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# Supplemental Information

Two-Stage Ultraviolet Degradation

of Perovskite Solar Cells Induced

# by the Oxygen Vacancy-Ti<sup>4+</sup> States

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## **Supplemental Information**

#### **Supplemental Figures**



**Figure S1. The SEM images of perovskite film deposided on glass substrate for 0, 30, 60, 90, 120, 150 days in argon-filled glovebox, related to Figure 1.**



**Figure S2. Schematic diagram of the mechanism that the oxygen vacancy-Ti3+ generation process (Xiong et al., 2012; Bennett et al., 2015; Yu et al., 2011; Zhang et al.2013),related to Figure 2.**



**Figure S3. The curve corresponding the formula of perovskite decomposition rate, related to Figure 2.**



**Figure S4. Perovskite film with different doping ratios of PbI2, MAI and I<sup>2</sup> for different UV exposure time (0 day and 5days), related to Figure 2.**



**Figure S5. XRD patterns of perovskite film with different doping ratios of PbI2, MAI and I<sup>2</sup> for different UV exposure time (0 day, 3 days and 5 days), related to Figure 2.**





(A) Schematic of the device structure and the molecular structure of PEIE.

(B) Top-view SEM images of perovskite films on PEIE-TiO2 ETL, and the inserted image is the

XRD patterns of the corresponding perovskite film.

(C) XPS pattern of N1s core level on the pure TiO<sub>2</sub> and PEIE-TiO<sub>2</sub> substrate.



**Figure S7. The AFM image of TiO<sup>2</sup> ETL surface morphology, related to Figure 3.**

 $(A)$  The pure TiO<sub>2</sub> ETL.

(B) The PEIE-modified TiO<sub>2</sub> ETL.



**Figure S8. XPS Ti(2p) spectra of (A) pure-TiO<sup>2</sup> film and (B) PEIE-TiO<sup>2</sup> film on glass under UV irradiation for 0 day and 10 days, related to Figure 3.**



**Figure S9. XRD patterns of perovskite film in PSCs based on (A) pure-TiO<sup>2</sup> ETL and (B) PEIE-TiO<sup>2</sup> ETL under UV irradiation, related to Figure 4.**



**Figure S10. Morphology evolution of perovskite films under UV exposure, related to Figure 4.** The scanning electron microscope (SEM) images of the perovskite films deposited on pure-TiO<sub>2</sub> ETL (top) and PEIE-TiO<sub>2</sub> (bottom) after UV irradiation for 0, 50, 65 days.



**Figure S11. Photoluminescence spectrum of perovskite film on pure TiO<sup>2</sup> ETL and PEIEmodified TiO<sup>2</sup> ETL under UV irradiation for 0 day and 50 days in glovebox. Related to Figure 5.**

- (A) Steady photoluminescence (PL) spectrum of perovskite film.
- (B) Transient photoluminescence (TRPL) decay of perovskite film.



**Figure S12. Forward (roundness) and reverse (square) scanned J-V curves of the PSCs with (red) and without (black) PEIE layer. Inset: Device performance parameters calculated from the curves. Related to Figure 5.**

**Table S1. The fitting values of R<sup>t</sup> and Rrec based on the EIS Nyquist plots, related to Figure 4.**

|                                  | $R_t(k\Omega)$ | $R_{rec}$ (k $\Omega$ ) |
|----------------------------------|----------------|-------------------------|
| Pure TiO <sub>2</sub> for 0 day  | 64.296         | 58.330                  |
| PEIE/TiO <sub>2</sub> for 0 day  | 61.370         | 76.690                  |
| Pure TiO <sub>2</sub> for 6 days | 89.330         | 48.230                  |
| PEIE/TiO <sub>2</sub> for 6 days | 65.748         | 69.330                  |
|                                  |                |                         |

#### **Transparent Methods**

#### **Materials:**

Methylammonium iodide, formamidinium iodide, 2,2',7,7'-tetrakis (N, N-di-pmethoxyphenylamine)-9,9' spirobifluorene (spiro-OMeTAD) and Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI) were purchased from Xi'an Polymer Light Technology Corp. (Purity: 99.5%). Lead iodide (Purity:99.999%), FK209, titanium tetrachloride (TiCl4, Purity:99.9%) precursor were purchased from Alfa Aesar. N, N-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and chlorobenzene were purchased from Acros Organics (Extra dry). Polyethylenimine, 80% ethoxylated (PEIE) was dissolved in H<sub>2</sub>O with a concentration of 37 wt. % in H<sub>2</sub>O when received from Aldrich.

### **Device Fabrication:**

*Solution Preparation:* TiO<sup>2</sup> solution was prepared according to the report of Wei et al (Dei et al., 2017). 1 mL of TiCl<sup>4</sup> precursor was dropwise added into 50 mL of ultrapure water, and stir it up. To prepare the perovskite precursor solution, 0.25 M of FAI, 0.75 M of MAI, and 1.025 M of PbI<sup>2</sup> were mixed in anhydrous dimethylformamide/dimethylsulfoxide (600 mg/78 mg) solution, which was stirred for 2 h at room temperature in the glove box. To prepare the HTM precursor, Spiro-OMeTAD was solved in chlorobenzene with the concentration of 80 mg·mL−1 and then tert-butylpyridine (28.5 μL in 1 mL chlorobenzene), and lithium bis- (trifluoromethanesulfonyl) imide (8.75 mg·mL−1 ) were added into the Spiro-OMeTAD solution as the additives, which was stirred in the glove box for 6 h as previous works (Song et al., 2016; Cui et al., 2017). To prepare the PEIE precursor solution, it was further diluted with 2 methoxyethanol (hereafter referred to as methoxyethanol) to a weight concentration of 0.1%.

*Perovskite Solar Cell Fabrication:* FTO glass (7 Ω·sq-1 ) was cleaned by sequential sonication with a detergent solution, deionized water, acetone, and isopropyl alcohol for 20 min, respectively. After dried by a nitrogen flow, the substrates were treated with UV-ozone for 15 min before use. TiO<sub>2</sub> films were fabricated by water-bath heating the precursor solution onto the FTO substrates at 70℃ for 30 min. The, TiO<sub>2</sub> films were further treated with UV-ozone for 15 min and then transferred into the  $N_2$ -filled glove box. To fabricate perovskite films, the perovskite precursor was spin coated directly on the TiO<sup>2</sup> substrate at 4000 rpm for 30 s. During the spin-coating step, 0.5 mL diethyl ether was poured on the surface at 22 s before the end. The light-yellow transparent films were converted into the brownish-red perovskite films by heating at 110 °C for 15 min. Then the Spiro-OMeTAD solution was spin-coated at 4000 rpm for 30 s on the perovskite films. Finally, 80 nm Au electrode was evaporated on the films. For the PEIE-modified PSCs, the diluted PEIE solution was spin coated on top of the compact TiO<sub>2</sub> layer at a speed of 5000 rpm for 30 s. Spin-coated PEIE films were annealed at 100 ºC for 10 min on a hotplate in glovebox. Finally, the modified PSCs were fabricated according to the above method.

#### **UV Aging and device monitored:**

We used Philip UV lamp (λ = 254 nm) with an intensity of ~50 mW·cm<sup>-2</sup> (equivalent to 11 suns of UV light below 400nm) to irradiate the PSCs from the  $TiO<sub>2</sub> ETL$  side at room temperature in an argon-filled glovebox. To achieve long-time efficiency monitoring, we designed and assembled an apparatus of stability test device. We attach the PSCs to the

platform of the apparatus so that it can be irradiated by UV light. Then, the apparatus containing the PSCs was transferred to the UV radiation chamber, which is installed in an argon-filled glovebox. The apparatus is sealed and removed every 24h to measure the current voltage curves under simulated AM 1.5G 100 mW·cm-2 irradiance.

#### **Device Characterization:**

Current-voltage curves were measured using a source meter (Keithley 2400) under AM 1.5G irradiation with a power density of 100 mW·cm<sup>-2</sup> from a solar simulator (XES-301S+EL-100) by forward (-0.1 to 1.2 V) or reverse (1.2 to-0.1 V) scans. The light intensity was calibrated with a NIM-certified Si reference cell. The step voltage was fixed at 12 mV and the delay time was set at 10 ms. All PSCs were fabricated with a metal mask that was used to define the active area, which is 0.1 cm<sup>2</sup>. XPS spectra were collected using a Thermo Fisher Scientific ESCALAB 250Xi under 10 $\cdot$ 9 Torr vacuum using a monochromic Al-Ka X-ray source. Fitting procedures to extract peak positions and relative element content from the XPS data were carried out using the Origin software. The UPS spectra were also measured by XPS (ESCSLAB 250Xi). All spectra were shifted to account for sample charging using inorganic Au as a reference. The steady PL spectra of the perovskite films on FTO substrates were measured by a spectrometer (Edinburg PLS 980) at 80 K. The EQE was measured using QE-R systems (Enli Tech.). The EIS patterns of the PSCs were measured by a electrochemical workstation (Zahner Zennium). The absorption spectrums were measured by UV-VIS spectrophotometer (UV-2600). The morphologies of the as-prepared MA<sub>0.75</sub>FA<sub>0.25</sub>PbI<sub>3</sub> were characterized by scanning electron microscopy (SEM) (FEI SIRION 200). The chemical compositions and structures of the MA0.75FA0.25PbI<sup>3</sup> films were analyzed by X-ray diffraction (XRD) (Bruker D8 Advance X-ray diffractometer, Cu-Kα radiation  $λ = 0.15406$  nm).

### **Formula derivation:**

*Reaction rate formula based on the mass action law:*

$$
v = kc_A^a c_B^b
$$
 Formula S1.

*The detail derivation process of the formula:*

$$
V = 8kx^4(1 + \frac{1}{Kc(I^-)})^3
$$

The decomposition procedures of perovskite material in terms of chemical equations:

$$
Ti^{3+} \stackrel{hv}{\rightarrow} Ti^{4+} + e^-
$$
 (1)

$$
2Ti^{4+} + Pb_2I_6^{2-} \stackrel{iv}{\rightarrow} 2Ti^{3+} + 2Pbl_2 + I_2 \tag{2}
$$

$$
I_2 + I^- = I_3^- \tag{3}
$$

$$
3CH_3NH_3^+ + I_3^- + 2e^- \rightarrow 3CH_3NH_2 + 3HI \quad (4)
$$

According to the mass action law, the reaction rate of Equation 4 can be calculated by  $V = kc_{MA}^3 c_{I_3}^1$ 

where V is the reaction rate,  $k$  is the chemical reaction rate constant,  $C_{MA}$  is the qualitative concentration of CH $_3$ NH $_3^+$ ,  $C_{I_3^-}$  is the qualitative concentration of I $_3$ . Based on Equation 2, the  $C_{MA}$  can be written as:  $C_{MA} = 2(C_{I_2} + C_{I_3^-}).$ 

Given that 
$$
x = c(I_3^-)
$$
,  $y = c(I_2)$ , the  $v = k(2(x + y))^3 x$ .

Then, 
$$
v=k(8(x^3+3x^2y+3xy^2+y^3)x
$$
,  $v=8k(x^4+3x^3y+3x^2y^2+xy^3)$ .

For the Equation 3, when it is in equilibrium,  $K = \frac{c(I_3^2)}{c(I_3) \epsilon(I_1)}$  $\frac{c(t_3)}{c(t_2)c(t^-)}$ , where K is the chemical equilibrium constant. Hence,  $K = \frac{x}{\sqrt{2}}$  $\frac{x}{\gamma c(I^-)}$ ,  $y = \frac{x}{\kappa c(I^-)}$  $\frac{\lambda}{Kc(I^-)}$ .

Therefore,  $v = 8k(x^4 + 3x^3 \frac{x}{\ln 6})$  $\frac{x}{Kc(I^-)} + 3x^2 \frac{x^2}{K^2c(I^-)}$  $\frac{x^2}{K^2c(I^-)^2} + x \frac{x^3}{K^3c(I^-)}$  $\frac{x}{K^3c(l^-)^3}$ .

Finally,  $v = 8kx^4(1 + \frac{1}{kx^2})$  $\frac{1}{Kc(I^-)}$ )<sup>3</sup>.

## **Supplemental References**

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