Supporting Information

Minimizing tin (II) oxidation using Ethylhydrazine oxalate for high-performance all-perovskite tandem solar cells

Jianhua Zhang[1], Xufeng Liao[1], Weisheng Li[1], Yutian Tian[1], Qinyang Huang[1], Yitong Ji[1], Guotang Hu[2], Qingguo Du[3], Wenchao Huang[1], Donghoe Kim[4], Yi-Bing Cheng[1,5], and Jinhui Tong[1+]

[1]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China.

[2]School of Art and Design, Wuhan University of Technology, Wuhan 430070, PR China.

[3]School of Information Engineering, Wuhan University of Technology, Wuhan 430070, PR China.

[4]Department of Materials Science and Engineering, Korea University, Seoul 02841, Republic of Korea

[5]Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory, Foshan 528200, PR China.

Email: jinhui.tong@whut.edu.cn

1.1 Materials

methylammonium iodide (MAI, 99.5%), formamidine iodide (FAI, 99.5%), cesium iodide (CsI, 99.99%), Methylammonium bromine (MABr, 99.5%), PEDOT: PSS (AI4083), C_{60} (>99.5%), and BCP were purchased from Xi'an p-OLED Crop. Lead iodide (PbI_2, 99.99%) and [4-(3,6-dimethyl-9H-carbazol-9-yl) butyl] phosphonic acid (Me-4PACz, >99.0%) were purchased from TCI. Ethylhydrazine oxalate (EDO) was purchased from Macklin. Other chemical reagents were obtained from Sigma-Aldrich unless otherwise notes. All of the purchased chemicals were used directly as received with no purification.

1.2 Device Fabrication

1.2.1 Precursor Preparation:

The NBG Sn–Pb $FA_{0.6}MA_{0.3}Cs_{0.1}Pb_{0.5}Sn_{0.5}I_3$(1.8M) perovskite precursor was prepared by resolving 14.1 mg of SnF_2, 85.8 mg of MAI, 185.7 mg of FAI, 46.8 mg of CsI, 414.9 mg of PbI_2,335.3 mg of SnI_2, 2.7 mg of NH_4SCN in 1 ml mixed solution of DMF and DMSO (DMF: DMSO = 3: 1, v/v). The precursor solution was stirred at 45°C for 2 hours and filtered through a 0.22 um PTFE filter before use.

1.2.2 Device Fabrication for NBG Sn–Pb PSCs:

Indium tin oxide (ITO) coated glass was purchased from Yingkou Youxuan Commercial & Trading Co., Ltd (Yingkou, Liaoning, China). Substrates are treated with UV ozone for 16 min prior to PEDOT:PSS deposition. PEDOT:PSS was spin-coated onto clean ITO substrates at 4000 rpm for 30s and then annealed at 130 °C for 30 min. Afterwards the substrate is transferred to the glove box for the next step. For spin-coating of the perovskite layer, we drop-coated 80ul of precursor solution onto the substrate. A two-step spin coating program was used. The first step was at 1000 rpm for 10s with an acceleration of 200 rpm · s^{-1}, and the second step was 4000 rpm for 60s with an acceleration of 1000 rpm · s^{-1} In the second step at 35s, 250μl of chlorobenzene was added dropwise to the substrate. After that, the substrate was annealed on a hot bench at 100°C for 20 min. For the EDO post-treatment, 0.2 mg EDO was added to 1.0

ml chlorobenzene. The solution is stirred overnight, then filtered through a 0.22 um PTFE filter before spin-coated. The surface posttreatment program was at 4000 rpm for 30 s with an acceleration of 1333 rpm · s^{-1}. 50ul of EDO solution was added dropwise to the substrate at 5s of spin-coating, followed by annealing at 100°C for 5min. and after annealing, the substrate was transferred to a vacuum chamber for thermal evaporation, and C60 (25 nm) and BCP (7 nm) were deposited sequentially under a vacuum pressure of less than 9×10^{-4} Pa, and then the area of the mask was replaced with an area of 0.11 cm^{-2} for the deposition of Ag (100 nm) in order to determine the effective area.

1.2.3 Fabrication for 2T all-perovskite tandem solar cells

The WBG PSCs ITO substrates were also cleaned as described above. Likewise, UV ozone treatment for 15 min. After that we spin-coated the NiOx onto the substrate at a spin-coating speed of 4000 rpm for 10s with an acceleration of 2000 rpm · s^{-1}. followed by annealing at 120°C for 15 min. (10 mg of NiOx was dissolved in 1 ml of water, Sonication for 20 min and filtered through a 0.22 um PTFE filter before use). Afterwards, Me-4PACz (0.5 mg/mL) was spin-coated on the substrate at a spin-coating speed of 3000 rpm for 30s. After spin coating, anneal the substrate at 100°C for 10min. The configured solution with a concentration of 1.2M perovskite precursor $(FA_{0.9}MA_{0.05}Cs_{0.05}Pb(I_{0.65}Br_{0.35})_3$ was dissolved in mixed solvents of DMF and DMSO (volume ratio of 4:1) was filtered through a 0.22 μm PTFE filter. Wide-bandgap perovskite films were deposited on top of Me-4PACz via a two-step procedure (1500 rpm for 10 s and 5000 rpm for 40 s), with 200 μl of chlorobenzene antisolvent added dropwise after 20s of the second step. The substrates were then transferred onto a hotplate and heated at 100°C for 15 min. After cooling to room temperature, they were transferred to a vacuum vapor deposition chamber (Wuhan PDVACUUM Technologies Co., Ltd.) for deposition of C_{60} (25 nm), after which the substrates were transferred to an atomic layer deposition (ALD) system (Jiaxing Komikro Electronic Equipment Co., Ltd.) for deposition of SnO_2 (20 nm) at 85 °C. After ALD, the substrates were transferred to a thermal evaporation system to deposit a 0.8 nm layer of

Au cluster on SnO2. NBG PSCs were then fabricated on this basis, and unlike single-junction Solar Cells, HTL spin-coating process used PEDOT:PSS mixed with isopropanol (PEDOT:PSS: IPA = 1: 2, v/v), and the annealing condition was changed to 110°C for 10 min. Above is how the 2T all-perovskite tandem solar cells is made

1.3 Characterizations

The X-ray photoelectron spectroscopy (XPS) spectra were tested by an X-ray photoelectron spectrometer (Thermo Fischer, ESCALAB Xiþ). The SEM images were tested by a Hitachi SU8010 field-emission scanning electron microscopy. The fourier-transform infrared spectroscopy (FTIR), which we measured using a Nicolet6700. Atomic force microscopy （AFM） and Kelvin probe force microscopy (KPFM) images of perovskite films were taken with Bruker Dimension Icon atomic force microscope. photoluminescence (PL) and time resolved PL spectra (TRPL, Micro Time 200 PicoQuant GmbH).The perovskite films were also characterized by X-ray diffractometer (XRD, D8 Advance) UV−Vis spectrometer (lambda 750 S, PerkinElmer), photoluminescence quantum yield (PLQY, Enlitech), The thickness of the perovskite films was measured by Filmetrics. The current density voltage *(J–V*) curves and dark current density of devices were measured by a Keithley 2450 source meter. The light source was a solar simulator (SS−XRC，Enlitech) matching AM 1.5G. All the devices were tested under AM 1.5G sunlight (100 mW · cm^{-2}) using a black metal aperture with a mask area of 0.058 cm^2. The EQE measurement was obtained on a computer-controlled quantum efficiency measuring instrument (QE−R, Enlitech). Photoluminescence quantum yield (PLQY) was tested by Enlitech with a 405 nm laser light source. Urbach energy was measured by Enlitech.

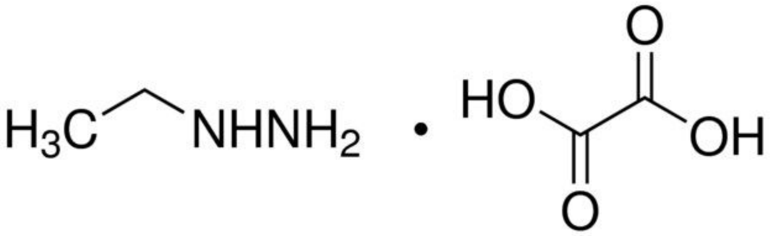

Fig. S1. The two-dimensional structure of EDO

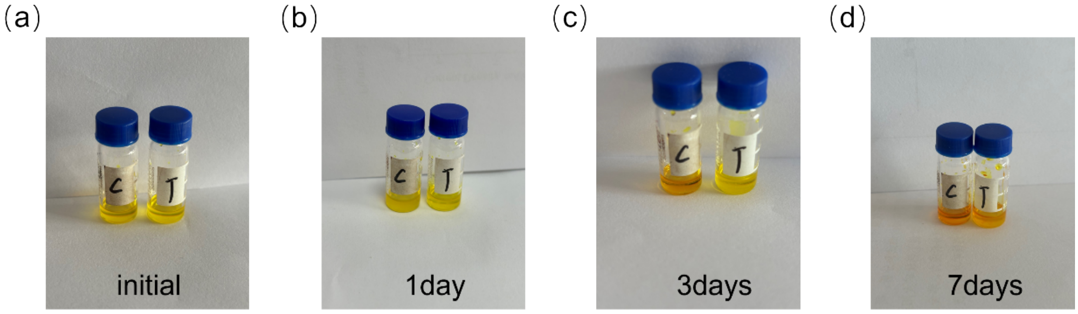

Fig. S2. (Color online) The color changes of the perovskite precursor solution without EDO (left image) and the precursor solution with EDO (right image) after being left in ambient air for one week.

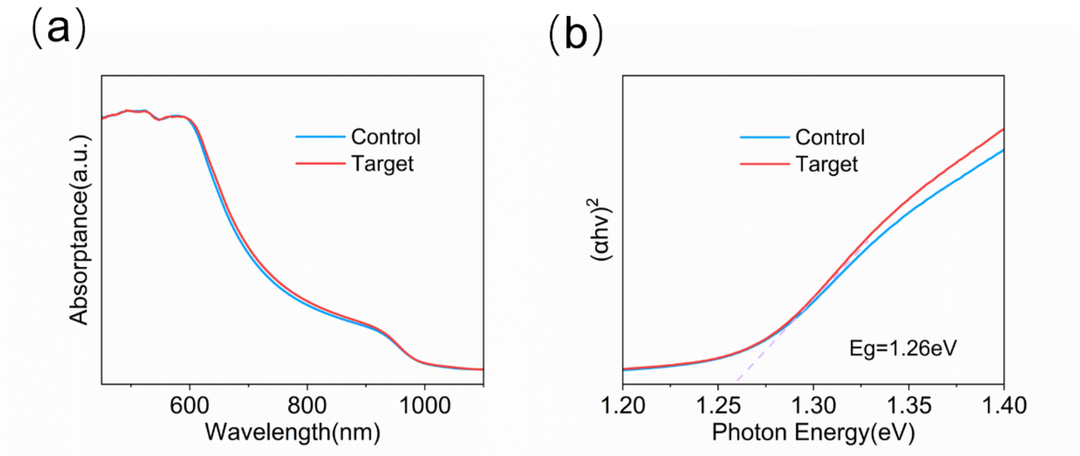

Fig. S3. (Color online) (a) UV−vis absorption spectra and (b) Tauc plots of perovskite films.

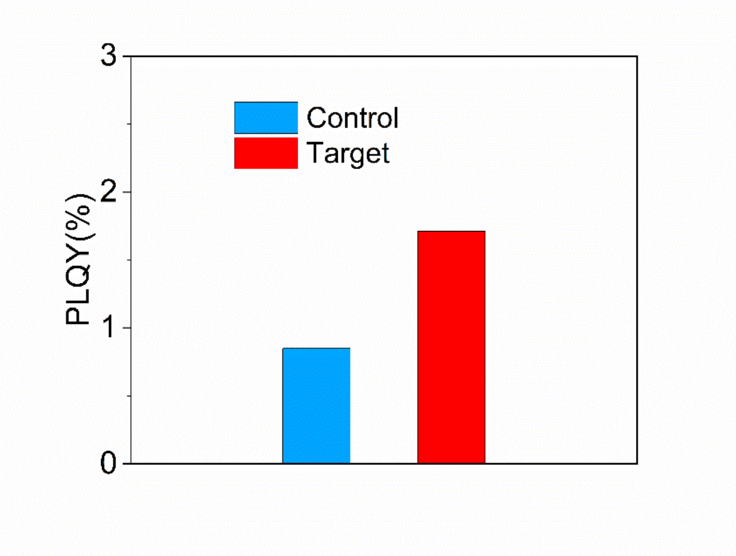

Fig. S4. (Color online) PLQY patterns of the control and target perovskite films.

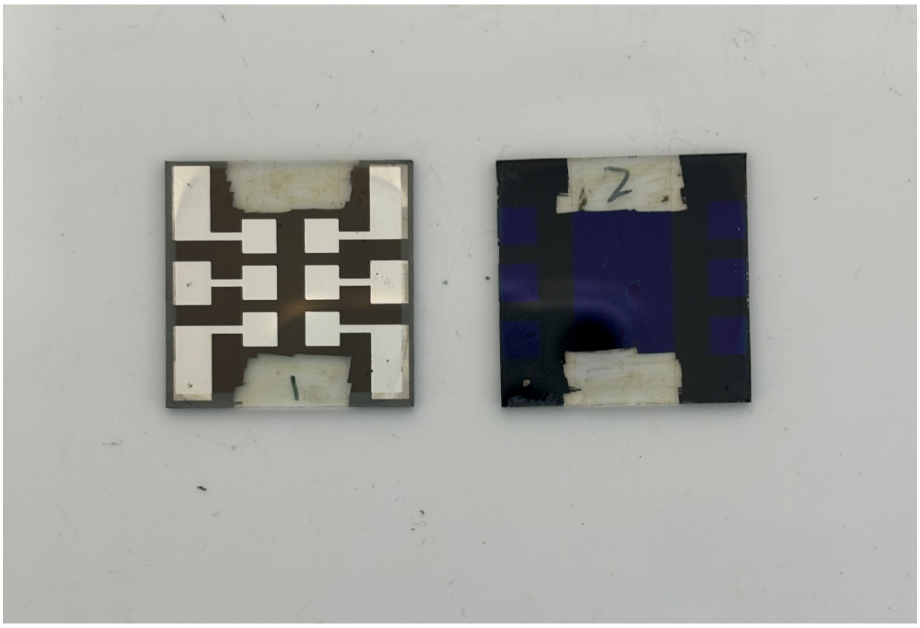

Fig. S5. Schematic of the front and back of a perovskite solar cell

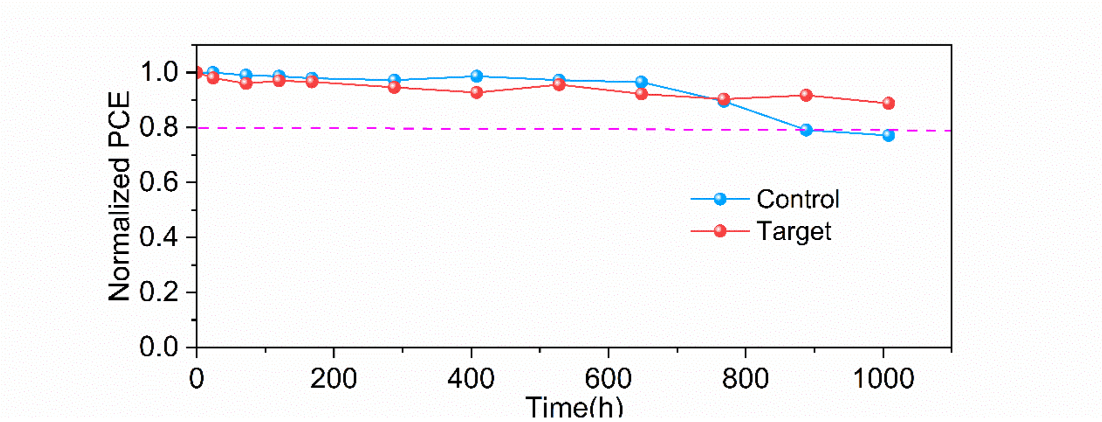

Fig. S6. (Color online) The long-term stability of unencapsulated control and target cells stored in an N2-filled glovebox.

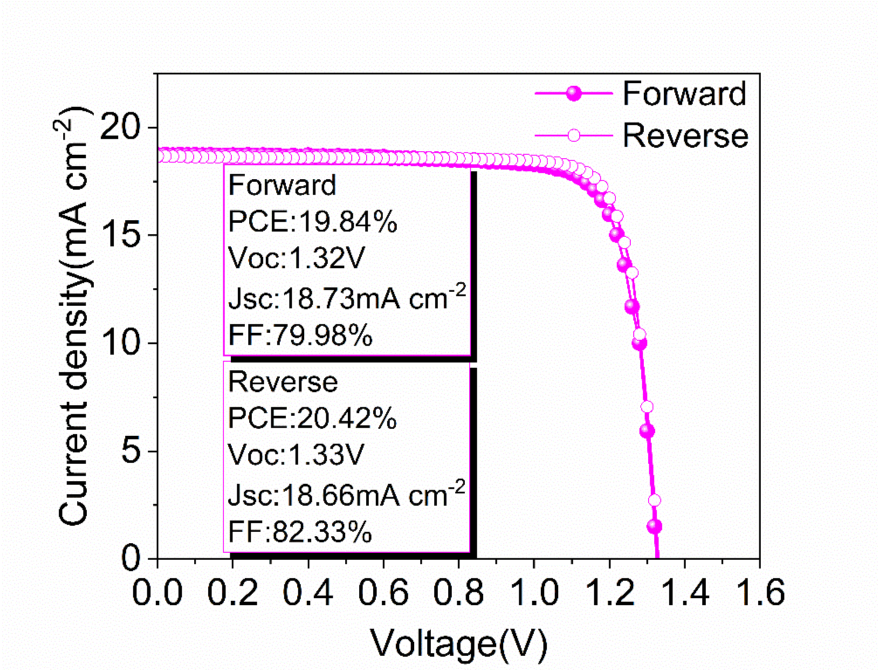

Fig. S7. (Color online) The $J-V$ curve of WBG Perovskite solar cells

Table S1. Fitting results from TRPL spectra of the Sn−Pb perovskite films with and without EDO-modified.

	A1	**τ1 (ns)**	**A2**	**τ2 (ns)**	**τ_{avg} (ns)**
Control	0.949	56.10	0.372	239.2	170.4
Target	0.605	215.76	0.455	413.4	332.3

Table S2. Detailed data on PCE, Voc, Jsc, FF for ten individual All-perovskite tandem solar cells

		PCE(%)	*Voc*(V)	*Jsc*(mA · cm^{-2})	FF(%)
1	Forward	26.242	2.107	15.485	80.404
	Reverse	26.988	2.112	15.443	82.711
2	Forward	26.459	2.161	15.153	80.781
	Reverse	26.622	2.159	15.096	81.649
3	Forward	27.248	2.134	15.821	80.707
	Reverse	27.538	2.133	15.708	82.193
4	Forward	26.572	2.139	15.846	78.381
	Reverse	26.938	2.140	15.851	79.407
5	Forward	26.664	2.159	16.575	74.492
	Reverse	27.074	2.159	16.542	75.806
6	Forward	26.862	2.168	16.184	76.555
	Reverse	27.405	2.169	16.052	78.684
7	Forward	27.410	2.119	15.899	81.344
	Reverse	27.588	2.121	15.852	82.031
8	Forward	27.668	2.150	16.154	79.650
	Reverse	27.899	2.150	16.138	80.371
9	Forward	27.284	2.145	16.638	76.423
	Reverse	27.777	2.147	16.373	79.013
10	Forward	27.577	2.163	15.750	80.921
	Reverse	27.771	2.161	15.682	81.908