Surface termination passivation of imidazole-based diiodide enabling efficient inverted perovskite solar cells

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Experimental Section

Materials

Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA, 99%), Formamidine hydroiodide (FAI, 99.5%), cesium iodide (CsI, 99.9%), lead bromide (PbBr₂, 99.99%), lead iodine (PbI₂, 99.99%), C₆₀ and bathocuproine (BCP, 99.9%) were purchased from Xi'an Polymer Light Technology (China). Dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.7%), isopropanol (IPA, 99.5%) and toluene (PhMe, 99.5%) were purchased from J&K. DMSO-d6 (99.95%) and Chlorobenzene (CB, 99.8%) were manufactured by Sigma-Aldrich. N-(3-Aminopropyl)-imidazole (API, 99.5%) was bought from Macklin. All materials were used as received without further purification.

Synthesis of N-(3-Aminopropyl)-imidazole Diiodide (APIDI)

N-(3-Aminopropyl)-imidazole (200 uL, 1.6 mmol) was dissolved in ethanol (25 mL) in a flask. Then, 57% hydroiodic acid solution in water (5.0 ml, 5 mmol) was added slowly under ice water bath, and the mixture solution was stirred at room temperature reacted for 6 h. After the evaporation of solvent, the crude product was washed by ethyl acetate for 3 times to obtain a white solid. Finally, the resulting white powder was placed to dry under vacuum for 72 h at 70 °C.

Device Fabrication

Solar cells were fabricated based on the FA_{0.83}Cs_{0.17}Pb(I_{0.86}Br_{0.14})₃ absorber layer, using the device structure with ITO/PTAA/FA_{0.83}Cs_{0.17}Pb(I_{0.86}Br_{0.14})₃/C₆₀/BCP/Ag. ITO (indium tin oxide, 1.5 cm \times 1.5 cm size, 1.1 mm thickness, 15 Ω /sq sheet resistance) substrates were cleaned by sonication with deionized water, acetone, ethanol and isopropanol for 15 min, sequentially, which are then dried with N₂. Then, the ITO were further treated by O₂ plasma for 6 minutes to remove the residual substances. PTAA (Mn≤6000) was dissolved in toluene (2 mg/ml) and spin-coated at the speed of 6000 rpm for 30 s and then PTAA (toluene) film annealed on the hotplate at 100 °C for 10 minutes. As for the perovskite precursor, we dissolved PbI₂ (493.7 mg), CsI (53.0 mg), PbBr₂ (66.1 mg) and FAI (171.3 mg) in 1 mL of mixed solvent (DMF/DMSO = 4:1, volume ratio). Then 60 µL of precursor solution was spun onto PTAA at 1000 rpm for 10 s and 6000 rpm for 30 s, note that 150 µL of CB was pipetted onto the spinning film at 15 s prior to the end of the second spinning step. Sequentially, the perovskite films were annealed 10 min with 100 °C. Finally, C₆₀, BCP and silver were sequentially deposited on top of perovskite films by vacuum evaporation under a vacuum pressure of less than 1×10^{-4} mbar. The target devices (perovskite surface treated by APDI) were prepared as follows: before depositing C₆₀, APDI/IPA solution was spin-coated on the perovskite film surface at 4000 rpm/30 s, and then C₆₀/BCP/Ag was deposited sequentially. All spin-coating steps were operated under N₂ atmosphere. The illumination area of devices is 0.0975 cm².

Characterization

The current density versus voltage (*J-V*) characteristics of the devices were measured in N_2 atmosphere using a Keithley 2400 source meter under AM 1.5G simulated 1 sun illumination (100 mW cm⁻²) from xenon lamp (Enli Technology Co.,Ltd.). The light source was calibrated using a standard silicon solar cell before the test. UV–vis absorption and transmission spectra were recorded using a Shimadzu UV2600 spectrophotometer. Steady-state photoluminescence (PL) spectra were obtained with fluorescence spectrophotometer (FLS980). Time-resolved PL (TRPL) spectra were measured with Lifespec II (Edinburgh Instrument, U.K.). Scanning electron microscopy (SEM) images were obtained on a Hitachi SU8010 instrument. Atomic force microscopy (AFM) images were obtained on a Dimension Icon (Bruker) in tapping mode. X-ray diffraction (XRD) measurement was performed on a Bruker D8 Advance instrument with a CuK α source ($\lambda = 0.15406$ nm). External quantum efficiency (EQE) was measured by a QE-R3011 instrument (Enli Technology Co., Ltd.). The stability test of devices is traced by storing the devices under the N₂ protection around ~25 °C or ambient condition with high relative humidity of ~50%. The maximum-power output stability of the devices was measured by monitoring the current output at a fixed bias voltage of 0.90 V (Control) and 0.92 V (Target), which is close to their maximum power voltage bias deduced from the reverse-scan J-V curves. XPS measurements were performed by the Thermo Scientific K-Alpha with a source of monochromatic Al-Ka (1486.6 eV). The electrochemical impedance spectra (EIS) and Mott-Schottky plots of solar cells were measured on an 608e Electrochemical Workstation (Chenhua, China).

Density functional theory, as implemented in Vienna ab initio simulation package, was used to carry out the calculations presented here. The projector augmented wave method was used to treat the effective interaction of the core electrons and nucleus with the valence electrons, while exchange and correlation were described using the generalized gradient approximation of the Perdew-Burke-Ernzerhof functional. The cut-off energy is set at 400 eV for the plane-wave basis restriction in the calculations. K-points are sampled under the Monkhorst-Pack scheme for the Brillouin-zone integration. K-points were sampled with 3x3x1 mesh.

The PL decay curve was fitted using the following equation 1¹:

$$f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + B$$

where τ_1 is the fast decay process related to bimolecular recombination, and τ_2 is the slow decay process associated with trap-assisted recombination. B is a constant for the

baseline offset. A_1 and A_2 are constants representing the contributions of the fast and slow components, respectively. The average PL decay lifetime (τ_{ave}) can be obtained using the following equation:

$$\tau_{\text{ave}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

The trap state density can be calculated by V_{TFL} using the following equation²:

$$N_{\rm trap} = 2 \varepsilon \varepsilon_0 V_{\rm TFL} / (q L^2)$$

where ε is the relative dielectric charge constant of perovskite, ε_0 is vacuum permittivity, q is the electric charge, and L is the thickness of perovskite film.

The exciton dissociation probability
$$(P_{diss})$$
 was calculated using the following
equation³: $J_{ph} = J_L - J_D$ (Eq. 1); $V_{eff} = V_0 - V_{app}$ (Eq. 2); $P_{diss} = J_{ph}/J_{sat}$
(Eq. 3)

where $J_{\rm L}$ is the photocurrent density measured under 1 sun illumination and $J_{\rm D}$ is the current density in the dark, V_0 and $V_{\rm app}$ are the voltage when $J_{\rm ph}$ equals zero and the applied bias, $J_{\rm sat}$ is the saturation photocurrent density. The $J_{\rm sat}$ is mainly related to the absorbed incident photons at high $V_{\rm eff}$, and it could be defined as the photocurrent, where the photogenerated excitons could be separated into free charge carriers and collected by corresponding electrodes. Therefore, the charge collection efficiency under different $V_{\rm eff}$ could be estimated by equation 3.

The slop value of J_{sc} vs. light intensity was calculated using the following equation⁴:

$$J_{\rm sc} \propto I^{\alpha}$$

where α is an exponential factor related to charge recombination.

The slop value of V_{oc} vs. light intensity was calculated using the following equation⁵:

$$V_{\rm oc} = ({\rm nkT/q}) \times {\rm ln}(I) + {\rm constant}$$

where n is an ideal factor, K is Boltzmann constant, T is the absolute temperature and q is elementary charge.



Figure S1. (a) Diagram of the state of perovskite film before and after dropping API and (b) structural formula of API and APDI.



Figure S2. H-NMR spectra of API, APDI and APDI-PbI₂ in DMSO-d6.



Figure S3. Scanning electron microscopy (SEM) images of the surface for (a) control and (b) target perovskite film with their related grain size measurements. Grain size distribution of perovskite films (c) without and (d) with API treatment. The grain sizes were estimated from the SEM images by the Nano Measurer 1.2 software.



Figure S4. (a) Top-view SEM images and water contact angles, (b) UV-vis spectra, AFM images and (d) calculated value of the E_g of perovskite (control) and perovskite/APDI (target).



Figure S5. The current density-voltage (*J-V*) curves of PSCs with different concentration of APDI: 0 mg/ml, 0.1 mg/ml, 0.3 mg/ml, and 0.5 mg/ml.



Figure S6. Statistics of PCE (a) / FF (b) / V_{oc} (c) / J_{sc} (d) distribution for PSCs without (control) and with (target) APDI treatment.



Figure S7. (a) J_{sc} vs. light intensity for the devices without (control) and with (target) APDI. (b) Recombination resistance (R_{rec}) of control and target devices obtained at different applied biases under dark conditions. (f) Charge collection probability as a function of internal voltage based on different devices.



Figure S8. Evolution of V_{oc} , J_{sc} and FF relative to the initial parameters for control and target device at N₂ conditions (a-c) and air conditions (d-f).



Figure S9. XRD patterns of (a) pristine (control) and (d) APDI-treated (target) perovskite films in air with an RH of ~35% for different time.

Structure of inverted PSCs	Components	PCE (%)	V _{oc} (V)	J _{SC} (mA/cm ²)	FF (%)	Area	Ref.
FTO/NiO _x /Me-4PACz/ PVK/PEAI/C ₆₀ /SnO ₂ /Ag	FA _{0.95} Cs _{0.05}	22.6	1.11	25.4	79	0.1	(
FTO/NiO _x /Me-4PACz / DPPP /PVK/PEAI/C ₆₀ /SnO ₂ /Ag	PbI ₃	24.5	1.16	25.6	82	0.1	U
ITO/NiO _x /PVK /C ₆₀ /BCP/Cu	C- EA Dh	15.30	1.28	15.5	76		
ITO/NiO _x /PVK+ TCMAI /C ₆₀ /BCP/Cu	$\begin{array}{c} Cs_{0.2}FA_{0.8}Pb\\ (I_{0.6}Br_{0.4})_3 \end{array}$	17.02	1.31	15.7	83		
ITO/NiO _x /PVK /C ₆₀ /BCP/Cu		19.02	1.06	21.9	82	0.04	7
ITO/NiO _x /PVK+ TCMAI /C ₆₀ /BCP/Cu	Cs _{0.1} FA _{0.9} PbI ₃	19.81	1.11	21.6	83		
ITO/NiO _x /PVK+ TCMAI	Cs _x FA _{1-x} PbI ₃	23.6	1.14	24.7	82		

Table S1 Summary of the photovoltaic performance of the reported Cs/FA-based perovskite devices.

/C ₆₀ /BCP/Cu							
ITO/PTAA(PhMe)-100°C/		10.25	1.00	22.7	70		
PVK/C ₆₀ /BCP/Ag		19.35	1.08	22.7	/8		
ITO/PTAA(Py)-60°C/	Cs _{0.2} FA _{0.8} Pb	20.52	1.10	22.1	0.1		0
PVK/C ₆₀ /BCP/Ag	(I _{0.95} Br _{0.05}) ₃	20.55	1.10	23.1	81	0.04	ð
ITO/PTAA(Py)-60°C/		21.21	1 1 4	22.4			
PVK/PEAI/C ₆₀ /BCP/Ag		21.51	1.14	23.4	/9		
ITO/PTAA/PVK/		20.8	1 10	72 7	80		
PEAI/PC ₆₁ BM/BCP/Ag	Cs _{0.15} FA _{0.85} Pb	20.8	1.10	23.7	80	0.00	0
ITO/ Py-PTAA /PVK/	$(I_{0.95}Br_{0.05})_3$	22.0	1 16	22.8	02	0.09	9
PEAI/ PC ₆₁ BM /BCP/Ag		22.0	1.10	23.0	85		
FTO/NiO _x /CuCrO ₂ /		16.28	1.07	22.1	66		
PVK/TiO ₂ /PC ₆₁ BM/BCP/Ag	Cs _{0.15} FA _{0.85} Pb	10.20	1.07	23.1	00	0.00	10
FTO/NiO _x / Mg: CuCrO ₂ /	(I _{0.9} Br _{0.1}) ₃	21.6	1 1 1 1	24.0	70	0.09	10
PVK/TiO ₂ /PC ₆₁ BM/BCP/Ag		21.0	1.14	24.0	19		
FTO/polyTPD/PVK/PC ₆₁ BM		16.6	1 1 1	10.5	75		
/BCP/Cr/Au	Cs _{0.17} FA _{0.83} Pb	10.0	1.11	19.5	/5	0.09	11
FTO/polyTPD/PVK+[BMP] ⁺ [BF ₄] ⁻ /	$(I_{0.77}Br_{0.23})_3$	17.3	1 16	19.5	77		
PC ₆₁ BM /BCP/Cr/Au			1.10				
FTO/polyTPD/PVK+[BMP] ⁺ [BF ₄] ⁻ /	$Cs_{0.17}FA_{0.83}Pb$		1 1 2				
PC ₆₁ BM /BCP/Cr/Au	$(I_{0.90}Br_{0.10})_3$	20.5	1.12	22.0	17		
ITO/PTAA/PVK/C ₆₀ /BCP/Cu	$FA_{0.83}Cs_{0.17}Pb$	19.10	1.04	22.7	81		
ITO/PTAA/PVK+ PFN-		20.32	1.10	22.9	81	0.07	12
Br/C ₆₀ /BCP/Cu	-2.72-0.3						
ITO/PTAA/PFN-Br/		17.85	1.08	21.4	77		
PVK/C ₆₀ /BCP/Ag	-						
ITO/PTAA/PFN-Br/		19.15	9.15 1.10	21.8	80	_	
PVK/PCBM/C ₆₀ /BCP/Ag	-						
ITO/PTAA/PFN-Br/		18.31	1.09	21.5	78		
PVK/mPy/C ₆₀ /BCP/Ag	$(Cs_{0.17}FA_{0.83})$					0.11	13
ITO/PTAA/PFN-Br/	$Pb(I_{0.8}Br_{0.2})_3$	19.24	1.12	21.5	80		
PVK/mPyI /C ₆₀ /BCP/Ag							
ITO/PTAA/PFN-Br/		20.04	1.12	22.1	81		
PVK/ bFP /C ₆₀ /BCP/Ag	-				81	-	
ITO/PTAA/PFN-Br/PVK/ bFPI		21.11	1.15	22.6			
/C ₆₀ /BCP/Ag							
FTO/polyTPD/PVK/PC ₆₁ BM/	FA _{0.83} Cs _{0.17} Pb	12.5	1.14	15.1	74	0.09	14
BCP/Ag	$(I_{0.6}Br_{0.4})_3)$						
FTO/NiMgLiO/PVK/PC ₆₁ BM		16.75	1.03	22.1	74		
/BCP/Ag	FA _{1x} Cs _x Pb					- 0.09	15
FTO/NiMgLiO/PVK/Acetylpyridine	I _y Br _{3-y}	20.05	1.08	23.2	80		
/ PC ₆₁ BM /BCP/Ag							
ITO/NiO/PVK/LiF/PC ₆₁ BM/SnO ₂	Cs _{0.17} FA _{0.83} Pb	14.5	0.98	18.7	79	0.95	16

/ZTO/ITO/Ag/LiF	(Br _{0.17} I _{0.83}) ₃						
ITO/PTAA/PVK/C ₆₀ /BCP/Ag	FA _{0.83} Cs _{0.17} Pb	20.01	1.09	22.64	80.6	0.00	This
ITO/PTAA/PVK/APDI/C ₆₀ /BCP/Ag	$(I_{0.86}Br_{0.14})_3$	21.41	1.12	23.29	82.0	0.09	work

Table S2. TRPL parameters of perovskite films from Fig. 4b.

Sample	$ au_1$ (ns)	$A_1(\%)$	$ au_2$ (ns)	$A_{2}(\%)$	$\tau_{\rm average}$ (ns)
Control	22.25	37.71	108.93	62.29	99.39
Target	15.45	28.24	176.77	71.76	115.78

Table S3. The photoelectric parameters of PSCs without and with APDI.

Sample	$V_{\rm OC}$ (V)	$J_{\rm SC}~({ m mA/cm^2})$	FF (%)	PCE (%)
0.0 mg/ml	1.097	22.64	80.56	20.01
0.1 mg/ml	1.133	22.59	82.08	21.01
0.3 mg/ml	1.121	23.29	82.03	21.41
0.5 mg/ml	1.123	22.41	81.26	20.44

Table S4. The photovoltaic parameters of PSC devices without and with APDI modification obtained from Figure S6. (The data in brackets is the champion value of the device, and the rest is the average value of the 20 groups of devices.)

Sample	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA/cm^2})$	FF (%)	PCE (%)
Control	1.089 ± 0.01	22.46 ± 0.43	79.0 ± 0.83	19.40 ± 0.33
Control	(1.097)	(22.64)	(80.56)	(20.01)
Tanat	1.107 ± 0.01	23.02 ± 0.36	81.0 ± 0.81	20.67 ± 0.48
Target	(1.121)	(23.29)	(82.03)	(21.41)

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