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## Unravelling the mechanism of interface passivation engineering for achieving high-efficient ZnO-based planar perovskite solar cells



Zhenyu Pang <sup>a,b</sup>, Yansen Sun <sup>a,b</sup>, Yanbo Gao <sup>c</sup>, Xinyuan Zhang <sup>a,b</sup>, Yunfei Sun <sup>c</sup>, Jinghai Yang <sup>c,\*</sup>, Fengyou Wang <sup>c,\*\*</sup>, Lili Yang <sup>c,\*\*\*</sup>

<sup>a</sup> Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130033, PR China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing, 100049, PR China

<sup>c</sup> Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun, 130103, PR China

#### HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T

- UV-O<sub>3</sub> treatment on ZnO ETLs results in higher PCE than annealing treatment.
- The O<sub>i</sub> and V<sup>+</sup><sub>O</sub> in ZnO ETLs strongly influence the charge collection in PSCs.
- A record PCE of 17.65% is achieved in ZnO-based PSCs with UV-O<sub>3</sub> treatment.



#### ARTICLE INFO

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#### ABSTRACT

Surface functional groups of ZnO electron transport layers are key factors to limit the power conversion efficiency of ZnO-based planar perovskite solar cells. We adopt ultraviolet ozone and annealing techniques to effectively remove parts of hydroxyl groups on the surface of ZnO layers, which improves the stability of perovskite layers in the crystallizing process, and reduces the number of pinholes and the crevices at the interface of ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Under the similar content of PbI<sub>2</sub>, the efficiency of the device based ZnO layers by ultraviolet ozone treatment for 20 min is not only three times of the device without treatment, but superior to that of the device based ZnO layers by annealing at 300 °C for 1 h. We find that the deep trap states and interstitial oxygen are the key factors to boost the photovoltaic performance of ZnO-based perovskite solar cells during the ultraviolet ozone treatment process, since they dominate the charge carries recombination lifetime at interface of ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and transport efficiency in the ZnO layers. When the treatment time of ultraviolet ozone ficiency of ZnO-based perovskite solar cells without any modified layers.

\* Corresponding author.

\*\* Corresponding author.

\*\*\* Corresponding author.

E-mail addresses: jhyang1@jlnu.edu.cn (J. Yang), wfy\_nku@163.com (F. Wang), llyang1980@126.com (L. Yang).

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#### 1. Introduction

Perovskite solar cells (PSCs) are promising as next-generation thin film photovoltaics attributed to the rapid promotion of power conversion efficiency (PCE) over the past few years [1–9]. The 23.3% certified PCE of PSCs has already been achieved [10], approaching monocrystalline silicon solar cells. Most high PCE devices are based on mesoporous TiO<sub>2</sub> electron transport layers (ETLs), which need high temperature (450 °C–500 °C) sinter process. Such high-cost technique limits the application of perovskite material in flexible devices. The planar structure device was generally processed at low-temperature, which can effectively solve above issues.

Recent studies have tried some low temperature processable and high conductivity material, such as PCBM,  $C_{60}$  and  $SnO_2$  were used as ETLs [11–13]. The inorganic  $SnO_2$  as ETLs obtain favorable effect for the low temperature process, high carrier mobility and suitable band alignment. However, the toxicity of elemental tin has gradually received attention. Regarding to processing temperature, conductivity, band alignment and toxicity, Zinc Oxide (ZnO) should be a better alternative since the bulk electron mobility is 205–300 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and it can be fabricated at room temperature [14–18].

However, there is a gap between the PCE of the ZnO based-PSCs without any modification to the ZnO ETL and the TiO2, SnO2 based-PSCs [19-23]. For instance, Kelly et al. used ZnO nanoparticle solution as the raw material of ZnO ETL, and prepared PSCs device with PCE of 15% [24]. Cao et al. prepared mesoporous ZnO PSCs and achieved PCE of 15.92% [25]. Two major issues have limited the increase of PCE of ZnO-PSCs. The first issue is that the surface functional groups of ZnO induce poorly chemical stability during crystallization process of perovskite film. The second issue is that the methylammonium is easily deprotonated by ZnO to decompose the perovskite [26]. Both issues induce charge carries recombination at the interface of ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. So far, people try to use surface modification technique with inorganic or organic materials as surface modifier to overcome the above two problems, including the inorganic or organic materials as surface modifier and other surface treatments [27]. For instant, Qingbo Meng research group used the atomic layer deposition technology to prepare the ultra-thin titanium dioxide inorganic modification layer on the ZnO nanorods and the PCE reached 13.4% [28]. Kwanghee Lee and Aram Amassian modified the ZnO/perovskite interface with PCBM and PEI, respectively, to obtain the PCE of 6.4% and 10.2% [29,30]. The introduction of inorganic and organic layer improves the stability of perovskite in the synthesis process, but the PCE is far lower than that of TiO2 and SnO2 based PSCs devices. The one important reason is the terrible band alignment and lower conductivity, which increases the Rs and degrades the open voltage (Voc) and filling factor (FF) of the devices [28-31]. Direct surface modification without introducing other materials should be the most promising method to improve the chemical stability of ZnO ETLs. Jung-Kun Lee et al. used ultraviolet ozone treatment and annealing treatment to passivate surface effects of ZnO ETL, the PCE reached 10% and 7%, respectively [32]. In fact, these studies are not comprehensive and there are a lot of significant issues on UV-O3 treatment such as conditional optimization and the physical mechanism of UV-O3 for boosting device performance, that need to be addressed.

Herein, on the basis of optimized synthesis technique of perovskite films, we select both UV-O<sub>3</sub> and annealing treatment techniques to perform the surface modification on ZnO ETLs and optimized treatment conditions to obtain a perovskite absorber layer with better crystal quality. We systematically study the effects of UV-O<sub>3</sub> treatment time and annealing temperature on the ZnO ETLs and the corresponding photovoltaic performance of ZnO-based PSCs. By utilizing such simple and low-cost technique, we achieved a record conversion efficiency of 17.65% for ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cells without any modified interlayer between the ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Meanwhile, a novel physical mechanism related to the deep trap states ( $V_{\rm O}^+$ ) and interstitial oxygen (O<sub>i</sub>) to determine the photovoltaic performance has been unveiled as well.

#### 2. Experimental section

#### 2.1. Materials

Zinc acetate dihydrate, methanol and Potassium hydroxide was purchased from Aldrich. Anhydrous chloroform and Anhydrous nbutanol were purchased from AcrosAll chemicals, which used as received without any further purification. These materials were used preparation ZnO nanoparticle solution.  $CH_3NH_3I$ , Lithium salts (>99.0%), tert-butylpyridine (tBP), Spiro-OMeTAD(2,20,7,70-tetrakis-(N,*N*-di-4-methoxyphenylamino)-9,90-spirobiuorene, >99.0%), and N, *N*-dimethyl formamide (DMF, >99.9%), Dimethyl sulfoxide (DMSO, >99.95%), chlorobenzene (>99.9%) were purchased from YouXuan Tech. Co. All the chemicals and solvents were kept in a glove-box and starting experiments.

#### 2.2. Preparation of ZnO NPs solution and ZnO film

The preparation process of ZnO dispersion is strictly in accordance with the method provided in Kelly et al. literature [24]. The X-ray diffraction pattern of as-prepared ZnO NPs was shown in Fig. S1(supporting information).

Patterned glass/F-doped SnO<sub>2</sub> substrates were sequentially cleaned in deionized water, ethanol and acetone respectively with duration of 20 min each. The ZnO dispersion filtered with a PVDF 0.45  $\mu$ m filter and spin coated on the FTO substrates at 3000 rpm for 30 s, the procedure was repeated three times to obtain a continuous smooth film. The ZnO films were separated into two categories, one set of films were annealed for 1 h at 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C in a nitrogen filled glove-box, which was named as AT-150 °C, AT-200 °C, AT-250 °C and AT-300 °C, AT-350 °C, AT-400 °C. The other set of films were treated with UV-O<sub>3</sub> for 5 min, 10 min, 15 min, 20 min and 25 min, 30 min which was named as UV-5min, UV-10min, UV-15min and UV-20min, UV-25min, UV-30min correspondingly. The ZnO films without any treatment is named as WT for reference. The environment humidity of ZnO ETLs processing is less than 35%.

#### 2.3. Device fabrication

The 85  $\mu$ L precursor solution of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I with equimolar were dissolved in DMF and DMSO with volume ratio of 700  $\mu$ L: 300  $\mu$ L) were spin coated on the prepared ZnO film at 5000 rpm. The 100  $\mu$ L anhydrous chlorobenzene was quickly dropped onto the center of the substrate at 30 s. The films were annealed at 65 °C for 5 min and 100 °C for 10 min [33]. A spiro-OMeTAD solution consist of 72 mg of spiro-OMeTAD, 29.5  $\mu$ L of 4-*tert*-butylpyridine (tBP), and 18.5  $\mu$ L of a lithium-bis (triuoromethanesulfonyl) imide (Li-TFSI) solution (520 mg Li-TFSI/1 mL acetonitrile) in 1 mL of chlorobenzene. It was spin-coated on the perovskite film with 1000 rpm for 10 s and 3000 rpm for 30 s. The samples were stored in the dry and dark circumstance overnight at room temperature. Finally, a 100 nm thick Ag electrode was deposited by thermal evaporation.

Two series solar cells of glass/FTO/ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Sprio-OMe-TAD/Ag have been fabricated in our case. One set of solar cells were fabricated with UV-5min, UV-10min, UV-15min and UV-20min, UV-25min, UV-30min ZnO ETLs. The other set of solar cells were fabricated with AT-150 °C, AT-200 °C, AT-250 °C and AT-300 °C, AT-350 °C, AT-400 °C ZnO ETLs.

#### 2.4. Thin film characterization

UV–Vis–NIR spectra were obtained using an UV–Vis–near-infrared (NIR) spectrophotometer (UV–3101PC) equipped with the integrating

sphere. The X-ray diffraction (XRD) measurements was performed on Japan Rigaku D/max-ga X-ray diffractometer with Cu Ka radiation ( $\lambda = 1.5418$  Å) at room temperature. The step size (2 $\theta$ ) is 0.01°. The SEM images were acquired by a field emission scanning electron microscope (Hitachi S-4800). The steady-state photoluminescence measurements and time-resolved PL measurements (TRPL) measurements were performed on Horiba Jobin Yvon Fluorolog-3 fluorescence spectrometer. We further utilized exponential function: I(t) = I\_0 exp(-(t\_i/\tau\_i)\beta\_i) to fit the decay curves, where  $\tau_i$  is the decay life time and  $\beta_i$  is a stretching parameter. Hall measurements were performed with van der Pauw configuration by Lake Shore 7704A at room temperature. The XPS measurements were carried on X-ray photoelectron spectrometer (ESCALAB MARK II, VG Inc.) with an Al K $\alpha$  monochromatized source.

#### 2.5. Device characterization

The Keithley 2400 source meter measurement system was used to acquire the J–V characteristics of PSCs under AM 1.5 G simulated sunlight illumination (100 mWcm<sup>-2</sup>, Model 91160, Oriel). The light source standard by silicon reference cell (91160V Oriel Instruments). The J–V measurement scan rate was  $0.1 V^{-1}$  and delay time was 10 m. The EQE set-up (QEX10, PV Measurement) was used the spectral responses of PSCs device, during which chopping frequency was 40 Hz and a lock-in amplifier was used. The EIS measurements were performed by Potentiostat Galvanostat EIS Analyzer 4000 at open circuit voltage applying 20 mV amplitude in the range of 1-1 MHz.

#### 3. Results and discussion

Current density-voltage (*J*–*V*) characteristics of two series of glass/ FTO/ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Sprio-OMeTAD/Ag PSCs under simulated AM1.5G illumination (100 mWcm<sup>-2</sup>) are shown in Fig. 1. Photovoltaic parameters of all the PSCs including V<sub>OC</sub>, J<sub>SC</sub>, FF, PCE, series resistance (R<sub>S</sub>) and shunt resistance (R<sub>SH</sub>) are summarized in Table 1. The statistical analysis results shown in Figs. S2 and S3 (Supporting Information) confirm the consistency of the performance trends. Obviously, both UV-

O<sub>3</sub> treatment and annealing treatment can effectively enhance the performance of ZnO-based PSCs, when the UV-O3 treatment time is shorter than 20 min and annealing temperature is lower than 300 °C. With prolonging the UV-O<sub>3</sub> treatment time and increasing the sintering temperature, the R<sub>S</sub> deceases but R<sub>SH</sub> increases, and the photovoltaic performance of the PSCs succession improved. In comparison with the WT PSCs, the Voc of UV-20 min PSCs increased by 18%, Jsc increased by 67%, and PCE increased by 161%. The annealing treatment shows a similar variation tendency to UV-O3 treatment. The Voc, Jsc and PCE of AT-300 °C PSC increased by 14%, 50% and 95% respectively. Obviously, the UV-O3 treatment can improve the performance of ZnO-based planar PSCs more effectively than those of solar cells with annealing treatment. The device performance degrades when the UV-O<sub>3</sub> treatment time exceeds 20 min and annealing temperature is higher than 300 °C. When UV-O<sub>3</sub> treatment time reaches up to 30 min, the Rs of device increases. which is 2 times than that of UV-20min sample. When the annealing temperature is 400 °C, the R<sub>SH</sub> of device decrease, which is 5 times lesser than that of AT-300 °C sample. We performed the stability tests of WT, AT-300 °C and UV-20min devices under simulated AM1.5G continuous illumination in air of RH 50%, as shown in Fig. S4 (Support Information). The stability of the device after annealing and UV-O<sub>3</sub> treatment has been greatly improved.

The EQE spectra of UV-20min, AT-300 °C and WT PSCs are shown in Fig. S5. The EQE spectral shapes for are close to full-conversion over the entire wavelength range. The highest EQE value at 480 nm was 49.5%, 74.2% and 84.7% for the WT, AT-300 °C and UV-20 min PSCs. The integration of EQE leads to integral current density of 11.34 mAcm<sup>-2</sup> (WT), 17.30 mAcm<sup>-2</sup> (AT-300 °C), and 20.11 mAcm<sup>-2</sup> (UV-20min), respectively, which is consistent with the trend of  $J_{SC}$  obtained from Fig. 1. Obviously, the integral current density of UV-20 min PSCs is better than that of AT-300 °C PSCs and WT PSCs. Similarly, UV-O<sub>3</sub> treatment also has obvious effect on promoting device performance.

The performance of perovskite solar cell is mainly determined by both the crystalline quality of perovskite absorption layer and the transport capacity of carriers at the interface [34]. To reveal the detailed influence mechanism for UV-O<sub>3</sub> treatment and annealing treatment on



Fig. 1. (a) (b) J–V curves of PSCs using WT, UV-5min, UV-10min, UV-15min, UV-20min, UV-25min and UV-30min (b) AT-150 °C, AT-200 °C, AT-250 °C, AT-300 °C, AT-350 °C and AT-400 °C.

Table 1

Photovoltaic properties of PSCs using	g UV-5min, UV-10min,	UV-15min, UV-20min,	AT-150 °C, AT-200 °C,	AT-250 °C, AT-300 °C, and WT.
The second				

Samples	Jsc [mA cm <sup>-2</sup> ]	Voc [V]	FF [%]	PCE [%]	Rs [Ωcm <sup>2</sup> ]	Rsh [Ωcm <sup>2</sup> ]
WT PSCs	13.37	0.90	40.0	4.90	26.7	260.4
UV-5min PSCs	17.42	0.98	42.0	7.30	19.3	300.5
UV-10 min PSCs	18.50	1.08	47.0	9.40	16.4	520.2
UV-15 min PSCs	22.61	1.08	53.0	13.00	10.0	1114.3
UV-20 min PSCs	22.86	1.13	68.0	17.65	6.4	1643.1
UV-25 min PSCs	22.20	1.12	51.0	13.48	17.0	1611.0
UV-30 min PSCs	21.48	1.10	45.0	11.42	20.0	689.0
AT-150 °C PSCs	17.36	0.95	41.4	6.87	20.3	249.8
AT-200 °C PSCs	18.65	1.01	44.7	8.43	19.3	443.4
AT-250 °C PSCs	19.97	1.03	47.7	9.90	14.6	530.0
AT-300 °C PSCs	21.72	1.07	50.0	11.80	12.3	748.7
AT-350 °C PSCs	20.60	0.98	40.3	8.20	19.1	199.7
AT-400 °C PSCs	19.82	0.87	35.0	6.20	23.0	117.0

the surface morphologies of perovskite absorption layers, the top-view and cross-sectional SEM images of two sets of samples were shown in Fig. 2 and Fig. 3. As indicated in Fig. S6 (Supporting Information), surface morphology of ZnO ETLs didn't change after the treatment. Fig. 2a illustrates the SEM image of WT perovskite film. Although perovskite film fully covers the ZnO ETLs, many small pin holes and voids exist in the entire film. Fig. 2b-e shows SEM images of perovskite films deposited on the UV-5min, UV-10min, UV-15min and UV-20min ZnO ETLs, respectively. By introducing UV-O<sub>3</sub> treatment, the small pin holes and voids between the ZnO/perovskite interface gradually disappeared via increasing the treatment time. In the case of UV-20min, the continuous compact perovskite film with larger grain size and decreased grain boundaries can be observed in Fig. 2e. Fig. 2f-i shows SEM images of perovskite films deposited on AT-150 °C, AT-200 °C, AT-250 °C and AT-300 °C ZnO ETLs. By annealing treatment, small pin holes and voids between the ZnO/perovskite interface gradually disappeared with increasing the annealing temperature. But even after 300 °C treatment, a few small pin holes still exist in the perovskite film. Agarwal and Liu et al. pointed out from the theoretical simulation and experimental point of view that the presence of pinholes on the surface of perovskites will lead to degradation of device performance [35,36]. The number of small pin holes in the films often induced poor repeatability of device

performance and increased recombination losses to reduce the FF and Voc. This may be one of the reasons why UV-20 min PSCs in Fig. 1 and Fig. S5 are superior to AT-300  $^{\circ}$ C PSCs and WT PSCs.

In order to further determine the treatment effects of ETLs on the interface contact between perovskite thin films and ZnO ETLs, Fig. 3 shows cross-sectional SEM images of the PSCs based on UV-O3 treated, annealing treated and WT ZnO ETLs. As shown in Fig. 3a, the interface of WT/perovskite contains a large number of crevices as well as significant reduction in contact area of perovskite and ETL, which is consistent with increased Rs. As shown in Fig. 3b-e and Fig. 3f-i, the crevices between perovskite and ZnO ETLs decreased significantly by UV-O<sub>3</sub> treatment and annealing treatment. Even though the interfaces of UV-20min/ MAPbI3 and AT-300 °C/MAPbI3 exhibit close contact as shown in Fig. 3e and i, a few crevices still exist at the interface of AT-300 °C sample, which is consistent with top-view SEM images. We also performed SEM measurement on the perovskite films deposited on UV-25min, UV-30min, AT-350 °C and AT-400 °C ZnO ETLs. However, the morphology of the perovskite film did not change significantly as shown in Figs. S7 and S8. Therefore, we believe that there might be some other factor to cause the degeneration of device performance, which will be discussed later.

To understand the formation mechanism of small pinholes in the



Fig. 2. Top-view SEM images of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films deposited on ZnO ETLs of (a) WT, (b) UV-5min, (c) UV-10min, (d) UV-15min, (e) UV-20min, (f)AT-150 °C, (g)AT-200 °C, (h)AT-250 °C, (i) AT-300 °C.



Fig. 3. Cross-sectional SEM images of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films deposited on ZnO ETLs of (a) WT, (b) UV-5min, (c) UV-10min, (d) UV-15min, (e) UV-20min, (f)AT-150 °C, (g)AT-200 °C, (h)AT-250 °C, (i) AT-300 °C.

perovskite films and crevices at the ZnO/perovskite interfaces, the XRD patterns of perovskite thin films deposited on UV-O<sub>3</sub> treated, annealing treated and WT ZnO ETLs were presented in Fig. 4. The strong diffraction peaks located at 14.1° and 28.3° can be assigned to (110) and (220) crystal planes of tetragonal phase CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite [37]. Obviously, a signature peak at 12.65° appears in all XRD patterns, which is attributed to the (001) diffraction peak of PbI<sub>2</sub>. To clearly see the intensity of this peak via UV-O<sub>3</sub> treatment time and annealing temperature, the enlarged XRD patterns at the region of 12–13° are presented in Fig. 4 b and e. It can be seen that the (001) peak intensity of PbI<sub>2</sub> decreased while extending the UV-O<sub>3</sub> treatment time or enhancing the annealing temperature of ZnO ETLs. To distinguish the detailed relative content of PbI<sub>2</sub> in perovskite films, the intensity ratio of (001) diffraction peak from PbI<sub>2</sub> to that of (110) diffraction peak from perovskite phase, i.

e. I<sub>Pb12</sub>/I<sub>MAPb13</sub>, are calculated and summarized in Fig. 4c and f. The intensity ratio exhibits a decrease tendency via extending the UV-O<sub>3</sub> treatment time or increasing the annealing temperature of ZnO ETLs, which indicates the decrease of PbI<sub>2</sub> content in perovskite films. Meanwhile, it is worth to note that the I<sub>Pb12</sub>/I<sub>MAPb13</sub> for the perovskite film on WT, AT-300 °C and UV-20min treated ZnO ETLs was 0.2, 0.025, and 0.019, respectively. The content of PbI<sub>2</sub> in perovskite films sharply reduced for AT-300 °C and UV-20min samples in comparison with that of WT sample, but the traces of lead iodide are still presented in the perovskite film, which can effective passivate interfacial trap states [37]. Perovskite phase is more stable on the surface of UV-20min and AT-300 °C ZnO ETLs in the synthesis process. When the UV-O<sub>3</sub> treatment time and annealing temperature are further increased, the variation tendency of PbI<sub>2</sub> content in the perovskite films is similar and steady as



**Fig. 4.** (a), (d) XRD patterns of the perovskite film based on WT, UV-5min, UV-10min, UV-15min, UV-20min, and AT-150 °C, AT-200 °C, AT-250 °C, AT-300 °C. (b), (e) the amplification of the XRD patterns at the peak position of PbI<sub>2</sub> (001). (c), (f) intensity ratio of the perovskite (110) plane and the PbI<sub>2</sub> (001) plane.

#### show in the Fig. S9.

The formation of PbI<sub>2</sub> in the perovskite film can be deduced based on the previous reports. Cheng et al. proposed reaction route of the decomposition of  $CH_3NH_3PbI_3$  promoted by –OH during thermal annealing process [29]. During the process of one-step synthesis method in our case, the –OH on the surface of ZnO-NPs promotes the decomposition of  $CH_3NH_3PbI_3$  especially at the interface of ZnO/ $CH_3NH_3PbI_3$ according to Eqs. (1) and (2), so that both PbI<sub>2</sub> and crevice are generated. Meanwhile, the  $CH_3NH_3OH$  is easily to decompose into  $CH_3NH_2$ and  $H_2O$  with gas phase, which induces small pin holes on the surface of  $CH_3NH_3PbI_3$ . Residual amounts of hydroxyl functional groups on the surface of the ZnO ETLs further decompose the perovskite absorber layer during device operation, and further deteriorating device performance. We consider this to be an important reason for the rapid performance degradation of WT-based PSCs (Fig. S4).

$$CH_3NH_3I + PbI_2 \Leftrightarrow CH_3NH_3PbI_3 \tag{1}$$

$$OH^{-}+CH_{3}NH_{3}I\rightarrow CH_{3}NH_{3}OH + I^{-}$$
(2)

$$CH_{3}NH_{3}OH \xrightarrow{heat} CH_{3}NH_{3}(g) \uparrow +H_{2}O(g) \uparrow$$
(3)

The XPS measurement was employed for quantitative characterizing the hydroxyl group on the ZnO ETLs. Both 20% Lorentzian and 80% Gaussian functions were utilized for deconvolution of all spectra. The O 1s XPS spectra in Fig. 5 show that the all the experimental curves can be consistently fitted by three curves with the peak center located at 532.00 eV (OIII), 531.20 eV (OII) and 530.30 eV (OI), which can be ascribed to chemisorbed oxygen species, oxygen-deficient regions  $(V_{\Omega}^{+})$ , and  $O^{2-}$  ions in wurtzite structure of ZnO [38,39]. The intensity ratio of  $I_{(OIII)}/I_{(OII)}$  is used to calculate the relative content proportional of hydroxyl on the surfaces of ZnO ETLs, which has been summarized in Fig. 5h. The XPS spectra of UV-25min, UV-30min, AT-350 °C and AT-400 °C samples shown in Fig. S10 (supporting information). The  $I_{(OIII)}/I_{(OI)}$  value of WT sample is 1.63. With prolonging the UV treatment time and enhancing the annealing temperature, the  $I_{(OII)}/I_{(OI)}$  value decreased and trend steady, indicating the relative content of hydroxyl groups on the surface of the ZnO ETLs decreases gradually. Thus, less degradation happened and relative content of lead iodide in the perovskite thin film decreased. Moreover, the I(OIII)/I(OI) value of UV-20min and AT-300 °C samples are only 0.71 and 0.85, implying that the relative content of hydroxyl group was reduced to 1/2 and 2/5, respectively. It is reasonable to deduce that relative content of -OH on the ZnO ETLs would be the key factor to influence the morphology of

perovskite films and photovoltaic performance of PSCs. The number of V<sub>0</sub><sup>+</sup> in the ZnO ETLs will lead charge carries recombination and hinder the separation efficiency of photogenerated carriers in solar cell. To evaluate the influence of treatment of ZnO ETLs on the concentration of  $V_{O}^{+}$ , the intensity ratio of  $I_{(OII)}/I_{(OI)}$  representing the relative content proportional of the  $V_0^+$  in the ZnO ETLs has been summarized in Fig. 5h. The  $I_{(OII)}/I_{(OI)}$  value of WT sample is 1.08. With prolonging the UV treatment time, the I<sub>(OII)</sub>/I<sub>(OI)</sub> value decreased, indicating the relative content of the V<sub>0</sub><sup>+</sup> in the ZnO ETLs decreases. The V<sub>0</sub><sup>+</sup> relative content exhibits gradually increase during annealing treatment. The  $I_{(OII)}/I_{(OI)}$ value of UV-20min and AT-300 °C samples is 0.51 and 1.01, implying that the relative content of the V<sub>0</sub><sup>+</sup> was reduced to 1/2 and gradually increased, respectively. The relative content of V<sub>0</sub><sup>+</sup> is not significant change when the UV-O $_3$  treatment time exceed 20 min. Annealing temperature higher than 300  $^{\circ}$ C, the relative content of V<sub>0</sub><sup>+</sup> obviously increased. Thus, UV-O3 treatment not only removes hydroxyl groups on the surface of ZnO ETLs but also filling the  $V_{O}^{+}$ , which is beneficial for enhancing the stability of perovskite films in the process and decreased charge carries interfacial recombination of ZnO ETLs. In our case, if we related the I<sub>OII</sub>/I<sub>OI</sub> and I<sub>OIII</sub>/I<sub>OI</sub> value for two series ETLs to the corresponding PCE of PSCs, it can be determined that when the  $I_{OUI}/I_{OI} < 1.2$ for ETLs, that is, the content of -OH on the surface of ZnO is less than 54%, the proportion of  $PbI_2$  in the perovskite film is < 0.041, and the  $I_{OII}/I_{OI} < 1$ , that is, the content of the  $V_0^+$  in the ZnO is less than 50%, the PCE of PSCs will be >10%.

In order to investigate the role of UV-O<sub>3</sub> and annealing treatment on dynamic process of photogenerated carriers in the ZnO/perovskite system, the steady-state and time-resolved photoluminescence measurements were carried out. The steady-state PL spectra of WT/MAPbI<sub>3</sub>, UV-5min/MAPbI<sub>3</sub>, UV-10min/MAPbI<sub>3</sub>, UV-15min/MAPbI<sub>3</sub>, UV-20min/MAPbI<sub>3</sub>, AT-150 °C/MAPbI<sub>3</sub>, AT-200 °C/MAPbI<sub>3</sub>, AT-250 °C/MAPbI<sub>3</sub> and AT-300 °C/MAPbI<sub>3</sub> are shown in Fig. 6a and b. The emission peak centered at 760 nm is originated from CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> [40]. Obviously, strong PL intensity quenching happened with prolonging the UV-O<sub>3</sub> treatment exhibits better PL quenching effect than annealing.

As shown in the UV–vis transmittance spectra of UV-O<sub>3</sub> treated, annealing treated and WT ZnO ETLs in Fig. S11 (Supporting Information), the transmittance for all samples did not exhibit obviously change. Accordingly, no obvious change happened in the absorbance spectra of ZnO/MAPbI<sub>3</sub> samples as well, as seen in Figs. S12 and S13 (Supporting Information). Thus, PL intensity was mainly decided by the carrier dynamics process. The PL intensity of UV-20min/MAPbI<sub>3</sub> and AT-300 °C/



Fig. 5. High-resolution of O 1s XPS core level spectra of (a) WT, (b)AT-150 °C, (c) AT-200 °C, (d) AT-300 °C, (e) UV-5min, (f) UV-10min, (g) UV-20min, (h) Summary of I<sub>(OIII)</sub>/I<sub>(OI)</sub> and I<sub>(OII)</sub>/I<sub>(OI)</sub> of ZnO ETLs samples.



Fig. 6. (a), (b)Photoluminescence spectra of MAPbI<sub>3</sub> deposited on the top of WT, UV-5min, UV-10min, UV-15min, UV-20min, and AT-150 °C, AT-200 °C, AT-250 °C and AT-300 °C. (c), (d)Photoluminescence decay curves of perovskite films prepared on WT, UV-5min, UV-10min, UV-15min, UV-20min and AT-150 °C, AT-200 °C, AT-200 °C, AT-250 °C and AT-300 °C.

MAPbI<sub>3</sub> was quenched by 4/5 and 1/2 in comparison with that of WT/MAPbI<sub>3</sub> sample, respectively, indicating UV-O<sub>3</sub> and annealing treatments can promote carrier extraction ability of the ZnO/MAPbI<sub>3</sub> system, but UV-O<sub>3</sub> treatment have the better effect.

To further unveil the origin of PL quenching effect, we performed time-resolved PL (TRPL) measurement on perovskite thin films deposited on UV-O<sub>3</sub> treated, annealing treated and WT ZnO ETLs. The TRPL spectra were presented in Fig. 6c and d. The biexponential decay function with a fast decay ( $\tau$ 1) and a slow decay ( $\tau$ 2) was used to fit the TRPL curves. The corresponding fitting parameters are summarized in Table 2 and Table S2. The fast decay and slow decay can be attributed to the quenching process caused by the charge separation and radiative recombination process of charge carriers, respectively [37,41]. For WT/MAPbI3, the fast decay time and slow decay time is 1.44 ns and 32.19 ns with corresponding fraction of 0.3 and 0.7, respectively. The radiative recombination became the domination process of charge carriers in the bulk. For the serials of UV-O<sub>3</sub> treatment samples, the  $\tau_1$  (fast decay time) unexpectedly rapidly decreased via prolonging the treating time. For the serials of annealing treatment samples,  $\tau_1$  gradually shortened. Such kind of obvious decay phenomena proved that both techniques can promote the ability to extract carries. At least two factors

Table 2
The decay parameter of ZnO/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> system WT, UV-5min, UV-10min, UV-
15min. UV-20min. AT-150 °C. AT-200 °C. AT-250 °C and AT-300 °C.

Samples	$\tau_1$ [ns]	$\tau_2$ [ns]	$\mathbf{f}_1$	$f_2$	$\tau_{avr} \; [ns]$
WT/MAPbI3	1.44	32.19	0.30	0.70	22.96
UV-5min/MAPbI <sub>3</sub>	0.91	17.35	0.62	0.38	7.15
UV-10min/MAPbI3	0.79	14.89	0.74	0.26	4.45
UV-15min/MAPbI3	0.74	12.39	0.75	0.25	3.64
UV-20min/MAPbI3	0.70	9.26	0.78	0.22	2.57
AT-150 °C/MAPbI3	1.36	26.02	0.50	0.50	13.69
AT-200 °C/MAPbI3	1.22	20.37	0.62	0.38	8.49
AT-250 °C/MAPbI3	0.88	12.35	0.69	0.31	4.43
AT-300 °C/MAPbI3	0.76	11.29	0.77	0.23	3.17

contribute to this excellent properties: On one hand, the passivation of the hydroxyl group on the ZnO ETLs can inhibit MAPbI<sub>3</sub> decomposition during the MAPbI<sub>3</sub> crystallization procession, reduce the number of pinhole in the MAPbI<sub>3</sub> film and disappear the crevice at the ZnO/-MAPbI<sub>3</sub> interface. On the other hand, the PbI<sub>2</sub> content gradually reduced on the MAPbI<sub>3</sub> crystal boundary, which preventing the formation of PbI<sub>2</sub> barriers at the interface ZnO/MAPbI<sub>3</sub> and grain boundaries. However, as indicated by SEM and XRD results, both surface morphology and PbI<sub>2</sub> contents of perovskite films tenderly turn better or lesser during the process of two kinds of treatments, which is consistent with the variation tendency of the serials of annealing treatment samples. Therefore, some other factor must contribute to the unexpectedly rapidly decreased of  $\tau_1$  during UV-O<sub>3</sub> treatment.

Meanwhile, it also can be seen from Fig. S14 a-b (Supporting Information) that the PL quenching effect is further attenuated when the UV-O<sub>3</sub> time and the annealing temperature exceed 20 min and 300 °C, respectively. At the same time, as shown in Fig. S14 **c-d** (Supporting Information), when the UV-O<sub>3</sub> treatment time and annealing temperature exceed 20min and 300 °C, respectively, the  $\tau_1$  of ZnO/MAPbI<sub>3</sub> heterojunction is prolonged as shown in Table S2, indicating that the carrier extraction ability of the heterojunction is weakened. These results are consistent with the J-V results but conflicts with the SEM results, which further implied the existence of other influence factor.

According to the above discussion, it can be found that we mainly pay attention to perovskite films, but lose sight of the contribution of ETLs. Except for passivating the surface functional groups of ZnO ETLs, the main difference that brings about by UV-O<sub>3</sub> treatment is the concentration of  $V_0^+$  testified by XPS analysis, i.e. UV-O<sub>3</sub> treatment can effectively fill  $V_0^+$  in ZnO ETLs. Thus, it can be deduced that the lessened  $V_0^+$  are another important factor to promote the faster extraction of charge carrier at the interface. In addition, the slow decay of  $\tau_2$  for two serials of samples exhibits gradually decrease tendency during the process of two kinds of treatments as well. Since the samples of UV-20min/ MAPbI<sub>3</sub> or AT-300 °C/MAPbI<sub>3</sub> heterojunction closely resembling the working devices, the majority of photogenerated carriers were rapidly separated and abstracted to ZnO ETLs so that the carriers taking part into the recombination process turn less. Thus, not only both decay lifetimes decrease, but also the fraction of the slow decay component turns smaller.

In order to better understand charge carries transport processes in the bulk perovskite and interface processes, we performed the EIS measurement on UV-20 min PSCs, AT-300 °C PSCs and WT PSCs at the open circuit potential under dark conditions. Fig. 7a shows the Nyquist plots of UV-20 min PSCs, AT-300 °C PSCs and WT PSCs. The inset of Fig. 7a shows the equivalent circuit of the curve fitting model, which has been used previously to investigate interfacial and bulk recombination in PSCs [42,43]. The equivalent circuit consists of a resistor in series to measure the overall Rs, and two resistor-capacitance (RC) element to identify the bulk and interface process. It was found that the Rs extracted from the UV-20min based PSCs (64  $\Omega$ ) is smaller than that of AT-300 °C based PSCs (122  $\Omega$ ) and WT-based PSCs (260  $\Omega$ ). In addition, the R<sub>rec</sub>  $(R_{tr})$  and  $C_{rec}~(C_{tr})$  for UV-20min based cells are 446  $\Omega~(27\,\Omega)$  and 1.8E-8 F (1.3E-8 F), while the  $R_{rec}$  (R\_{tr}) and  $C_{rec}$  (C\_{tr}) for AT-300  $^\circ C$  based cells are 310  $\Omega$  (67  $\Omega$ ) and 3.2E-8 F (1.1E-9 F), WT based PSCs are 100  $\Omega$  $(125 \Omega)$  and 4.8E-8 F (3.2E-10 F) (Table 3). The WT based PSCs exhibits an increased Rtr, which suggests the extraction of the charge carriers is unfavorable at the ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface. It is consistent with the weak photoluminescence quenching observed for the WT/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> sample in contrast to the UV-20min/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and AT-300 °C/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> analogue. Previous work has shown that decomposition of perovskites caused by ZnO induced the losses in Voc and FF due to surface charge carries recombination, which leaded to seriously degenerate device performance [44]. We found that the bulk charge recombination lifetime ( $\tau_{rec} = R_{rec} * C_{rec}$ ) for UV-20 min PSCs and AT-300 °C PSCs did not show significant difference [43]. However, the surface charge carries lifetime ( $\tau_{tr} = R_{tr} {}^{*}C_{tr}$ ) for UV-20min based PSCs is ~5 times higher than that of for AT-300  $^\circ C$  PSCs, the longer  $\tau_{tr}$  mean fewer surface trap states which is consistent with TRPL measurement, indicating it has the better charge extraction capability. The charge extraction is depending on the crystal quality of both perovskite films and ZnO ETL which decide the heterojunction of ZnO/perovskite

#### Table 3

Fitted values of different parameters from Nyquist plot of the Perovskite solar devices at open circuit potential under dark conditions.

Samples	Rs (Ω)	$R_{tr}(\Omega)$	$R_{rec}(\Omega)$	C <sub>tr</sub> (F)	C <sub>rec</sub> (F)	$ au_{tr}$	$\tau_{rec}$
UV- 20min	64	27	446	1.3E-8	1.8E-8	3.5E-7	8.02E- 6
AT- 300 °C	122	67	310	1.1E-9	3.2E-8	7.03E- 8	7.8E-6
WT	260	125	100	3.2E- 10	4.8E-8	3.84E- 8	4.8E-6

performance. It is worth to notice that the decomposition degree of both perovskites is similar as verified by XRD patterns. Thus, some other factor should contribute to the big difference of  $\tau_{tr}$ . We further perform the Hall Effect measurement to obtain the electronic properties of the ZnO ETLs after different treatment. The results summarized in Table S1 (Supporting Information) indicate that the conductivity of UV-20min ZnO ETL is higher than that of AT-300 °C ZnO ETL. As proved by XPS spectra analysis, UV-O<sub>3</sub> treatment effectively reduced Vo<sup>+</sup> deep trap states of ZnO ETL, which can decrease charge carrier mobility and induce carrier recombination at ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface (Fig. 8a b). Thus, the improved charge extraction and enhanced PSCs performance for UV-20 min PSCs should be originated from both the improved interface properties and higher conductivity of the ZnO ETL. Moreover, higher carrier interface extraction capability can effectively reduce hysteresis, so that the UV-20 min PSCs behave weaken hysteresis effect as shown in the Fig. 7b-c and Table 4.

Besides the hydroxyl groups, the defects of  $V_D^{\rm o}$  and  $O_i$  are the key factors to influence the ZnO-based PSCs since they dominate the processes of charge carries transport and extraction. As shown in the Fig. 8a and b, the  $V_D^{\rm o}$  trap states can act as recombination center to induce the electron and hole recombination at the interface of ZnO/perovskite. When the annealing temperature exceeds 300 °C, the ratio of  $V_D^{\rm o}$  in the ZnO ETLs increased as indicated in XPS spectra, which induced the obviously decrease of  $R_{\rm sh}$  of PSCs device due to the emergence of serious



Fig. 7. (a) Electronic impedance spectroscopy characteristics of the UV-20min, AT-300 °C and WT devices at open circuit potential under dark condition. (b) (c) (d) J–V curve of PSCs using UV-20min, AT-300 °C and WT ZnO ETLs.



Fig. 8. (a) (b) Energy band diagram demonstrating charge carries recombination due to V<sub>0</sub><sup>+</sup>, (c) The schematic illustration of electrons capturing process and scattering process.

# Table 4 Parameter of champion devices based on different ETLs with forward and backward scan directions.

Sample	Voc [V]	JSC [mAcm <sup>-2</sup> ]	FF [%]	PCE [%]	Hysteresis index [%]
UV-20 min PSCs- backward	1.13	22.86	68	17.65	22
UV-20 min PSCs- forward	1.08	22.09	57	13.7	
AT-300 °C PSCs- backward	1.07	21.72	50	11.8	30
AT-300 °C PSCs- forward	1.01	20.55	39	8.28	
WT PSCs- backward	0.90	13.37	40	4.9	41
WT PSCs-forward	0.73	11.98	32	2.86	

recombination. The UV-O<sub>3</sub> treatment can fill in the  $V_O^+$  to decrease the number of the recombination centers of the electrons and holes, which is beneficial for enhancing charge carries extraction between the ZnO and perovskite layers, as shown in Fig. 8b. But along with prolonging the treatment time, the interstitial oxygen ion O<sub>i</sub> with negative charge will increase. As shown in the Fig. 8c, the O<sub>i</sub> acts as the electron scattering center, which decreases the charge carries mobility and conductivity of ZnO ETLs, which is consistent with the increased Rs of device proved by J-V measurement when the time of UV-O<sub>3</sub> treatment exceeds 20 min (Fig. 1d). Thus, the hydroxyl groups principally control the decomposition of perovskite, while adjusting the concentration of V<sub>O</sub><sup>+</sup> and O<sub>i</sub> in ZnO ETLs can further improve the photovoltaic performance of PSCs devices.

#### 4. Conclusion

In summary, the approaches of UV-O<sub>3</sub> and annealing process were respectively utilized to deal with ZnO ETLs to solve the decomposition problem of perovskite films fabricated by one-step method. Both methods can bring the enhancement of photovoltaic performance of ZnO-based planar PSCs due to the passivation of surface functional groups of ZnO ETLs. The deep trap states (V<sup>+</sup><sub>0</sub>) and interstitial oxygen (O<sub>1</sub>) of ZnO ETLs are revealed to be another two key factors to dominate charge carries recombination lifetime at interface of ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and transport in the ZnO ETLs. The UV-O<sub>3</sub> treatment can effectively reduce the concentration of  $V^+_0$  to improve the photovoltaic performance of PSCs, but longer treatment will bring more oxygen interstitials to dramatically degrade the photovoltaic performance of PSCs. With treating ZnO ETLs with UV-O<sub>3</sub> for 20 min, 17.65% PCE of ZnO-based planar PSCs of without any modified layers. These results not only unveil the detailed physical mechanism of the  $UV-O_3$  treatment, but also prove  $UV-O_3$  treatment indeed an effective approach to enhance the PCE of ZnO based-PSCs, which exhibits promising potential for the industrial production due to its low-cost and simple fabricating process.

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#### Appendix A. Supplementary data

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