Materials Today Energy 31 (2023) 101227

Contents lists available at ScienceDirect

Materials Today Energy

journal homepage: www.journals.elsevier.com/materials-today-energy/

Modifying the buried interface with azodicarbonamide for highefficiency MA-free perovskite solar cells



Jin Kang ^a, Huan Bi ^{b, *}, Mengna Guo ^c, Yao Guo ^d, Hanjun Zou ^e, Gaoyi Han ^{c, **}, Wenjing Hou ^{c, ***}

^a Department of Chemistry and Chemical Engineering, Collaborative Innovation Center for Functional Chemicals, High Value Fine Chemicals Research Center, Jinzhong University, Jinzhong, 030619, China

^b Faculty of Informatics and Engineering, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo, 182-8585, Japan

^c Institute of Molecular Science, Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province, Shanxi University, Taiyuan, 030006, China

^d School of Materials Science and Engineering, Henan Joint International Research Laboratory of Nanocomposite Sensing Materials, Anyang Institute of Technology, Anyang, 455000, China

^e Analytical and Testing Center, Chongqing University, Chongqing, 401331, China

ARTICLE INFO

Article history: Received 10 September 2022 Received in revised form 6 December 2022 Accepted 7 December 2022 Available online 10 December 2022

Keywords: MA-free perovskite solar cell Interface engineering Defect passivation Multifunctional modifier Weak chemical intercation

ABSTRACT

Although perovskite solar cells have achieved huge progress, there is still unprecedented room for improvement since there exist non-radiative recombinations at the interface. Herein, we employed azodicarbonamide to modify the buried interface for promoting power conversion efficiency and stability. Azodicarbonamide can not only reduce the defects at the buried interface but also can improve the quality of the perovskite film due to the possible chemical interaction with perovskite. In addition, a matched interfacial energy level is conducive to the transport of charge carriers. Finally, the perovskite solar cells achieved a power conversion efficiency of 22.52% and attractive stability. This work demonstrates a simple interface modification strategy for the highly-performed perovskite solar cells, which is beneficial to their commercialization process.

© 2022 Elsevier Ltd. All rights reserved.

1. Introduction

Due to the long carrier lifetime, high light absorption, tunable bandgaps, and so on, organic—inorganic perovskite solar cells (PSCs) have captured a sea of attention and have been regarded as one of the most potential photovoltaic devices [1]. Up to now, the power conversion efficiency (PCE) of single junction PSCs has achieved 25.7%, which can compare favorably with silicon solar cells and has greatly promoted the development of third-generation solar cells [2,3]. A lot of solutions have been developed to improve the PCE of the PSCs, such as introducing the additive and buffer layer, adjusting composition, or applying a physical field [4—9]. However, there is still a certain gap compared

with the Shockley Queisser theoretical limit efficiency. So, it is an urgent need to find some strategies to enhance the performances of the PSCs in order to further meet the requirements of practical application.

Reducing interfacial non-radiative recombination and improving film quality are also important to enhance the PCE of the PSCs. As one of the interfaces of PSCs, the buried interface between the electron transport layer (ETL) and perovskite layer has been regarded as a key point for perovskite photovoltaic devices. However, poor contact, defects existance, and mismatched interface energy level always cause poor performance of the PSCs. Over the past decade, an army of materials has been chosen to modify the buried interface, for instance, Lewis acids and bases, ionic liquids, polymers, two-dimensional materials, and so on. [10–13] Among them, Lewis acids and bases buffer layers have been widely proven to be effective in reducing film defects, improving film quality, and augmenting interface links. Lewis's acids, including phosphoric acid, sulfonic groups, and ammonium groups, can neutralize undercoordinated halides by forming coordinated Lewis adducts



^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: hbi.trans.sci@uec.ac.jp (H. Bi), han_gaoyis@sxu.edu.cn (G. Han), houwenjing@sxu.edu.cn (W. Hou).

[14]. Lewis bases with amine, carboxylate, and electron-rich aromatic structures have been reported to reduce undercoordinated metal defects in SnO₂ ETL or perovskite film by donating electrons [14]. Chen and his co-workers improve the device performance by forming an oriented dipole layer on the substrate using aliphatic 5amino-valeric acid (5-AVA) [15]. In addition, it is highly expected to build a suitable energy level to make the carrier's transport easier by introducing the buffer layer. Our previous works have confirmed that appropriate interface material could make the energy level between ETL and perovskite became more suitable [2,16,17]. However, there is only a few peoples pour their attention into the buried interface. Therefore, it is highly desirable to passivate the interface defects and change the energy level simultaneously by developing one simple and effective strategy.

Herein, a multifunctional buffer layer was developed by spin coating the organic compound named azodicarbonamide (ADC) on the TiO₂ layer. The defect density of perovskite film was reduced after ADC modification because the several functional groups in ADC (such as -N-H, -C=O, and -N=N-) can passivate these defects. Meanwhile, the energy level matched better after ADC modification, which facilitates the transport of charge carriers. Finally, a PCE of 22.52% was obtained. In addition, the unencapsulated device exhibited attractive humidity and thermal stability.

2. Results and discussion

Mixed perovskites with the component of $Rb_{0.02}(FA_{0.95}Cs_{0.05})_{0.98}PbI_{2.91}Br_{0.03}Cl_{0.06}$ are prepared in the present work. Fig. 1a shows the structure of the PSCs employed in this study (FTO/TiO2/ADC/perovskite/Spiro-OMeTAD/Ag), in which, multifunctional groups (such as $-NH_2$, -C=0, and -N=N) are considered to be effective to passivate film defects and improve the film quality. The corresponding atomic charge distributions are presented in Fig. 1b, among them, there are redundant electrons in N and O, so it is expected that the undercoordinated Pb^{2+} defects can be passivated. At the same time, H is expected to participate in the formation of hydrogen bonds with perovskite. Hereinafter, the perovskite films or devices without or with ADC modification are defined as control or target, respectively. As a powerful technique to characterize the chemical interactions between molecules, X-ray photoelectron spectroscopy (XPS) was adopted to reveal the interaction between perovskite and ADC. In Fig. 1c, the control film of perovskite shows two typical peaks corresponding to Pb $4f_{7/2}$ and $4f_{5/2}$, while the peaks of the target film shifted to lower binding energies. Generally, the decreased binding energy indicates that the density of the electron cloud around Pb increases, which confirms the coordination interaction between ACD and Pb²⁺ of perovskite. Further, the I



Fig. 1. (a) Device structure in present work. (b) Atomic charge distribution of the azodicarbonamide (ADC); XPS of (c) Pb 4*f*, and (d) I 3*d* core-level spectra of control and target film. (e) XPS and (f) FT-IR spectra of ADC and perovskite film deposited on ADC-modified TiO₂. (g) XPS spectra of TiO₂ film modified without/with ADC. (h) Schematically illustrated defect passivation and ion migration inhibition mechanism.

3*d* shifted toward higher binding energies after ADC was modified, proving the interaction between ADC and perovskite again. Fig. 1e exhibited the XPS peaks of C 1 s, which can be split into several peaks, where the peak situated in 288.84 eV is assigned to -C=0. The binding energy of -C=0 shifted to 288.35 eV after ADC was modified, indicating that ADC could passivate the undercoordinated Pb²⁺ defects in perovskite thin films [2]. Fourier transform infrared spectrum (FT-IR) in Fig. 1f also gave evidence of interaction between ADC and perovskite. After ADC was modified, the scissoring peak of $-NH_2$ at 1725 cm⁻¹ shifted to 1699 cm⁻¹ and the stretching vibration peak of $-NH_2$ at 3332 cm⁻¹ shifted to the lower wavenumber of 3317 cm^{-1} , which can be a result of the existence of chemical interaction between perovskite and ADC by forming the -N-H or -C=O···H hydrogen bondingWhich indicated the chemical interaction existence in perovskite and ADC [17]. In addition, the peak of -C=O located in 1635 cm⁻¹ shows the same trend. Both FT-IR and XPS results proved that there exists a chemical interaction between perovskite and ADC. The interaction between TiO₂ and ADC was demonstrated via XPS in Fig. 1f. An obvious shift in the binding energy of Ti 2p can be observed after spin coating the ADC on TiO₂, which proves that there is indeed a chemical interaction between the ETL and ADC. And we classify the interaction as a hydrogen bond (N–H···O) and coordination bond (C=O···Ti). Fig. 1h schematically illustrates the diagram of the interaction between the functional layer (perovskite and TiO₂) and the buffer layer. As we discussed above, C=O in ADC can not only passivate the uncoordinated Pb²⁺ defect in the perovskite but also can eliminate the oxygen vacancy defect in TiO₂; The formation of hydrogen bond (N–H···O) and halogen bond (N–H···I) can passivate the oxygen vacancy in TiO₂ and suppress the iodine ions migration in perovskite film, which would be affirmed subsequently [18,19].

X-ray diffraction (XRD) patterns were performed for evaluating the crystallinity of the perovskite films with and without ADC modification (Fig. 2a). The characteristic diffraction peaks of



Fig. 2. (a) XRD patterns of perovskite film deposited on glass with or without ADC modification. (b) UV–vis absorption spectra of the perovskite films spin-coated on the TiO_2 and ADC-modified TiO_2 (TiO_2 /ADC). Top-view SEM images and cross-sectional SEM images of the perovskite films deposited on (c, e) TiO_2 and (d, f) TiO_2 /ADC.

perovskite deposited on glass substrates without and with ADC modification were compared. Neither shifts in the characteristic diffraction peaks were observed and there are no new peaks that can be seen in the control and target film XRD patterns. However, the XRD peak intensity of the target film increased after ADC modification compared with bare perovskite film, demonstrating the crystallization of the perovskite film was enhanced by ADC. The previous report has also illustrated that the crystallization of perovskite film could be improved after changing the substrates. Ultraviolet-visible (UV-vis) absorption measurement was further carried out to evaluate the influences of the ADC modification on the light-harvesting property. As revealed in Fig. 2b, the absorption intensity of the perovskite film increased after ADC modification. The top-view and cross-sectional scanning electron microscopy (SEM) images of the perovskite films on ETL and ADC-modified ETL are exhibited in Fig. 2c-f. Some pinholes exist in the control perovskite film, while a tighter grain arrangement was obtained in the modified one (Fig. 2c and d). The cross-sectional SEM in Fig. 2e and f also depicted that the thickness of perovskite films increases from the original 616 nm–636 nm after ADC modification, which can explain the increased UV–vis absorbance intensity by ADC modification in Fig. 2b. And the results of atomic force microscope in Fig. S1 indicate that ADC-modified perovskite film shows the lower roughness (Rq = 28.4) than the control perovskite thin film (Rq = 35.4) (Fig. 2e and f). Concisely, the ADC can improve the quality and morphology of the perovskite film without changing the crystal structure. It implies that introducing the ADC as the buffer layer has a positive effect.

The steady-state and time-resolved photoluminescence (PL and TRPL) technology was employed to reveal the effect of ADC modification on the defects and carrier lifetimes of the perovskite films on glass or ADC-modified glass. In Fig. 3a, the PL intensity of the perovskite film has a significant increase after introducing the ADC to the interface. Besides, the PL peak of the target film shows a slight blue shift. The stronger PL intensity and shifted PL peak sustained that the defect of the target film decreased. TRPL results



Fig. 3. (a) PL and (b) TRPL spectra of the perovskite films deposited on the glass without and with ADC modification. PL mapping images of the perovskite films prepared on the glass (c) without and (d) with ADC modification. Dark *I*–*V* curves of the electron-only devices (e) without or (f) with ADC modification.

display the important difference in the lifetime of free charge carriers between the control and target film (Fig. 3b). The double exponential function equation of $I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_1)$ $(-t/\tau_2)$ was used to fit the TRPL response. The average carrier lifetime (au_{ave}) was calculated by employing the equation of au_{ave} = $(A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. The control sample shows much shorter carriers lifetimes (au_1 = 23.88 ns, au_2 = 107.63 ns, $\tau_{\rm ave} = 86.57$ ns) than those of the target film ($\tau_1 = 18.17$ ns, $\tau_2 = 110.84$ ns, $\tau_{ave} = 99.68$ ns) (Table S1), which coincides with PL test. In the PL mapping images exhibited in Fig. 3c and d, the PL intensity of perovskite film increased remarkably after ADC modification, which was following the single-point PL measurement results (Fig. 3a). Meanwhile, PL peak position mapping and PL peak full width at half maxima (FWHM) mapping are illustrated in Figs. S2 and S3, respectively. The PL emission peak position of the target film shifted to a lower wavelength than those of the control film in a large range. Besides, the FWHM of the film narrowed down when ADC was introduced into the interface between TiO₂ and perovskite. The lower wavelength and narrower peak FWHM indicate that the reduced defects were reduced, and the film quality was significantly improved, which is also consistent with the results of single-point PL and TRPL.

Subsequently, the trap density of the two kinds of perovskite was calculated via the space charge limited current (SCLC) method. As presented in Fig. 3e and f, the dark current–voltage (I-V) curves of electron-only devices (FTO/TiO₂/(without/with ADC)/perovskite/ PCBM/Ag) were measured to test the defect density according to the equation of $n_{\rm t} = (2\epsilon\epsilon_0 V_{\rm TFL})/(eL^2)$, where ϵ and ϵ_0 are the dielectric constants of the perovskite and the vacuum dielectric constant, L is the thickness of the perovskite, V_{TFL} is the trap-filled limit voltage, and e is the elementary charge [20]. Moreover, the n_t values of devices without and with ADC were 4.77×10^{15} cm⁻³ and $2.86\times 10^{15}\,\text{cm}^{-3}$, which was consistent with increased PL intensity (Fig. 3a). Reduced film defects indicate that the quality of the thin film was improved. The enhanced film quality could be attributed to the that the iodine defects and vacancy defects could be passivated by -C=O, -N=N, and -NH₂. In addition, the weak interaction between ADC and perovskite helps to improve the quality of the film.

PL and TRPL methods were further implemented to uncover the interfacial charge dynamics (Fig. 4a and b). Dropped PL intensity and carrier lifetimes (control: $\tau_1 = 5.47$ ns, $\tau_2 = 23.79$ ns, $\tau_{ave} = 15.85$ ns; target: $\tau_1 = 4.40$ ns, $\tau_2 = 19.61$ ns, $\tau_{ave} = 11.27$ ns) confirmed that improved electron extraction by ADC (Table S2). PL



Fig. 4. (a) PL and (b) TRPL of the perovskite films with the structure of FTO/TiO₂/(ADC)/perovskite to evaluate the effect of the charge extraction of the PSCs. PL intensity mapping of the (c) control and (d) target perovskite films. PL peak position mapping of the (e) control and (f) target perovskite films. (g) Nyquist plots and (h) Mott–Schottky plots of the control and target devices. (i) Energy-level scheme for the devices.

mapping image exhibited that the PL intensity indeed reduced after ADC modification in a large range (Fig. 4c and d). Besides, the peak of the target film shifted to the lower wavelength also means that the electron extraction was enhanced (Fig. 4e and f). Electrochemical impedance spectroscopy (EIS) was performed to evaluate carrier transfer and recombination. In Fig. 4g, the Nyquist plots were measured at a bias of 0 V in the frequency range of 1 MHz to 0.1 Hz under dark conditions. It has been confirmed that the semicircles at the high-frequency and low-frequency regions are related to charge-transfer resistance (R_{ct}) and recombination resistance (R_{rec}). The reduced R_{ct} and the increased R_{rec} by ADC proved that they promoted interfacial charge transfer and effectively suppressed charge recombination. Decreased R_{ct} could be owing to the improved perovskite crystallization. In addition, the increased R_{rec} can explain the increased carrier lifetime and reduced non-radiative recombination. The ideality factor (n) ob-

tained from light intensity (I)-dependent V_{OC} curves was used to

study the carrier dynamics. As the V_{OC} versus light intensity curves shown in Fig. S4, the target device shows a lower n of 1.21 compared with the control device (1.68), which also supports that the non-radiative recombination was suppressed by ADC modification. C–V characteristics of a typical device based on the perovskite/(with or without ADC)/TiO2 heterojunction have been measured at 1000 Hz in the dark and at room temperature. Fig. 4h displays the Mott-Schottky plots of the device without or with ADC modification. The built-in potentials $(V_{\rm bi})$ of the target devices is 0.85 V, which is higher than that of the control device (0.78 V). This result indicates ADC modification is conducive to promoting carrier transfer, which is consistent with TRPL and EIS results [21,22]. In a nutshell, ADC can accelerate charge transfer and suppress charge recombination at the buried interface. Ultraviolet photoelectron spectroscopy (UPS) measurement was utilized to estimate the surface energy-level changes caused by ADC (Fig. 4i and Fig. S5). The energy levels of the conduction band (CB) and valence band



Fig. 5. (a) Statistical PCE data based on 15 individual cells. (b) *J*-*V* curves and (c) IPCE spectra and (d) maximum power point tracking of the champion control and target devices; PCE evolution of the unencapsulated devices aged in different air conditions: (e) with a relative humidity of 40–45% at room temperature in the dark (f) With a relative humidity of 15–20% and a temperature of 60 °C.

(VB) can be calculated according to the previous work. As Fig. 4i shows that after ADC modification, the energy levels of the ADC/ perovskite (PVSK) have no obvious changes, while conduction band energy levels of TiO₂/ADC shift to a higher value than TiO₂. After ADC modification, the better-matched energy level between ETL and perovskite can reduce the interface charge accumulation.

We then explore the photovoltaic performance in Fig. 5a and Fig. S6. All photovoltaic parameters (J_{SC}, V_{OC}, FF, and PCE) firstly increase, maximize at 0.5 mg/mL, and then reduce as the concentration further increases. The statistical parameters are summarized in Table S3. The average PCE is increased from $(20.69 \pm 0.146)\%$ of the control devices to $(22.32 \pm 0.196)\%$ of the ADC-modified devices. The increased J_{SC} is mainly due to ameliorated quality and reduced pinhole of the perovskite film (can be seen from SEM images). The improved V_{OC} and FF can be attributed to reduced defect density (proved by PL, TRPL, and SCLC) and increased carrier lifetime (confirmed via PL, TRPL, and EIS). The J-V curves of the devices are displayed in Fig. 5b. The champion target device shows a J_{SC} of 25.38 mA/cm², a V_{OC} of 1.098 V, and an FF of 0.820, corresponding to a PCE of 22.52%, while the champion control device exhibited a Jsc of 24.67 mA/cm², a Voc of 1.047 V, and an FF of 0.806, corresponding to a PCE of 20.82%. In Fig. 5c, the integrated J_{SC} from incident photon-to-current efficiency (IPCE) for the control and target device are 24.06 mA/cm² and 24.99 mA/cm², respectively, which is consistent with the J_{SC} got from the J-V curves. Fig. 5d displays the stable output PCE of control and target devices measured at the maximum power point with a bias of 830 mV and 890 mV, respectively. Finally, control and target devices got a PCE of 20.07% and 22.15%, respectively, after 300 s. Much enhanced V_{OC} and I_{SC} along with slightly improved FF contributed to the improved PCE. Improved JSC could be explained by the enhanced light-harvesting ability and slightly increased film thickness. Improved carrier transport should be mainly responsible for the enhanced, supported by the EIS test. The improved V_{OC} was mainly put down to the reduced non-radiative recombination. The present reports have proved that reduced non-radiative recombination in the device is a prerequisite for achieving highperformance PSC [23,24]. Photoluminescence quantum yield (PLQY) has been used as a useful tool to investigate non-radiative recombination owing to that PLQY can be expressed in terms of the radiative (R_{oad}) and non-radiative (R_{nr}) recombination rates $PLQY = R_{rad}/(R_{rad} + R_{nr})$ [25]. The previous reports have indicated that a high PLQY value will lead to enlarged quasi-fermi level splitting ($\Delta E_{\rm F}$), decreased V_{OC} loss, and reduced non-radiative recombination loss [24,26]. As shown in Fig. S7, the ADCmodified perovskite film shows a higher PLQY value (1.02%) than the control perovskite film (0.56%), indicating the reduced nonradiative recombination loss by ADC. In a word, ADC has been proven to be an effective modifier for the buried interface.

Except for the high PCE of the PSCs, long time stability of the device also should be a concern of commercialization. First, the unencapsulated device was placed in a condition with a relative humidity of around 40-45% to evaluate the humidity stability (Fig. 5e and Fig. S8). After aging for 500 h, the ADC-based PSCs retained 94% of their initial PCE, whereas the control PSCs decreased to 80% of their original PCE. Obviously, the humidity stability of PSCs was improved after ADC was introduced. Further, the PSCs were holed at the temperature of 60 °C with a relative humidity of 15–20% (air condition) to test the thermal stability. After aging 100 h, the PCE of the target device decreased by 5.2% while the control device decreased by 20% (Fig. 5f and Fig. S9). Slower degraded device efficiency by ADC indicates that the thermal stability of the target device was improved significantly compared with the control device. Enhanced stability of PSCs mainly due to the fewer defects in the perovskite film. Besides,

reducing trap-assisted non-radiative recombination also results in the lower degradation of perovskite films.

3. Conclusions

We developed a feasible and effective bottom-up holistic carrier management strategy induced synergistically by multiple chemical bonds to reduce the energy losses in bulk and interfacial. Experimental results reveal that the ADC can not only passivate reduce the film defect and improve the perovskite film morphology but also can improve carrier transport. This is mainly due to the possible chemical interaction between ADC and perovskite or TiO₂. The target device with ADC modification exhibited a high PCE of 22.52% and good thermal and humidity stability. The present work lays the foundation for the development of multifunctional interface modifiers for highly efficient MA-free PSCs.

3.1. Device fabrication

Laser patterned FTO glasses were ultrasonically cleaned with detergent water and ethanol for 20 min in sequence and blown dry by nitrogen (99.99%). Then, the FTO was treated with ultraviolet ozone $(UV-O_3)$ for 30 min. For TiO₂, we put the FTO into the TiCl₄ in an aqueous solution (TiCl₄:H₂O = 2.25:1, V: V) for 45 min under 70 °C, and then annealed at 200 °C for 30 min. The cold substrates were then treated with UV-O₃ for 20 min. For ADC treatment, different concentrations of ADC (0, 0.25, 0.5, and 0.75 mg/mL) were dissolved in DMF, and then 30 uL of ADC was spin-coated on the TiO₂ film at a speed of 5000 rpm for the 30 s. Then, the perovskite was deposited in an argon-filled glovebox. The perovskite precursor solution with a concentration of 1.55 M was prepared by dissolving 248.16 mg FAI, 6.58 mg RbI, 19.73 mg CsI, 8.53 mg PbBr₂, 682.73 mg PbI₂, 12.74 mg PbCl₂, and 35 mg MACl additive in the mixed solvents of DMF and DMSO (V_{DMF} : $V_{DMSO} = 4$: 1) and filtering by the 0.22 μ m PTFE filter. The perovskite film was deposited by the consecutively spin-coating process at 4000 rpm for 30 s where 80 µL CB antisolvent was dripped on perovskite films at 16 s before ending the program, and the film was then annealed at 130 °C for 30 min. The Spiro-OMeTAD solution was prepared by mixing 72.3 mg spiro-OMeTAD, 17.5 µL of lithium bis(trifluoromethane sulfonyl)imide (Li-TFSI) stock solution (520 mg/mL in acetonitrile), and 28.8 µL of 4-tert-butyl pyridine (tBP) in 1 mL CB. Subsequently, the hole transport layer was prepared by spin-coating the 20 μ L Spiro-OMeTAD solution at 4000 rpm for 33 s. Finally, a 100 nm metal counter electrode was thermally evaporated under a vacuum of 3 \times 10⁻⁵ Pa.

3.2. Characterization

I–V curves were recorded using a Keithley 2400 source meterequipped solar simulator. The active area of the device is to be 0.1 cm², which is defined by the black metal mask. *I-V* curves were measured with a scan rate of 120 mV/s under air conditions. Fourier-transformed infrared (FT-IR) spectra were obtained on an FT-IR spectrometer (Tensor 27, BRUKER, Germany). UV-Vis spectra were measured on an Agilent 8453 UV-Vis G1103A spectrometer. XPS spectra were collected from a Physical Electronics Model 5700 XPS instrument, and the data were analyzed and processed by Thermo Avantage (v5.9921) software. Photoluminescence (PL) was tested by a Confocal Raman system (iHR 550 HORIBA) with a laser of 532 nm. SEM was observed on SEM (FESEM, JEOL-JSM-6701F) in ADD mode. The structures were characterized by using an X-ray diffract meter (XRD) (D2 PHASER Desktop XRD, BRUKER, Germany). Ultraviolet Photoelectron Spectroscopy (UPS) was performed by PHI 5000 VersaProbe III with He I source (21.22 eV) under an

applied negative bias of 9.0 V. The energy-dispersive X-ray spectroscopy (EDS) measurement was carried out on a field emission scanning electron microscope (JEM-7900F, Japan) with EDS equipment. The Pb concentration in the water was detected by an ICP–MS instrument (NexION 350, PerkinElmer). Time-resolved photoluminescence (TRPL) was measured by using a self-built scanning confocal system based on an inverted microscope (Nikon, TE2000-U) with a 450 nm laser in the State Key Laboratory of Quantum Optics and Quantum Optics Devices of Shanxi University. The Photoluminescence Quantum Yield (PLQY) of the layer structure glass/FTO/TiO₂/(without or with ADC)/perovskite was tested by the Edinburgh Instruments (FS5) assembled with an integrating sphere under 532 nm excitation.

Credit author statement

Jin Kang: Validation; Investigation; Writing – Original Draft; Huan Bi: Conceptualization; Validation; Investigation; Writing

- Original Draft; Supervision; Writing - Review and Editing.

Mengna Guo: Validation.

Yao Guo: Supervision.

Hanjun Zou: Resources.

Gaoyi Han: Validation; Resources; Supervision; Funding acquisition.

Wenjing Hou: Validation; Resources; Writing – Review and Editing; Supervision; Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (61804091 and U21A6004), Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (2020L0002), and the Natural Science Foundation of Shanxi Province under Grant (201901D211127), Program of State Key Laboratory of Quantum Optics and Quantum Optics Devices (No: KF201910), Scientific Research Start-up Funds of Shanxi University and the Hundred Talents Plan of Shanxi Province. We would like to acknowledge Prof. Qing Shen (Faculty of Informatics and Engineering, The University of Electro-Communications) and Dr. Chao Ding (Faculty of Informatics and Engineering, The University of Electro-Communications) for the useful discussion. The authors also thanks for the support of Shiyanjia Lab (www.shiyanjia.com).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtener.2022.101227.

References

- J. Chen, N.G. Park, Causes and solutions of recombination in perovskite solar cells, Adv. Mater. 31 (2019), 1803019, https://doi.org/10.1002/ adma.201803019.
- [2] H. Bi, B. Liu, D. He, L. Bai, W. Wang, Z. Zang, J. Chen, Interfacial defect passivation and stress release by multifunctional KPF₆ modification for planar

perovskite solar cells with enhanced efficiency and stability, Chem. Eng. J. 418 (2021), 129375, https://doi.org/10.1016/j.cej.2021.129375.

- [3] NREL. https://www.nrel.gov/pv/cell-efficiency.html, 2021.
- [4] H. Zhen, C. Xu, L.J. Li, A.M. Liu, T.L. Ma, L.G. Gao, Highly efficient and stable perovskite solar cells induced by novel bulk organosulfur ammonium, Mater, Today Energy 26 (2022), 101004, https://doi.org/10.1016/ i.mtener.2022.101004.
- [5] P. Zhu, S. Gu, X. Luo, Y. Gao, S. Li, J. Zhu, H. Tan, Simultaneous contact and grain-boundary passivation in planar perovskite solar cells using SnO₂-KCl composite electron transport layer, Adv. Energy Mater. 10 (2019), 1903083, https://doi.org/10.1002/aenm.201903083.
- [6] M. Azadinia, M. Ameri, R.T. Ghahrizjani, M. Fathollahi, Maximizing the performance of single and multijunction MA and lead-free perovskite solar cell, Mater. Today Energy 20 (2021), 100647, https://doi.org/10.1016/ j.mtener.2021.100647.
- [7] X. Zuo, B. Kim, B. Liu, D. He, L. Bai, W. Wang, C. Xu, Q. Song, C. Jia, Z. Zang, D. Lee, X. Li, J. Chen, Passivating buried interface via self-assembled novel sulfonium salt toward stable and efficient perovskite solar cells, Chem. Eng. J. 431 (2021), 133209, https://doi.org/10.1016/j.cej.2021.133209.
- [8] F. Zhang, S. Ye, H. Zhang, F. Zhou, Y. Hao, H. Cai, J. Song, J. Qu, Comprehensive passivation strategy for achieving inverted perovskite solar cells with efficiency exceeding 23% by trap passivation and ion constraint, Nano Energy 89 (2021), 106370, https://doi.org/10.1016/j.nanoen.2021.106370.
- [9] S. Liu, Y. Guan, Y. Sheng, Y. Hu, Y. Rong, A. Mei, H. Han, A review on additives for halide perovskite solar cells, Adv. Energy Mater. 10 (2020) 345–351, https://doi.org/10.1002/aenm.201902492.
- [10] T. Zhu, D. Zheng, M.N. Rager, T. Pauporté, The stabilization of formamidinium lead tri-iodide perovskite through a methylammonium-based additive for high efficiency solar cells, Sol. RRL 4 (2020), 2000348, https://doi.org/10.1002/ solr.202000348.
- [11] A. Mahapatra, D. Prochowicz, M.M. Tavakoli, S. Trivedi, P. Kumar, P. Yadav, A review of aspects of additive engineering in perovskite solar cells, J. Mater. Chem. 8 (2020) 27–54, https://doi.org/10.1039/c9ta07657c.
- [12] B. Liu, H. Bi, D. He, L. Bai, W. Wang, H. Yuan, Q. Song, P. Su, Z. Zang, T. Zhou, J. Chen, Interfacial defect passivation and stress release via multi-active-site ligand anchoring enables efficient and stable methylammonium-free perovskite solar cells, ACS Energy Lett. 6 (2021) 2526–2538, https://doi.org/10.1021/acsenergylett.1c00794.
- [13] H. Wang, C. Zhu, L. Liu, S. Ma, P. Liu, J. Wu, C. Shi, Q. Du, Y. Hao, S. Xiang, H. Chen, P. Chen, Y. Bai, H. Zhou, Y. Li, Q. Chen, Interfacial residual stress relaxation in perovskite solar cells with improved stability, Adv. Mater. 31 (2019), 1904408, https://doi.org/10.1002/adma.201904408.
- [14] Z. Gao, Y. Wang, W. Choy, Buried interface modification in perovskite solar cells: a materials perspective, Adv. Energy Mater. 12 (2022), 2104030, https:// doi.org/10.1002/aenm.202104030.
- [15] Y. Zhang, S. Zhang, S. Wu, C. Chen, H. Zhu, Z. Xiong, W. Chen, R. Chen, S. Fang, W. Chen, Bifunctional molecular modification improving efficiency and stability of inverted perovskite solar cells, Adv. Mater. Interfac. 5 (2018), 1800645, https://doi.org/10.1002/admi.201800645.
- [16] H. Bi, Y. Guo, M. Guo, C. Ding, S. Hayase, T. Mou, Q. Shen, G. Han, W. Hou, Highly efficient and low hysteresis methylammonium-free perovskite solar cells based on multifunctional oteracil potassium interface modification, Chem. Eng. J. 439 (2022), 135671, https://doi.org/10.1016/ j.cej.2022.135671.
- [17] H. Bi, X. Zuo, B. Liu, D. He, L. Bai, W. Wang, X. Li, Z. Xiao, K. Sun, Q. Song, Z. Zang, J. Chen, Multifunctional organic ammonium salt-modified SnO₂ nanoparticles toward efficient and stable planar perovskite solar cells, J. Mater. Chem. 9 (2021) 3940–3951, https://doi.org/10.1039/D0TA12612H.
- [18] X. Guo, B. Zhao, K. Xu, S. Yang, Z. Liu, Y. Han, J. Xu, D. Xu, Z. Tan, S. Liu, p-type carbon dots for effective surface optimization for near-record-efficiency CsPbl₂Br solar cells, Small 17 (2021), 2102272, https://doi.org/10.1002/ smll.202102272.
- [19] S. Nanayakkara, Y. Tao, E. Kraka, Comment on "exploring nature and predicting strength of hydrogen bonds: a correlation analysis between atoms-inmolecules descriptors, binding energies, and energy components of symmetry-adapted perturbation theory", J. Comput. Chem. 42 (2021) 516–521, https://doi.org/10.1002/jcc.26475.
- [20] J. Huang, S. He, W. Zhang, A. Saparbaev, Y. Wang, Y. Gao, L. Shang, G. Dong, L. Nurumbetova, G. Yue, Y. Tu, Efficient and stable all-inorganic CsPblBr₂ perovskite solar cells enabled by dynamic vacuum-assisted low-temperature engineering, Sol. RRL 6 (2022), 2100839, https://doi.org/10.1002/ solr.202100839.
- [21] X. Ding, H. Wang, Y. Miao, C. Chen, M. Zhai, C. Yang, B. Wang, Y. Tian, M. Cheng, Bi(trifluoromethyl) benzoic acid-assisted shallow defect passivation for perovskite solar cells with an efficiency exceeding 21, ACS Appl. Mater. Interfaces 14 (2022) 3930–3938, https://doi.org/10.1021/ acsami.1c18035.
- [22] X. Ding, H. Wang, C. Chen, H. Li, Y. Tian, Q. Li, C. Wu, L. Ding, X. Yang, M. Cheng, Passivation functionalized phenothiazine-based hole transport material for highly efficient perovskite solar cell with efficiency exceeding 22, Chem. Eng. J. 410 (2021), 128328, https://doi.org/10.1016/j.cej.2020.128328.
- [23] I. Brały, D. deQuilettes, L. Pazos-Outón, S. Burke, M. Ziffer, D. Ginger, H. Hillhouse, Hybrid perovskite films approaching the radiative limit with over 90% photoluminescence quantum efficiency, Nat. Photonics 12 (2018) 355–361, https://doi.org/10.1038/s41566-018-0154-z.

- [24] D. Luo, R. Su, W. Zhang, Q. Gong, R. Zhu, Minimizing non-radiative recombination losses in perovskite solar cells, Nat. Rev. Mater. 5 (2020) 44–60, https://doi.org/10.1038/s41578-019-0151-y.
- [25] H. Zhu, Y. Liu, F. Eickeneyer, L. Pan, D. Ren, M. Ruiz-Preciado, B. Carlsen, W. Yang, X. Dong, Z. Wang, H. Liu, S. Wang, S. Zakeeruddin, A. Hagfeldt, M. Dar, X. Li, M. Grätzel, Tailored amphiphilic molecular mitigators for stable

perovskite solar cells with 23.5% efficiency, Adv. Mater. (2020), 1907757, https://doi.org/10.1002/adma.201907757.

[26] A. Ren, H. Lai, X. Hao, Z. Tang, H. Xu, B. Jeco, K. Watanabe, L. Wu, J. Zhang, M. Sugiyama, J. Wu, D. Zhao, Efficient perovskite solar modules with minimized nonradiative recombination and local carrier transport losses, Joule 4 (2020) 1263–1277, https://doi.org/10.1016/j.joule.2020.04.013.