Supporting information for

Existence of ligands within Sol-gel-derived ZnO films and Their Effect on Perovskite Solar Cells

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Contents

1. Experimental section

Solar Cell Fabrication: Fluorine-doped Fluorine-doped Tin Oxide (FTO) glass substrates with dimension of 2.0 cm × 2.0 cm were patterned by etching with zinc powder and 2 M hydrochloric acid. The substrates were then cleaned in ultrasonic baths of acetone, distilled water and ethanol, sequentially. The precursor solution of 169 mg of $ZnAc_2 \cdot 2H_2O$ and 60 μL EA dissolved in 3.0 mL 2-methoxyethanol (2-ME) was spin-coated on the prepared FTO substrate at 3,000 rpm for 25 s. The substrate was then annealed at different temperatures to construct a ZnO film as electron transport layer in PSCs. After cooling down to room temperature, The $Cs_{0.05}(MA_{0.17}FA_{0.83})_{(100-x)}Pb(I_{0.83}Br_{0.17})_3$ precursor solution prepared by the reported ratio[S1] was spin-coated on the prepared FTO substrate at 4,000 rpm for 25 s, when 0.5 mL of diethyl ether was slowly dropped on the rotating substrate in 8 s. The obtained transparent film was then heated at 120 °C for 5 min to form a dense perovskite film. After preparation of the perovskite layer, the Co porphyrin[S1]/chlorobenzene (30 mg/mL) solution was spin-coated by solution process at 3,000 rpm for 30 s. Finally, an Au counter electrode with 80-nm thickness was deposited by thermal evaporation under reduced pressure of 1×10^{-7} Torr. The active area was 0.10 cm^2.

Device Characterization: The current-voltage characteristics were measured by using a solar simulator (the aperture of 40 × 40 cm^2) equipped with a Keithley 2400 source meter and 300 W collimated Xenon lamp (Newport) and calibrated with the light intensity to 100 $mW \cdot cm^{-2}$ under simulated AM 1.5G illumination by a certified

silicon solar cell. Incident photon-to-electron conversion efficiencies (IPCE) were recorded with a computer-controlled IPCE system (Newport) containing a monochromator, a Xenon lamp and a Keithley multimeter. The system was determined using a certified silicon solar cell and the IPCE data were collected at DC mode. XRD patterns were collected at an X-ray diffractometer (Rigaku, RINT-2500) with a Cu Kα radiation source. The surface morphologies were recorded by a SEM-4800 field-emission scanning electron microscope (SEM). The organic species were verified by TPD-MS characterization. The tested samples were placed in a quartz U-shaped reactor tube and pre-treated for 1 hour, and then heated from room temperature to 800 °C (heating rate of 10 °C/min). Evolution of organic species was monitored by a mass spectrometer by following the m/z fragments.

2. Supporting Figures

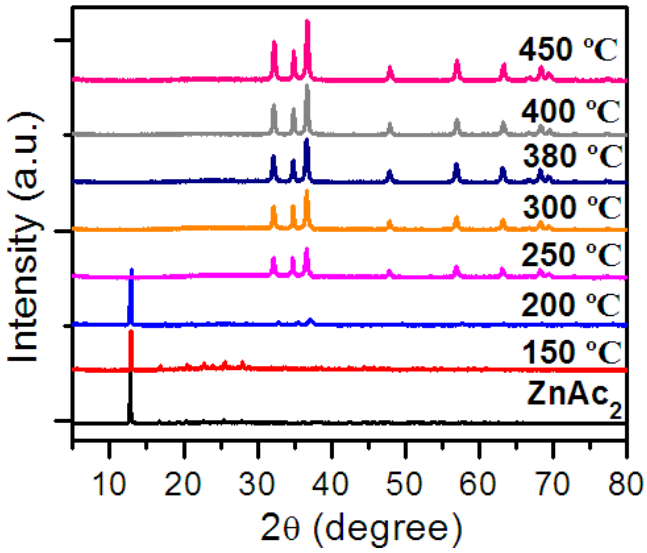

Figure S1. XRD patterns of precursor samples treated at different temperatures.

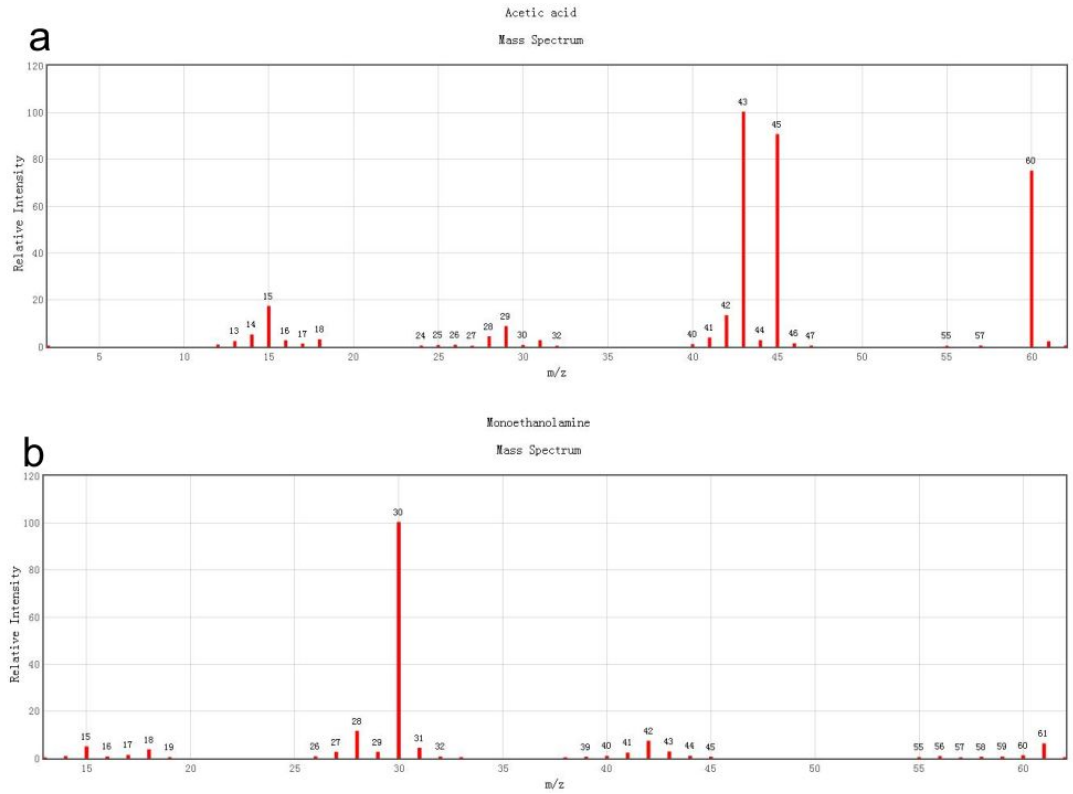

Figure S2. Standard mass spectra of acetic acid (a) and monoethanolamine (EA, b).

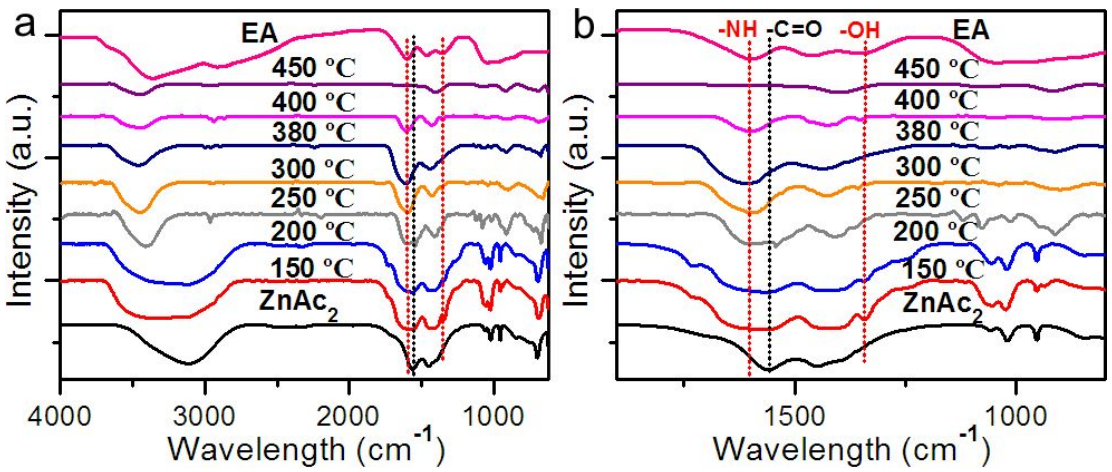

Figure S3. IR spectra (a and enlarged spectra in b) of precursor samples by treatment at different temperatures.

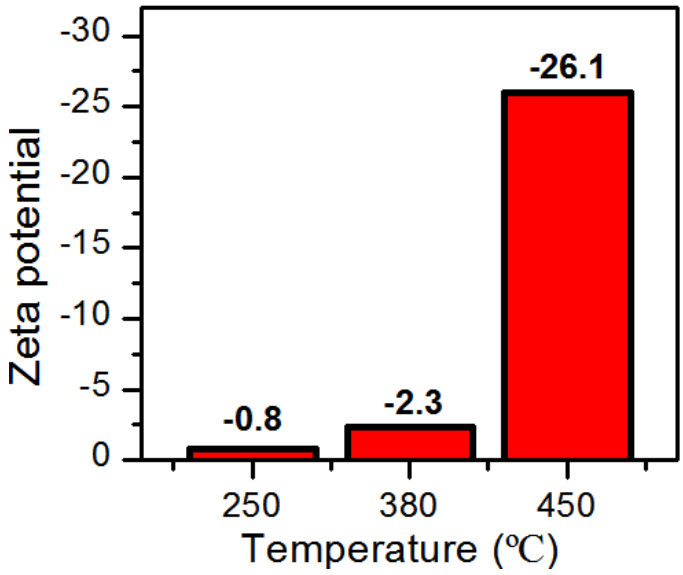

Figure S4. Zeta potential of precursor samples by treatment at different temperatures.

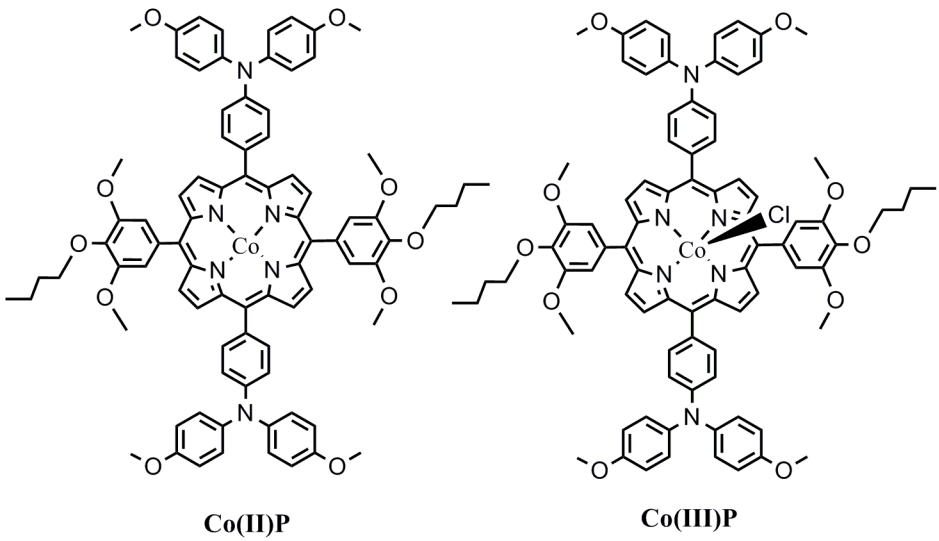

Figure S5. Structures of Co(II) porphyrin (Co(II)P, left) and Co(III) porphyrin (Co(III)P, right).

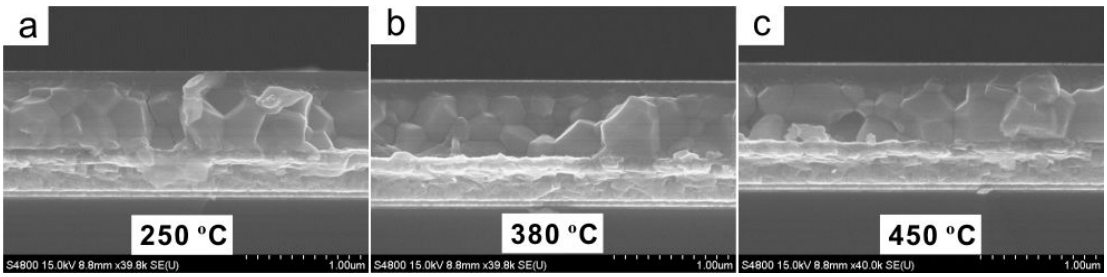

Figure S6. Cross-sectional SEM images of PSCs with ZnO treated at 250 °C (a), 380 °C (b) and 450 °C (c).

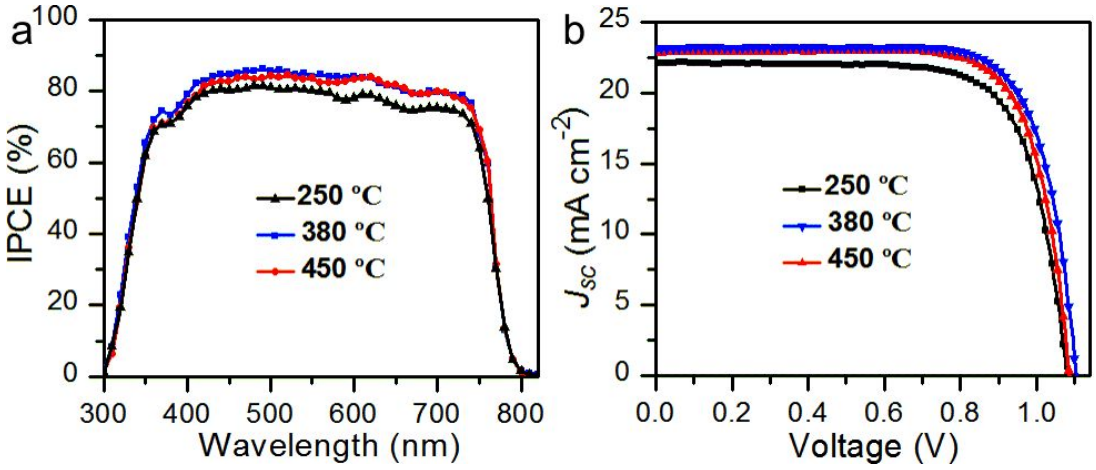

Figure S7. (a) IPCE and (b) histograms of cell efficiencies among 30 cells of planar PSC devices with ZnO at different T_a.

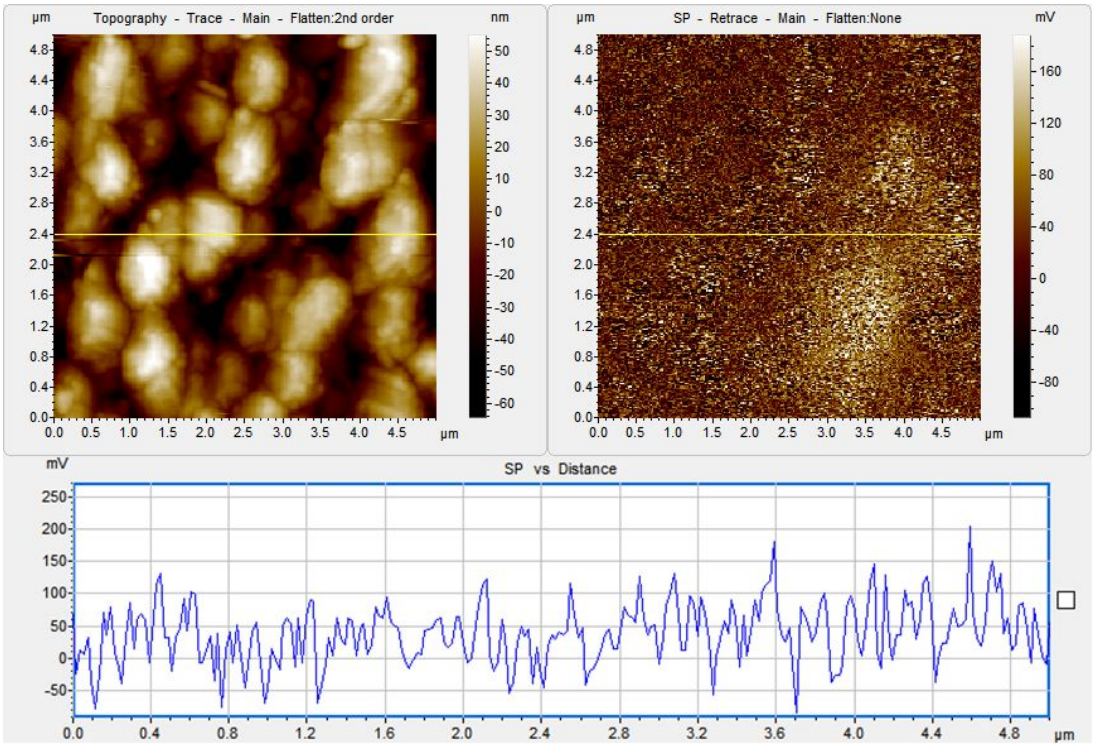

Figure S8. Contact potential differences (CPD) measured on the surface of ZnO powders treated at 250 °C.

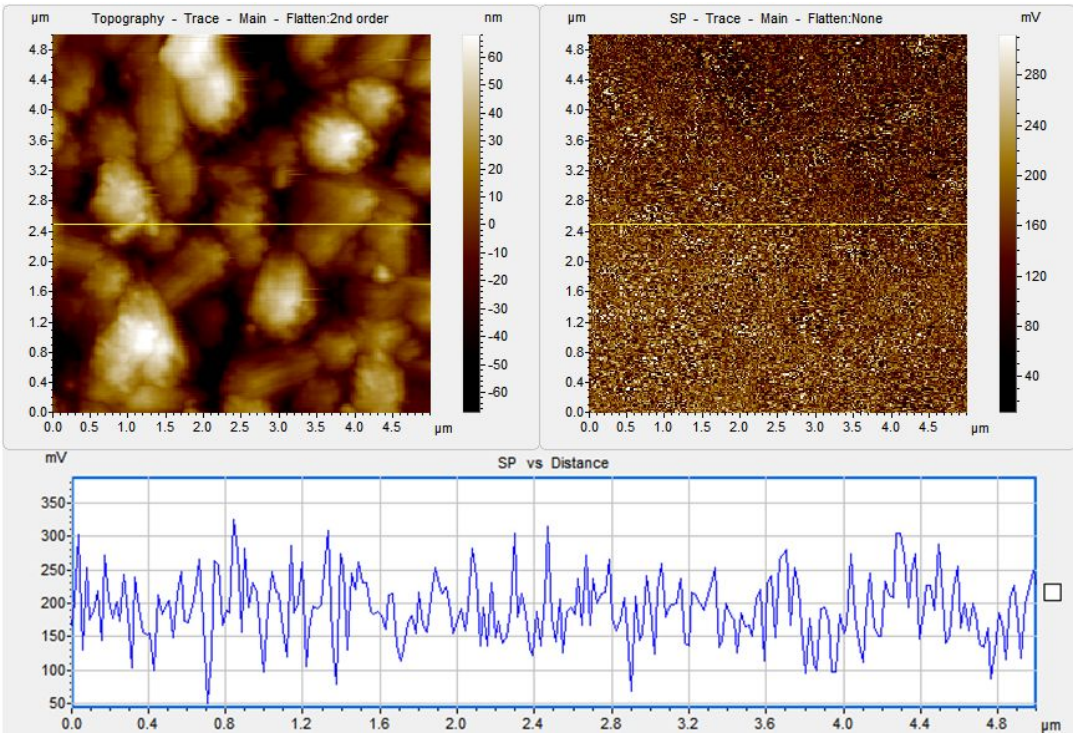

Figure S9. Contact potential differences (CPD) measured on the surface of ZnO powders treated at 380 °C.

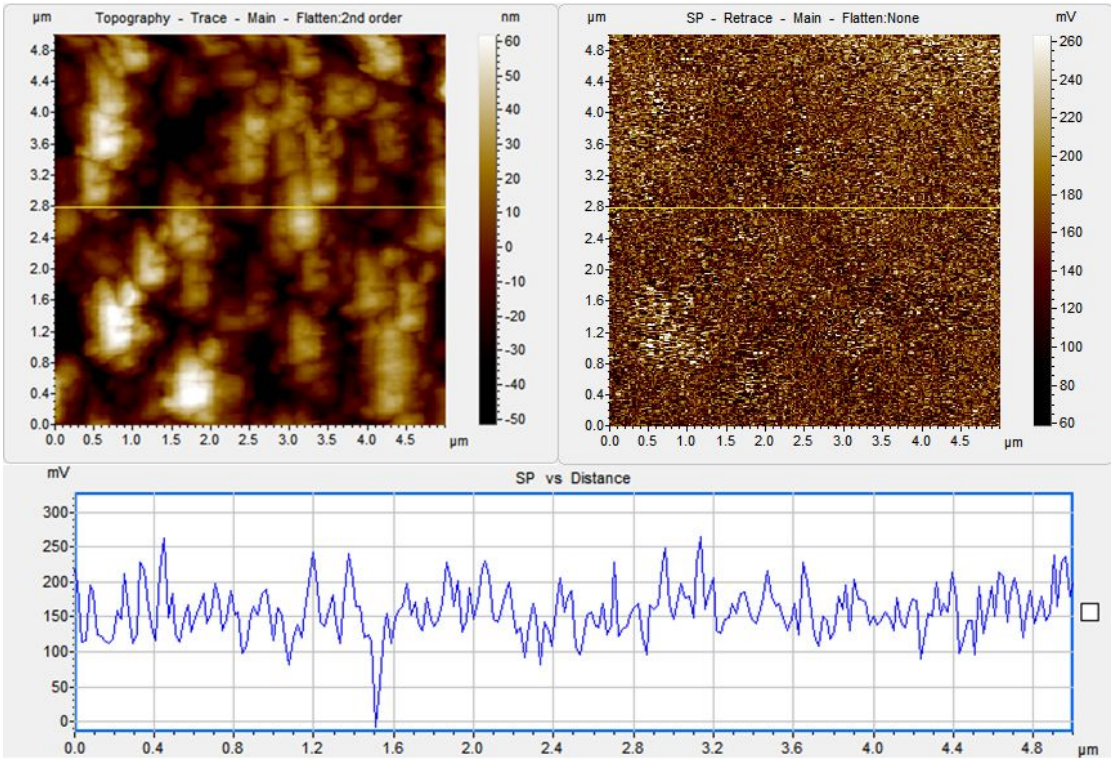

Figure S10. Contact potential differences (CPD) measured on the surface of ZnO powders treated at 450 °C.

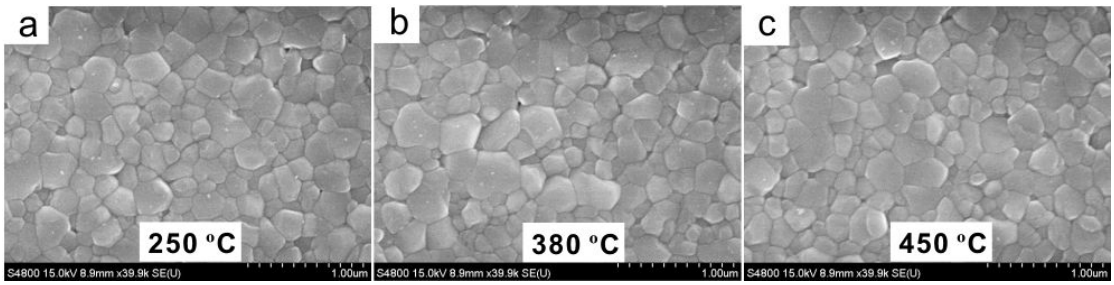

Figure S11. SEM images of perovskite films grown on ZnO treated at 250 °C (a), 380 °C (b) and 450 °C (c).

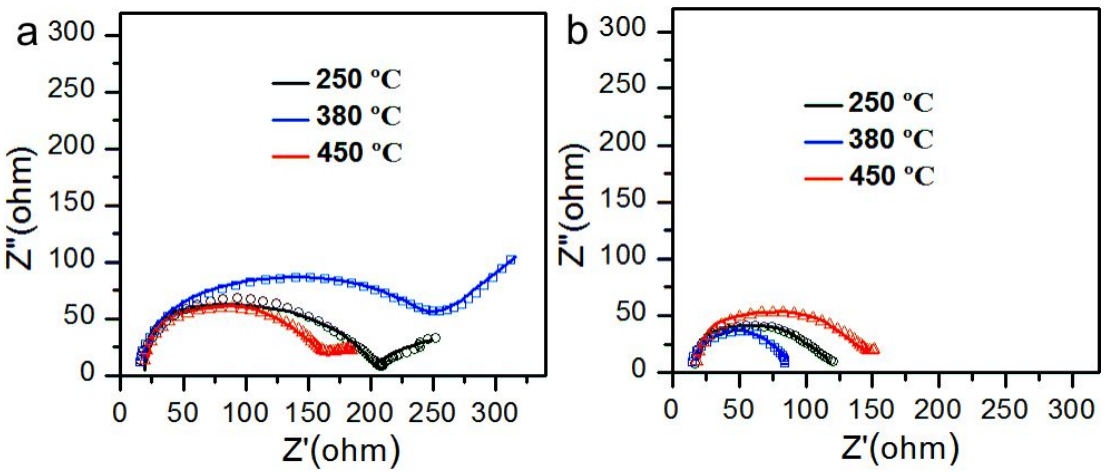

Figure S12. EIS of the PSCs based on ZnO treated at different temperatures measured at (a) 0 V and (b) 0.9 V bias voltage (Dotted lines were experimental data and solid lines were fitting data).

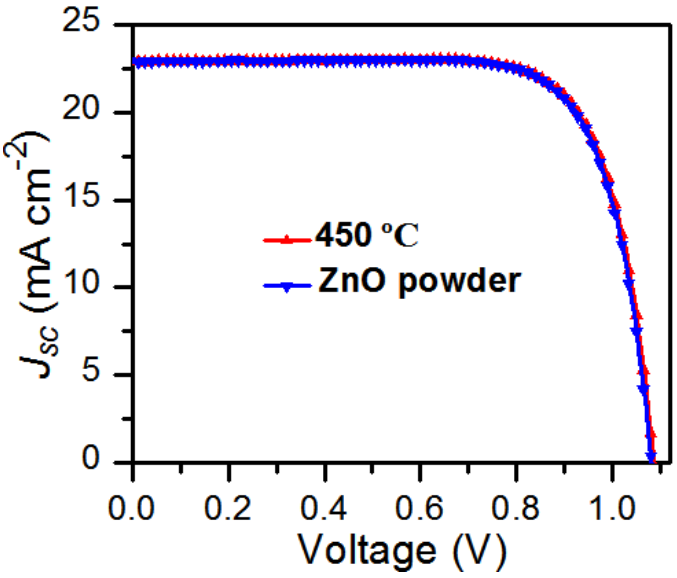

Figure S13. Best *J*−*V* data of planar PSC devices with ZnO treated at 450 °C and the as-prepared ZnO powder.

3. Supporting Tables

Table S1. List of the corresponding literatures and detailed experimental information of ZnO films prepared by sol-gel method.

Precursor	Temperature (°C)	References
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	600	*Nano Lett.* 2008, 8, 1501
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	550	*Nano Lett.* 2011, 11, 3355
$ZnAc_2 \cdot 2H_2O$, EtOH, EA	550	*RSC Adv.* 2014, 4, 4363
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	500	*Adv. Mater.* 2006, 18, 1617; *Mater. Sci. Semicond. Process.* 2019, 89, 149.
$ZnAc_2 \cdot 2H_2O$, EtOH, EA	500	*Adv. Funct. Mater.* 2008, 18, 1832
$ZnAc_2 \cdot 2H_2O$, IPA, EA	450	*Phys. Status Solidi A* 2008, 205, 1938
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	350	*Adv. Funct. Mater.* 2012, 22, 2194
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	300	*Nanoscale* 2014, 6, 1011
$ZnAc_2 \cdot 2H_2O$, EtOH, EA	300	*Nanoscale* 2017, 9, 11574
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	290	*Adv. Energy. Mater.* 2014, 4, 1301404
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	280	*Adv. Mater.* 2018, 30, 1801720
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	275	*Organic Electron.* 2009, 10, 1473
$ZnAc_2 \cdot 2H_2O$, DMF, DEA	250	*Adv. Func. Mater.* 2017, 27, 1604720
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	200	*J. Am. Chem. Soc.* 2015, 137, 6995; *ACS Appl. Mater. Interfaces* 2015, 7, 6273; *ACS Appl. Mater. Interfaces* 2018, 10, 20196; *Nature Photon.* 2016, 10, 521; *ACS Appl. Mater. Interfaces* 2017, 9, 26234; *J. Phys. Chem. C* 2017, 122, 236
$ZnAc_2 \cdot 2H_2O$, EtOH, EA	200	*Adv. Mater.* 2013, 25, 2397
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA,	200	*J. Phys. Chem. C* 2014, 118, 21819

NH_4OH		
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	180	*Adv. Funct. Mater.* 2015, 25, 7309; *ACS Appl. Mater. Interfaces* 2016, 8, 28750; *Sci. Rep.* 2014, 4, 6813
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	180	*ACS Appl. Mater. Interfaces* 2018, 10, 26805
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	170	*Adv. Energy. Mater.* 2014, 4, 1301938
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	160	*J. Am. Chem. Soc.* 2015, 137, 2674
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	150	*Nat. Commun.* 2016, 7, 10279; *Adv. Energy. Mater.* 2016, 6, 1502146; *J. Mater. Chem. A* 2013, 1, 6446; *Adv. Optical Mater.* 2018, 1801153; *Adv. Mater.* 2015, 27, 1035; *J. Mater. Chem.* 2012, 22, 22781; *Adv. Energy Mater.* 2014, 4, 1301777; *ACS Appl. Mater. Interfaces* 2017, 9, 26045; *ACS Appl. Mater. Interfaces* 2017, 9, 10743; *Nat. Commun.* 2017, 8, 15640.
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA,	150	*Sci. Rep.* 2018, 8, 3925
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	140	*RSC Adv.* 2016, 6, 46915
$Zn(NO_3) \cdot 6H_2O$, citric acid	600	*Sci. Rep.* 2018, 8, 10691
$ZnAc_2 \cdot 2H_2O$, 2-ME, EA	150	*J. Mater. Chem. A* 2018, 6, 6542

Table S2. Photovoltaic parameters of planar PSCs with ZnO treated at different temperatures in forward (FS) and reverse (RS) scans.

Devices		J_{sc}/mA·cm^{-2}	V_{oc}/V	*FF*/%	η/%	*Rs*/Ω·cm^{-2}
250 °C	Reverse	22.01	1.08	73.68	17.64	4.85
	Forward	22.26	1.06	69.68	16.37	5.19
380 °C	Reverse	23.11	1.10	76.40	19.38	4.35
	Forward	23.10	1.10	76.38	19.26	4.39
450 °C	Reverse	22.84	1.08	75.68	18.83	4.42
	Forward	22.80	1.08	70.24	17.31	5.22

Table S3. Photovoltaic parameters of planar PSCs with ZnO treated at 450 °C and the as-prepared ZnO powder.

Devices	J_{sc}/mA·cm^{-2}	V_{oc}/V	*FF*/%	η/%	*Rs*/Ω·cm^{-2}
450 °C	22.84	1.08	75.68	18.83	4.42
ZnO powder	22.79	1.08	75.59	18.76	4.43

4. References

[S1] Cao, J.; Lv, X.; Zhang, P.; Chuong, T. T.; Wu, B.; Feng, X.; Shan, C.; Liu, J.; Tang, Y., Plant Sunscreen and Co(II)/(III) Porphyrins for UV-Resistant and Thermally Stable Perovskite Solar Cells: From Natural to Artificial. *Adv. Mater.* **2018**, *30*, 1800568.