Supporting Information

Low-Temperature Aqueous Solution Processed ZnO as an Electron Transporting Layer for efficient Perovskite Solar Cells

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Experimental Section

Materials: 4-tert-butylpyridine (TBP) and Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI) were purchased from Aladdin-reagent. PbI_2 (99.99%), hydroiodic acid (57% wt. in water, 99.99%) and methylamine (33% wt. in absolute ethanol) were purchased from Sigma-Aldrich. Ethanol, diethyl ether, acetonitrile, dimethyl formamide and chlorobenzene were purchased from Alfa Aesar. 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine) -9,9'-spirobifluorene (spiro-OMeTAD) (≥99.0%) was purchased from Shenzhen Feiming Science and Technology Co., Ltd. Indiumtinoxide (ITO) glass with a sheet resistance of 14 G sq^{-1} was purchased from Huanan Xiangcheng. The purity of silver wire is 99.99%. All of the used reagents were analytical grade.

Measurements: Transmission spectra were characterized by an ultraviolet-visible (UV-Vis) spectrophotometer (Lambda 950, PerkinElmer) at room temperature. The morphologies of the ZnO nanocrystalline and perovskite films were imaged by scanning electron microscopy (SEM) on a JEOL-6701F microscope. The crystalline structures of perovskite films were identified using an X-ray diffractometer (XRD, Bruker D8 Advance) with a monochromatized source of Cu Kα radiation (λ = 0.15406 nm) at 1.6 kW (40 kV, 40 mA). UPS measurements were analyzed on Thermo Scientific ESCA Lab 250 Xi. The gas discharge lamp with helium as admitted and the HeI (21.22 eV) emission line was used. The helium pressure was about 2E-8 mbar and the data were acquired at -10 V bias.

ZnO Precursor Synthesis. Zn solutions were prepared by dissolving $Zn(NO_3)_2$ $6H_2O$ in distilled H_2O to a total concentration of 0.5 M Zn. 10 mL of 2.5 M NaOH was added dropwise to 15 mL of this solution in 5 min. The resulting $Zn(OH)_2$ precipitate was centrifuged and the supernatant removed. The precipitate was then suspended in 20 mL of H_2O, followed by centrifugation and supernatant removal. Rinse and separation steps were repeated three times to remove Na^+ and NO_3^-. After the final centrifugation, the $Zn(OH)_2$ precipitate was dissolved in 60 mL of 6.6 M NH_3(aq) to form a stock solution.

Synthesis of CH_3NH_3I. A concentrated aqueous solution of hydroiodic acid (HI) (15.0 mL, 57 wt% in water, Alfa Aesar) was reacted with methylamine (CH_3NH_2) (13.5 mL, 40 wt% in aqueous solution, Alfa Aesar) at 0 ℃ for 2 h with constant stirring under nitrogen atmosphere. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing the solvents at 50 ℃. The generated white powder was washed with diethyl ether three times and dried in vacuum overnight.

Fabrication and Characterization of PSCs. Planar n-i-p PSC structure based on ITO/ZnO/(urea)/Perovskite/Spiro-OMeTAD/Ag was used. The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then treated with UVO for 20 min. Then ZnO was deposited by spin-coating the prepared aqueous solution (2000 rpm, 30s) and annealed at 150 ℃ for 10 min in air. The ZnO coated glass/ITO substrates were transferred into the glovebox for further deposition of urea (2 mg/mL in methanol, 5000 rpm, 30s). In the following, freshly prepared $CH_3NH_3PbI_3$ solution was spin-coated at 5000 rpm and after six seconds anhydrous chlorobenzene (150 μL) was quickly dropped onto the center of the substrate. The solution of perovskite was prepared by mixing PbI_2 and CH_3NH_3I (molar ratio is 1:1) in N,N-dimethylformamide (DMF) with concentration of 47%. The as spun films were annealed at 70 ℃ for 30 min. Lithium doped 2,2',7,7'-tetrakis(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) was deposited from the solution of chlorobenzene by spin-coating (2500 rpm, 30s). The substrates were deposited 70 nm Ag to finish the device fabrication process. The device area is defined around 0.09 cm^2 by the cross section of the electrodes. The *J-V* characteristic of PVSC was recorded on Keithley 2400. All the cells were measured under a 100 mW cm^{-2} (AM1.5 simulated irradiation) illumination with a standard Newport Solar Simulator. A standard silicon solar cell was used to calibrate the light intensity.

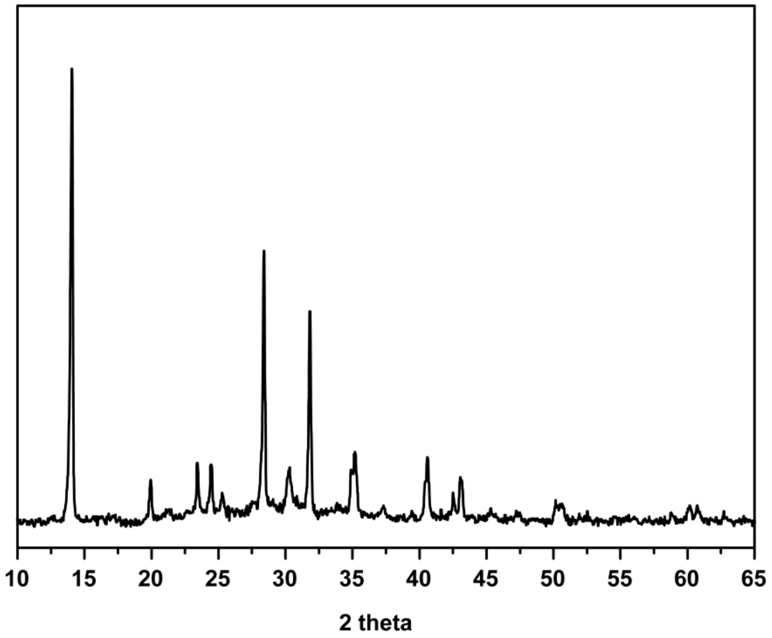

Figure S1 XRD of the perovskite film on ZnO/Urea.

XRD images of the prepared perovskite film on ZnO/Urea is shown in Figure S1, indicating that the perovskites with high crystalline were successfully prepared by the one-step method.

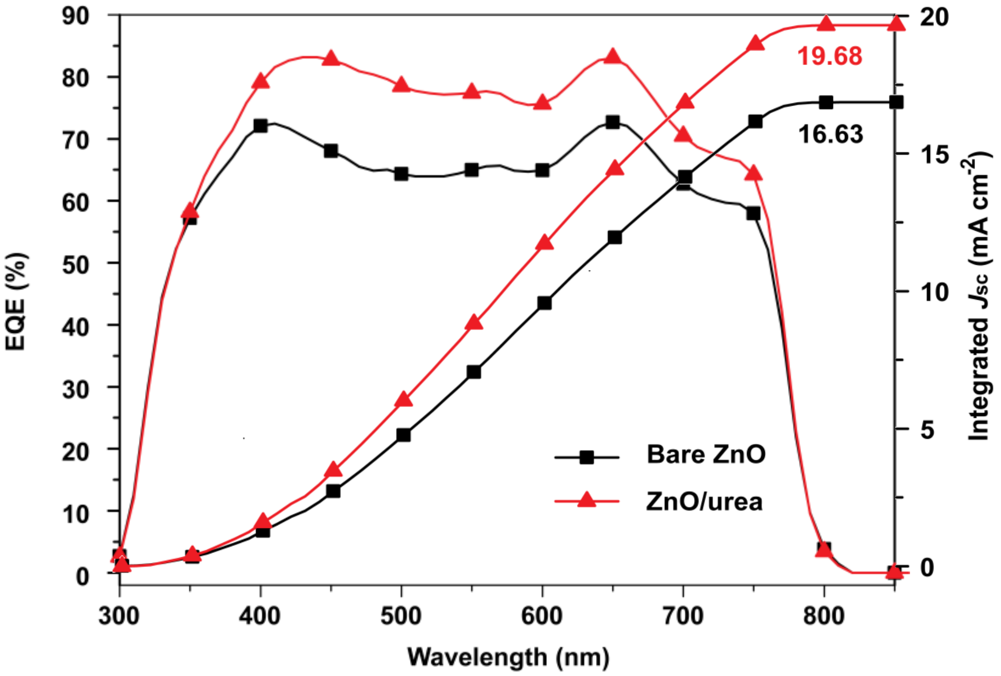

Figure S2 EQE spectra of the solar cells using the ZnO ETL with or without urea modification.

Figure S2 shows the external quantum efficiency (EQE) spectra of the solar cells using the ZnO ETL with or without urea modification. The EQE spectrum of the solar cell with urea modification shows a broad peak with EQE value of above 75% in the range from 370 to 670 nm, in reasonable agreement with the high J_{sc} measured from the *J*-*V* curves.

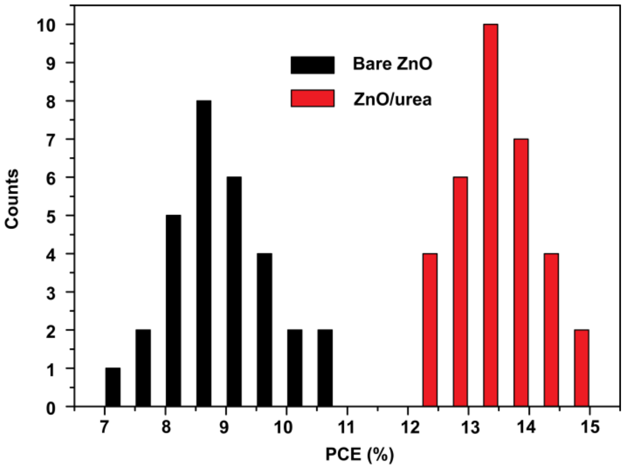

Figure S3 Histograms of PCEs measured for 30 cells using the ZnO ETLs with or without urea modification.

To check the reproducibility of the performance of the perovskite solar cells using the ZnO ETLs with or without urea modification, we fabricated and measured 30 separate devices. Figure S3 shows the statistic histograms of the PCEs measured with reverse voltage scan and a scan rate of 0.1 V/s. The device performance of PVSC with urea modified ZnO ETL showed a narrow distribution of PCE (range: 12.1% to 14.6%, with the average value of 13.4%). In comparison, without the urea modification, much lower PCE (average value of 9.1%) with a wide range (from 7.2% to 10.6%) was obtained. We attributed the improved reproducibility to the evolved morphology of $CH_3NH_3PbI_3$ film on the urea surface.

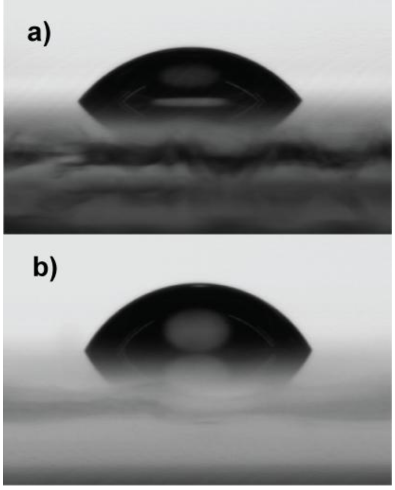

Figure S4 the contacting angles of water on the ZnO films a) without urea modification and b) with urea modification

To investigate the wetting capability of the prepared ZnO film, we measured the contacting angles of water on the ZnO films with or without urea modification (see Figure S4). The contacting angle of water on the prepared ZnO film is 52.1°. After modification with urea, the contacting angle is increased to 61.9°, which is higher than that of PEDOT:PSS (12°), indicating the hydrophobic nature of the prepared ZnO film. The non-wetting surface of the prepared ZnO film will improve the grain size and crystallinity of MAPbI3, resulting in higher photovoltaic performance.

Table S1. Transient PL Species of Perovskite on bare ZnO and ZnO/Urea.

substrates	τ1		τ2		τ3	
	lifetime (ns)	content (%)	lifetime (ns)	content (%)	lifetime (ns)	content (%)
Bare ZnO	9.6	9.25	142.2	80.83	555.4	9.92
ZnO/Urea	8.8	16.56	84.7	62.31	307.7	21.13

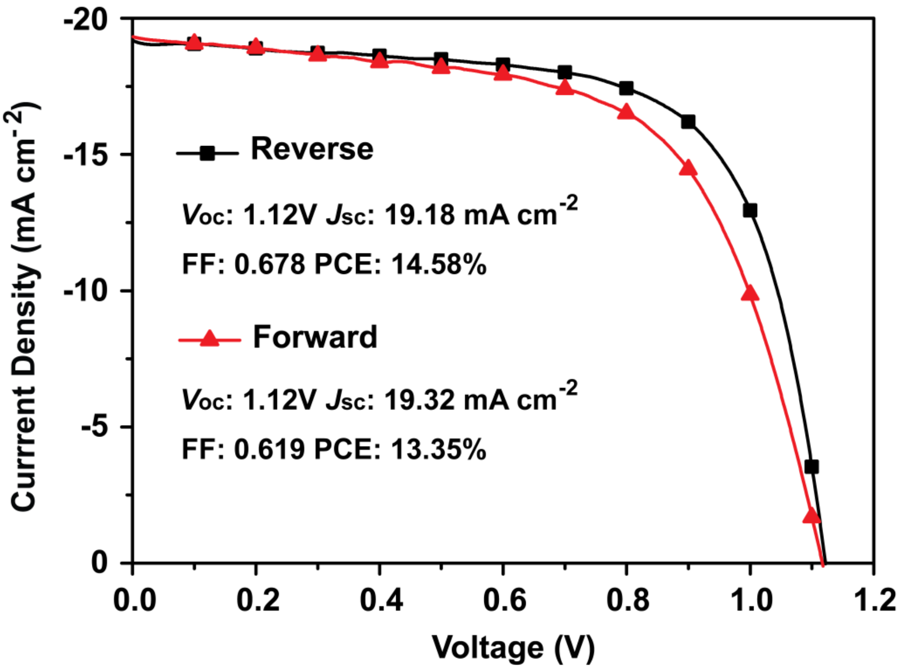

Figure S5 *J-V* curves of the PSCs based on ZnO/urea with the forward and reverse scan.

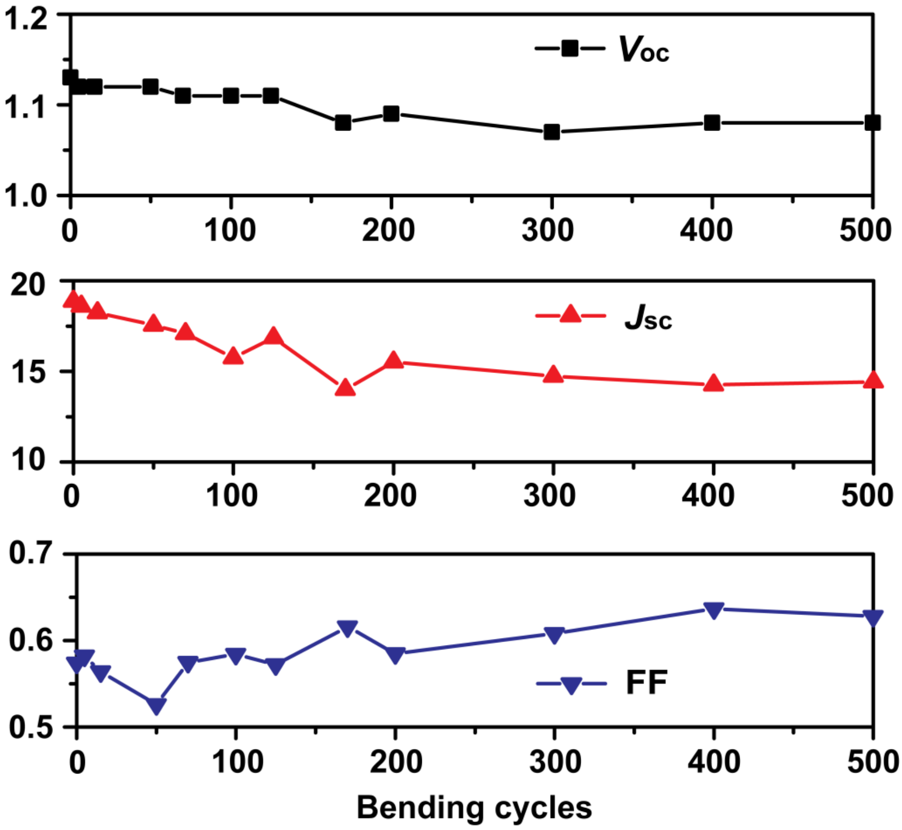

Figure S6 Device parameters of ZnO-based flexible PSCs as a function of bending cycles.

Table S2 Device parameters of ZnO-based flexible PSCs as a function of bending cycles.

Bending cycles	V_{oc}[V]	J_{sc}[mA/cm^2]	FF	PCE [%]
0	1.13	18.86	0.574	12.23
5	1.12	18.60	0.582	12.13
15	1.12	18.24	0.564	11.52
50	1.12	17.55	0.526	10.34
70	1.11	17.08	0.575	10.90
100	1.11	15.74	0.584	10.20
125	1.11	16.86	0.572	10.70
170	1.08	14.00	0.616	9.62
200	1.09	15.52	0.585	9.89
300	1.07	14.73	0.608	9.58
400	1.08	14.25	0.637	9.80
500	1.08	14.43	0.628	9.78

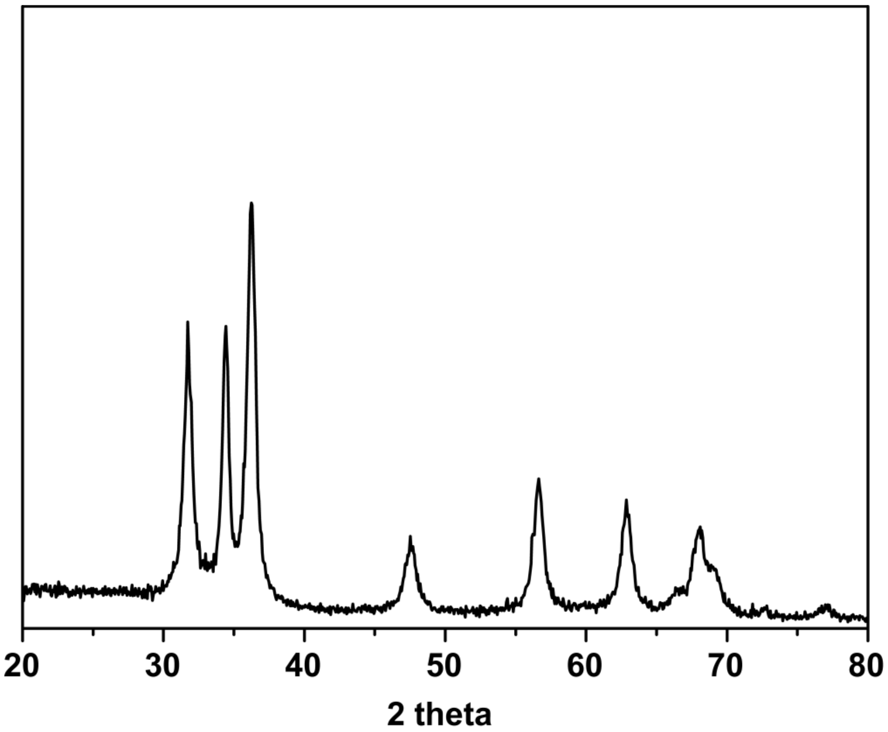

Figure S7 XRD of the prepared ZnO film.