyl-1,10-phenanthroline (Bphen, Nichem Fine Technology Co., Ltd.) solution at a concentration of 0.7 mg/mL in ethanol. The fabrication processes were performed in a nitrogen-filled glovebox, except for the HTL deposition and the thermal annealing of the films.

2.2. Material and device characterization

The current density–voltage (*J–V*) values of the perovskite solar cells were obtained using a Keithley 2400 source meter under simulated AM 1.5 sunlight (Zolix Sirius-SS) at 100 mW cm^{-2} with an active area

of 0.12 cm^2. For convenience and brevity, the current density–voltage test performed under sunlight is called the "light-IV test," while that in the dark is called the "dark-IV test" in this paper. The monochromatic incident photon to current efficiency (IPCE) was measured using the same measurement system combined with a mono-chromator (Zolix Omni-λ). The light source was adjusted using a calibrated silicon photodiode (ABET Technology). Electrochemical impedance measurements (EIS) were performed in the dark as a function of the applied voltage at frequencies of $1–1 \times 10^6$ Hz, using an electrochemical system (Princeton Applied Research, Parstat 2273). These characterization were carried out in an ultra-clean room with a stable ambient atmosphere (65% RH, 25 °C).

The morphology of the perovskite films and the cross-section of the device were observed using a scanning electron microscope (SEM, HITACHI SU8010), while the crystalline structures of the perovskite films were analyzed using an X-Ray diffractometer (XRD, Bruker QUANTAX 200). The chemical compositions of the deposited films were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher, PHI 5000 VersaProbe II). For the XPS characterization, an Al Ka X-ray source was used with a C 1s peak at 284.6 eV as calibration reference. The high-resolution cross-section and corresponding elemental map of the device were obtained using a focused ion beam-assisted SEM (FIB-SEM, Helios Nanolab 660).

3. Results and discussion

3.1. Light-current-induced degradation acceleration

This work investigated the degradation progress of an inverted planar solar cell without encapsulation. The cell structure and morphology of the pinhole-free perovskite film are shown in Fig. 1a. The photocurrent–voltage (*IV*) curves of the non-encapsulated PSC measured after exposure to the ambient atmosphere (approx. 65% RH) in the dark for 15 min (1st test) and 30 min (2nd test) exhibit a clear performance decrease, as shown in Fig. 1c. In the 1st test, the PSC maintains an excellent level of performance (PCE of 16%), with a short-circuit current (J_{sc}) of about 21.4 mA cm^{-2}, a V_{oc} of 0.98 V, and a fill factor (*FF*) of about 77%. When the storage term is increased to 30 min, however, J_{sc}, V_{oc}, and *FF* decrease to 15.4 mA cm^{-2}, 0.96 V, and about 70%, respectively, corresponding to a nearly 37% PCE loss in the 2nd test. Relative to V_{oc} and *FF*, J_{sc} appears to be more sensitive to the length of time in storage. The photovoltaic performance parameters are listed in Table 1.

To further study the degradation kinetics of the PSCs, the IPCE was measured and the rate of the integrated short-circuit current change was used to evaluate the performance degradation progress as D_{rate}. Fig. 2a shows the IPCE curves of a non-encapsulated PSC before and after the light-IV testing for a storage time of 5–15 min. D_{rate} is also shown and the distribution of D_{rate} can be found in Fig. S1. The value of D_{rate} is found to change, being about 0.02 mA cm^{-2}·min^{-1} before the light-IV testing, and about 0.35 mA cm^{-2}·min^{-1} after, corresponding to an order of magnitude increase. It would be reasonable to suppose that the different D_{rate} value was the result of a different degradation mechanism, but the rate of degradation caused by a single factor can also change suddenly depending on the conditions, as in the case of moisture-induced degradation [22]. Given that oxygen requires a timescale in the order of hours to induce degradation [25] while degradation caused by light can be repaired by placing the PSCs in the dark, we can assume that this acceleration in the degradation is caused by either moisture or an electric field. To verify this assumption, the D_{rate} values of PSCs exposed to the ambient atmosphere in the dark for 60 min and after dark-IV testing (with a voltage scan from -0.1 to 1.0 V) for 15 min were measured, as shown in Fig. 2b and c. No obvious change can be observed between the three samples, that is, the D_{rate} before light-IV testing, that of the sample stored for 60 min without IV testing, and that of the sample after dark-IV testing. Meanwhile, for the