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COMMUNICATION

Supporting Information

Defects Passivation of Perovskite Film by $ZnIn_2S_4$ Nanosheets for Efficient and Stable Perovskite Solar Cells

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Experimental Section

Materials

All the commercial materials were used as received without further purification. $Zn(NO_3)_2\cdot 6H_2O$, $In(NO_3)_3\cdot 4.5H_2O$, L-cysteine, titanium diisopropoxide bis(acetylacetonate) and PbI_2 (99.9985%) were purchased from Alfa Aesar. TiO_2 paste (Dyesol, 30NRD), $HC(NH_2)_2I$ (FAI) and CH_3NH_3I (MAI), FK209-cobalt(III)-TFSI, Li-TFSI, CsI, $PbBr_2$, Spiro-OMeTAD were purchased from Xi'an Polymer Light Technology Corp. Chlorobenzene (CB), titanium diisopropoxide bis(acetylacetonate), 1-Butanol, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 4-tert-butylpyridine were purchased from Sigma-Aldrich. Glass substrates with a transparent F-SnO_2 (FTO) (14 Ω/square) layer were purchased from Wuhan Jingge Solar Technology Co., Ltd.

The preparation of $ZnIn_2S_4$ nanosheets

$ZnIn_2S_4$ nanosheets were synthesized by using a hydrothermal method. Firstly, 0.25 mmol of zinc nitrate ($Zn(NO_3)_2\cdot 6H_2O$, Alfa-Aesar), 0.5 mmol of indium nitrate ($In(NO_3)_3\cdot 4.5H_2O$, Alfa-Aesar) and 2 mmol of L-cysteine (L-cys, Alfa-Aesar) were added to 30 mL of distilled water, and the mixture was stirred magnetically until completely dissolved. Then, the solution was transferred to a 50 mL autoclave, kept it at 200 ^oC for 18 h. The product was washed three times by deionized water and ethanol each.

The preparation of $ZnIn_2S_4$ anti-solvent

The 2 mg of $ZnIn_2S_4$ nanosheets were dissolved in 2 mL of DMF, the mixture was dispersed by ultrasound with 6 h, after filtered, the DMF solution of ZIS (ZIS-DMF) was obtained. The solution was dispersed in CB with volume ratios of 0.25%, 0.5%, 1% and 2 %, and the different concentrations of anti-solvent (ZIS-DMF/CB) are 0.005 $mg\cdot mL^{-1}$, 0.01 $mg\cdot mL^{-1}$, 0.02 $mg\cdot mL^{-1}$ and 0.04 $mg\cdot mL^{-1}$, respectively.

Preparation of FTO substrate and compact layer

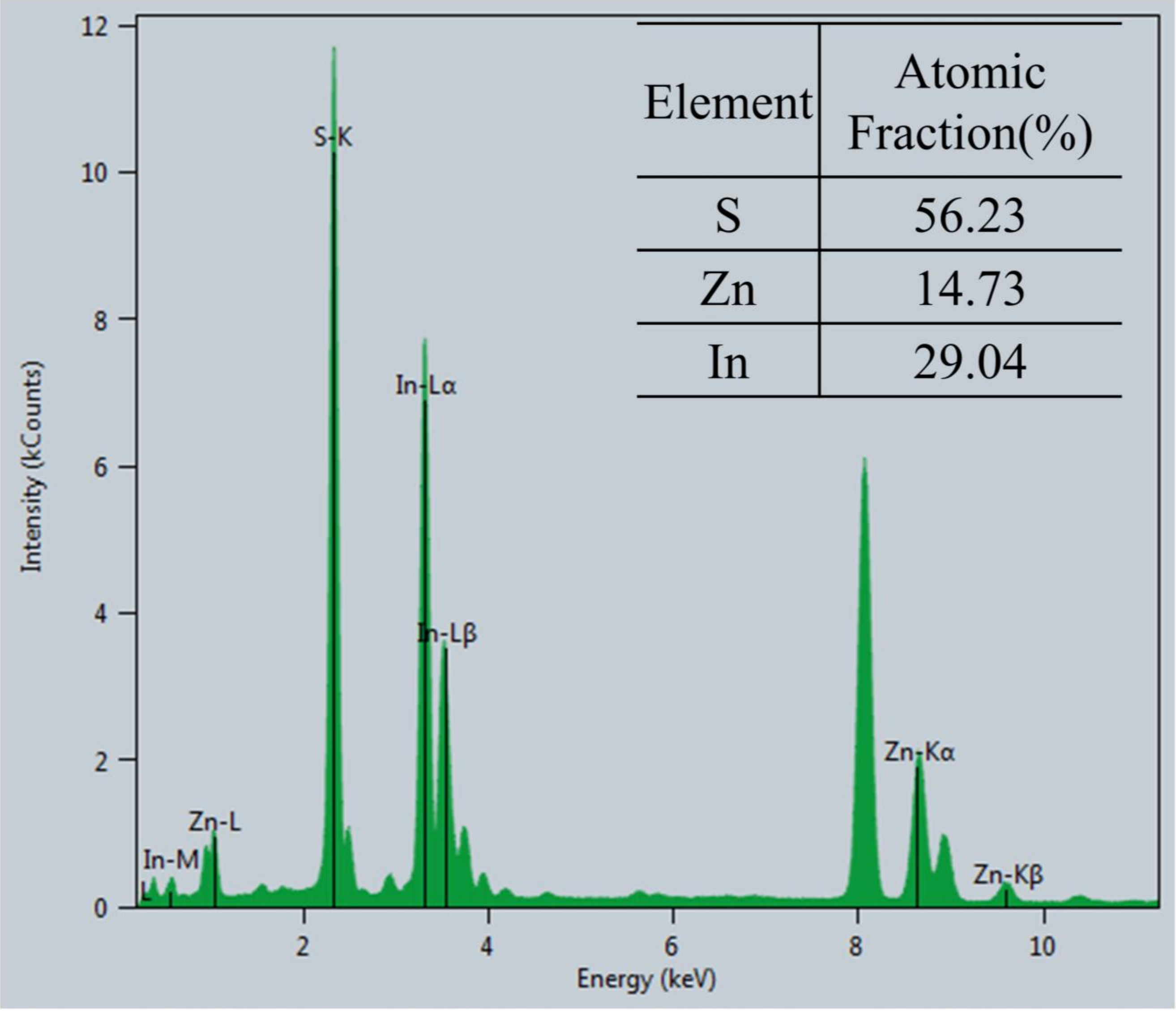
Firstly, fluorine doped tin oxide coated glass (FTO) was patterned by etching with 2 M HCl and Zn powder. The patterned FTO was cleaned by ultra-sonication and rinsed with detergent, deionized water, ethanol, acetone and isopropanol for 30 min, respectively. Then, the FTO was dried by clean air and treated with a UV-ozone machine for 15 min. The TiO_2 compact layer (c-TiO_2) was prepared by a spin-coating precursor solution of 0.15 M titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol) in 1-butanol (99.9%). After spin-coating, the substrates were annealed at 150 ^oC for 15 min and then left to cool down to room temperature. The mesoporous TiO_2 (m-TiO_2) layer was deposited by spin coating for 30 s at 2000 rpm. Finally, the substrate was immediately dried at 150 ^oC for 30 min and sintered again at 550 ^oC for 30 min.

The fabrication of PSC devices

The perovskite film was deposited by using a single-step deposition method from the precursor solution, which was prepared in nitrogen atmosphere and the perovskite precursor solution is composed of 1.38 M of FAI, 0.24 M of MAI, 0.15 M of CsI, 1.49 M of PbI_2, and 0.26 M of $PbBr_2$ in a volume ratio of 4:1 for DMF/DMSO in anhydrous state. The perovskite solution was spin coated in a two-step program at 1000 and 4000 rpm, respectively. CB as anti-solvent (125 μL) was dropped on the spinning substrate, and followed by annealing at 120 ^oC for 25 min. The Spiro-OMeTAD chlorobenzene solution (60 mM) was mixed with 4-tertbutylpyridine (28.8 μL), lithium bis(trifluoromethylsulfonyl) imide (17.5 μL, 520 $mg\cdot mL^{-1}$ in acetonitrile), and cobalt bis(trifluoromethylsulfonyl) imide (29.0 μL, 300 $mg\cdot mL^{-1}$ in acetonitrile) was spincoated (3000 rpm for 20 s) on top as the hole transporting layer. At the end, the gold layer was added by thermal evaporation to form a back electrode.

Characterization

The X-ray powder diffraction (XRD) patterns of sample were measured by Rigaku Ultima IV with Cu Kα radiation (1.5418 Å). The scanning electron microscope (SEM) and Energy Dispersive Spectrometer (EDS) measurement were observed by field emission scanning electron microscope (FESEM, Hitachi S4800). The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern images were recorded on a FEI Talos F200S G2 instrument. The photovoltaic performance of PSCs was recorded using a source meter (Keithley 2400), a PEC-L11 1.5 solar simulator with a 1000 W Xe lamp and an AM 1.5 filter (Peccell) was applied as the light source (100 $mW\cdot cm^{-2}$). The J-V curves were measured from both forward and reverse scan directions, and the scan rate was 20 $mV\cdot s^{-1}$, a mask with a window of 0.06 cm^2 was utilized to define the active area of the devices. The Incident photon-to-electron conversion efficiency (IPCE) spectrum was recorded using an instrument of PEC-S20 (Peccell). Atomic force microscopy (AFM) measurements were obtained using a SPA-300 AFM (Bruker) and scanning range of the AFM images was 5 μm×5 μm. The UV-vis transmission spectra were measureed with a UV-vis spectrometer (Shimadzu UV-2450). The steady-state photoluminescence (PL) and time-resolved photoluminescence spectroscopy (TRPL) of perovskite films were performed using Edinburgh FLS 980 instrument with the excitation at 405 nm. Electrochemical Impedance Spectroscopy (EIS) spectrum was measured by an electrochemical workstation (IM6, Zahner) and fitting use software called Z-view. XPS measurements were performed on a Thermo ESCALAB 250Xi instrument with a monochromatized Al Kα X-ray source in vacuum.



Element	Atomic Fraction(%)
S	56.23
Zn	14.73
In	29.04

Figure S1. Energy-Dispersive X-ray spectroscopy (EDX) spectrum of ZIS.

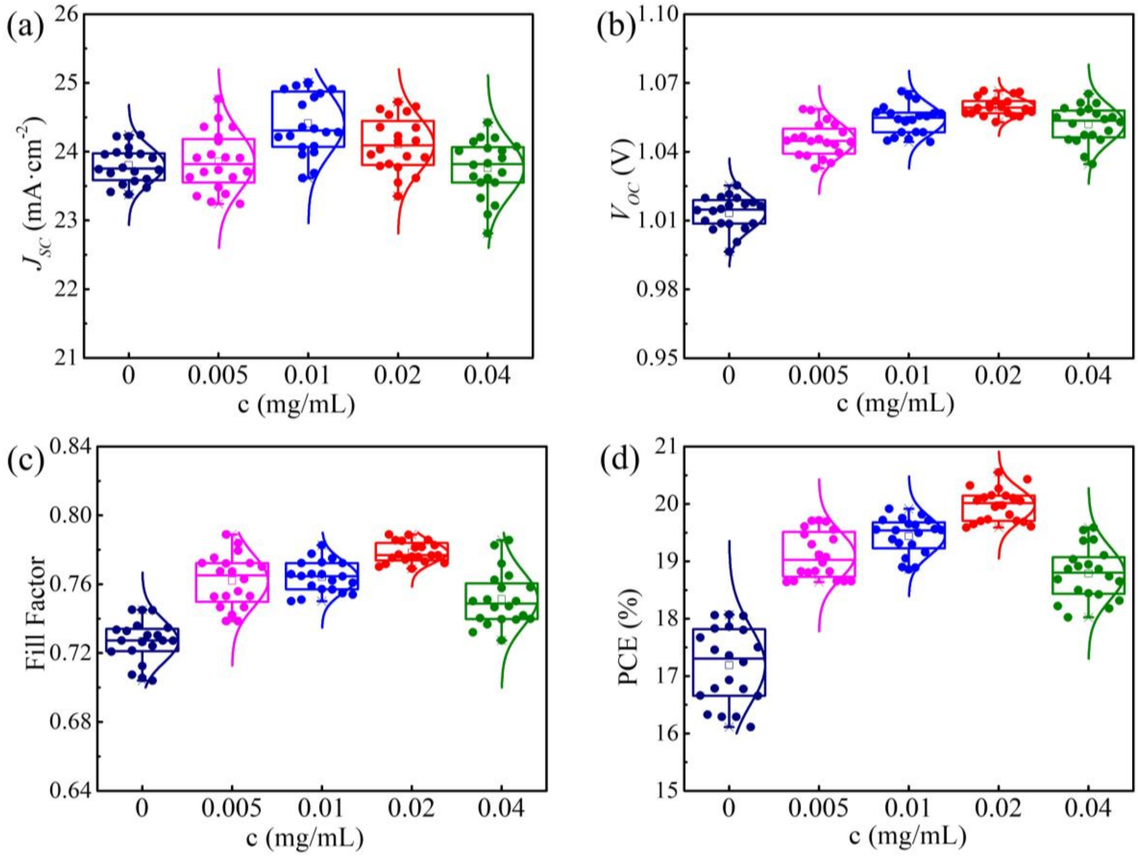


Figure S2. Box diagrams summarizing the statistics of (a) J_{SC}, (b) V_{OC}, (c) FF, and (d) PCE of twenty devices with different concentrations of ZIS modification.

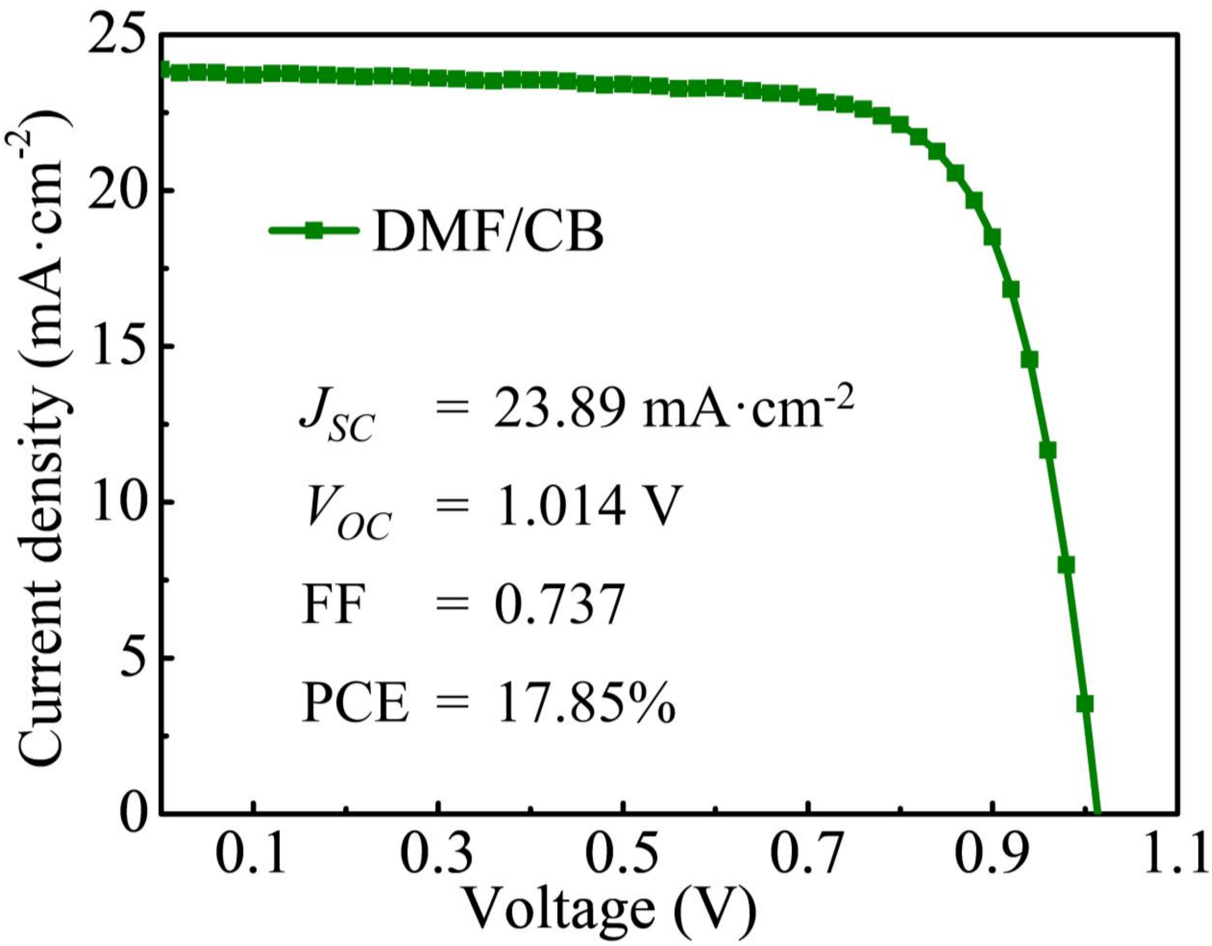


Figure S3. The *J*-*V* curve of the champion device with an anti-solvent of DMF/CB.

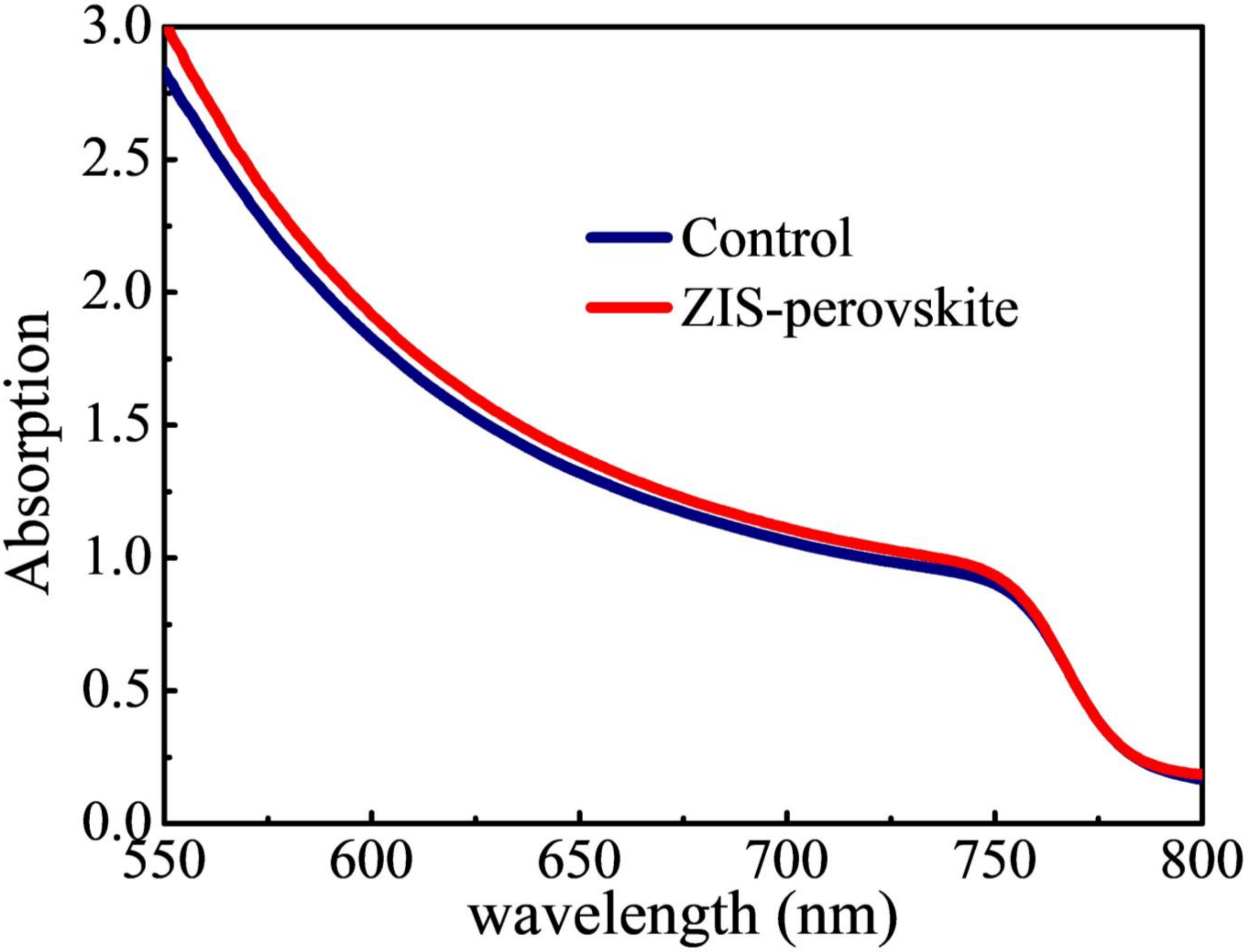


Figure S4. UV-vis absorption spectra of the perovskite films with and without ZIS modification.

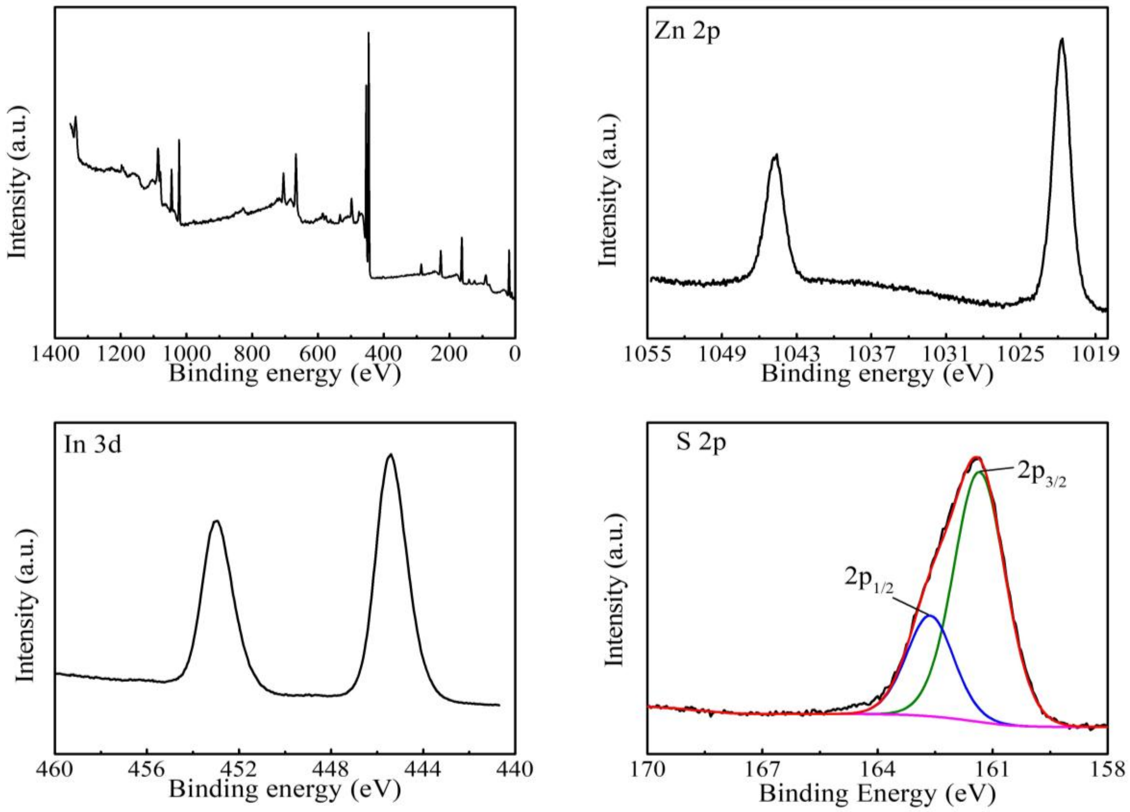


Figure S5. (a) XPS survey spectra of ZIS and high-resolution spectra of (b) Zn 2p, (c) In 3d, and (d) S 2p.

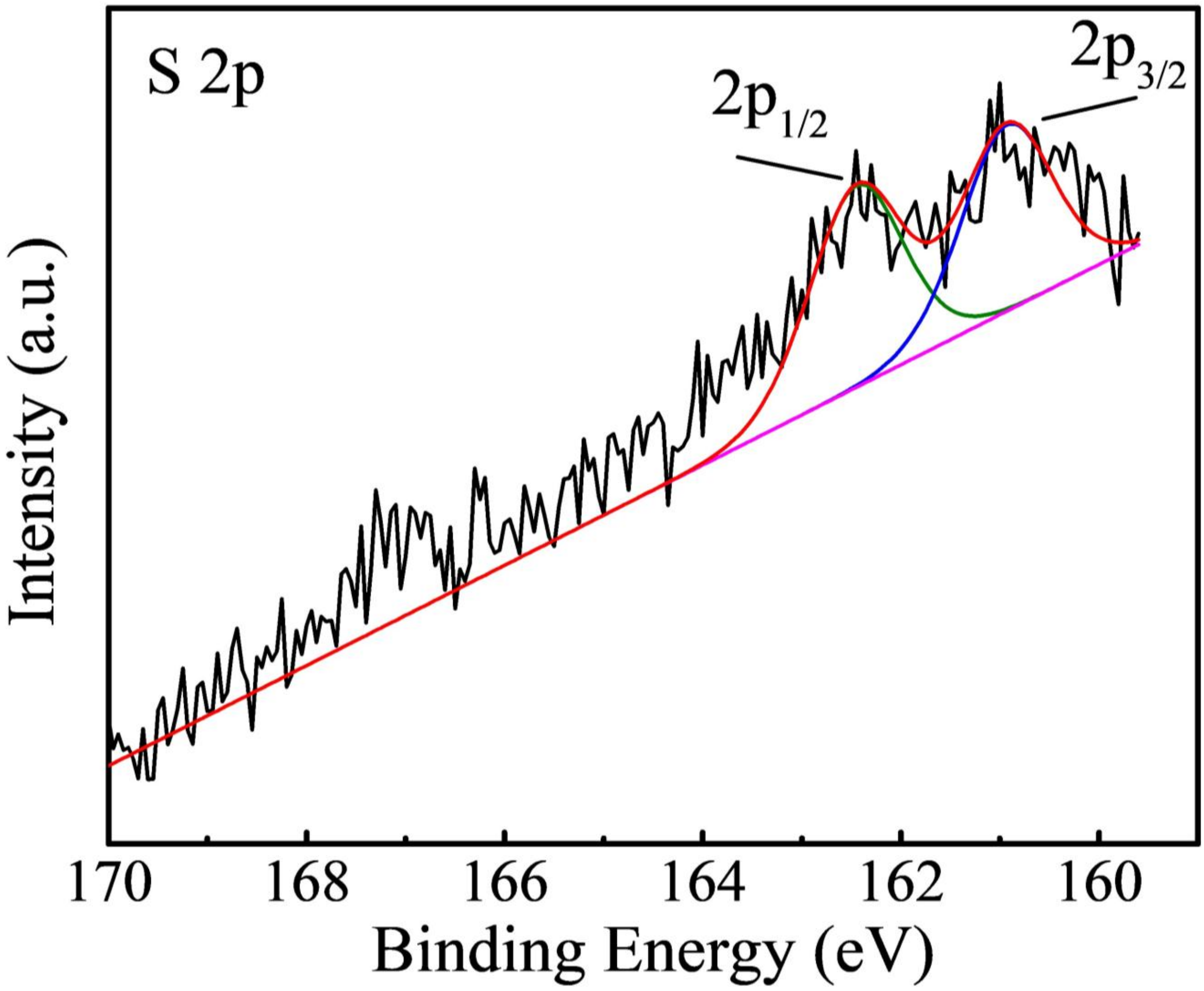


Figure S6. XPS spectra pf the S 2p spectrum of perovskite film with ZIS modification.

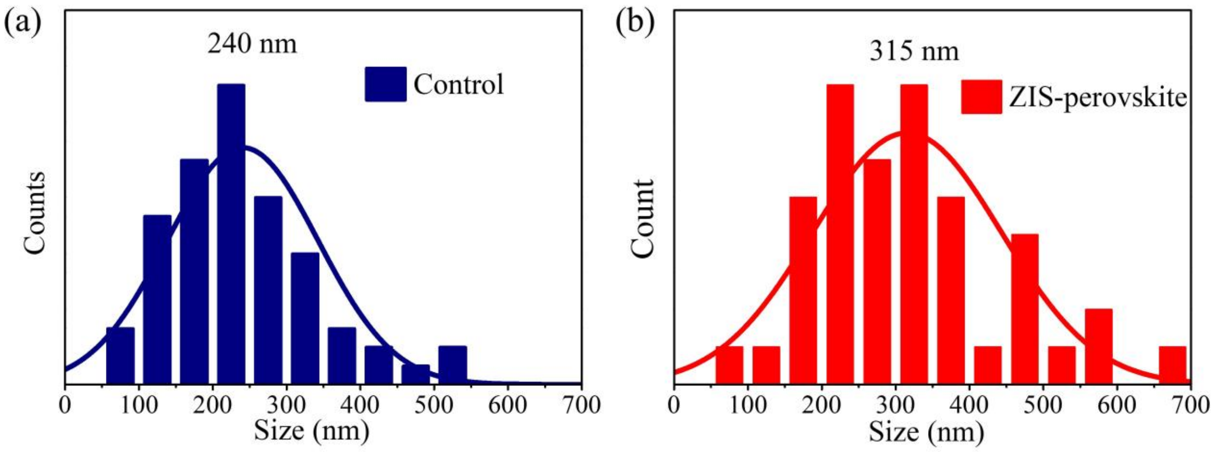


Figure S7. The statistical distribution histograms of perovskite grain sizes without and with ZIS modification.

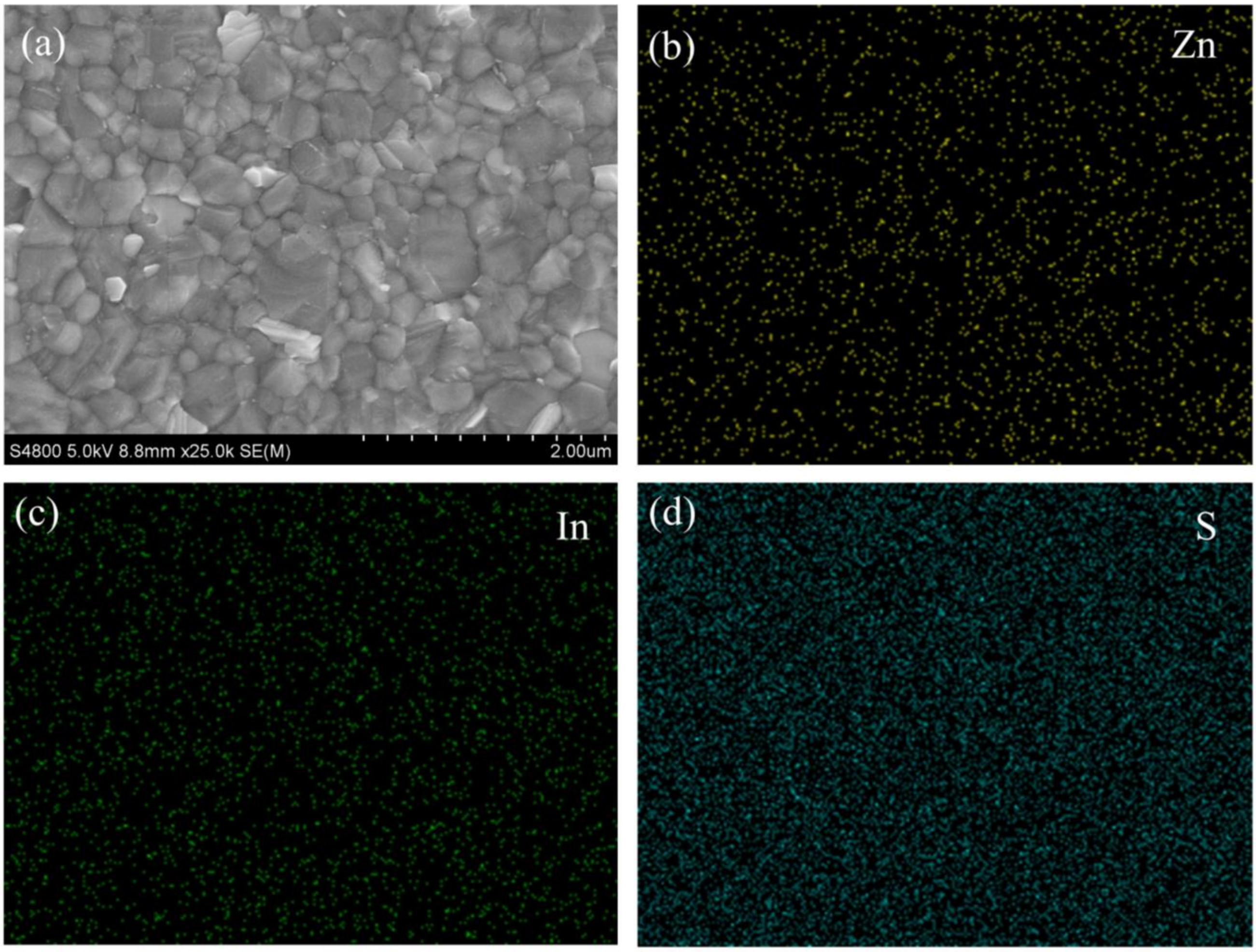


Figure S8. (a) The top view SEM image, and (b-d) energy dispersive spectroscopy (EDS) elemental mapping images of perovskite films decorated by ZIS (the yellow, green and blue balls represent Zn, In and S atoms, respectively.).

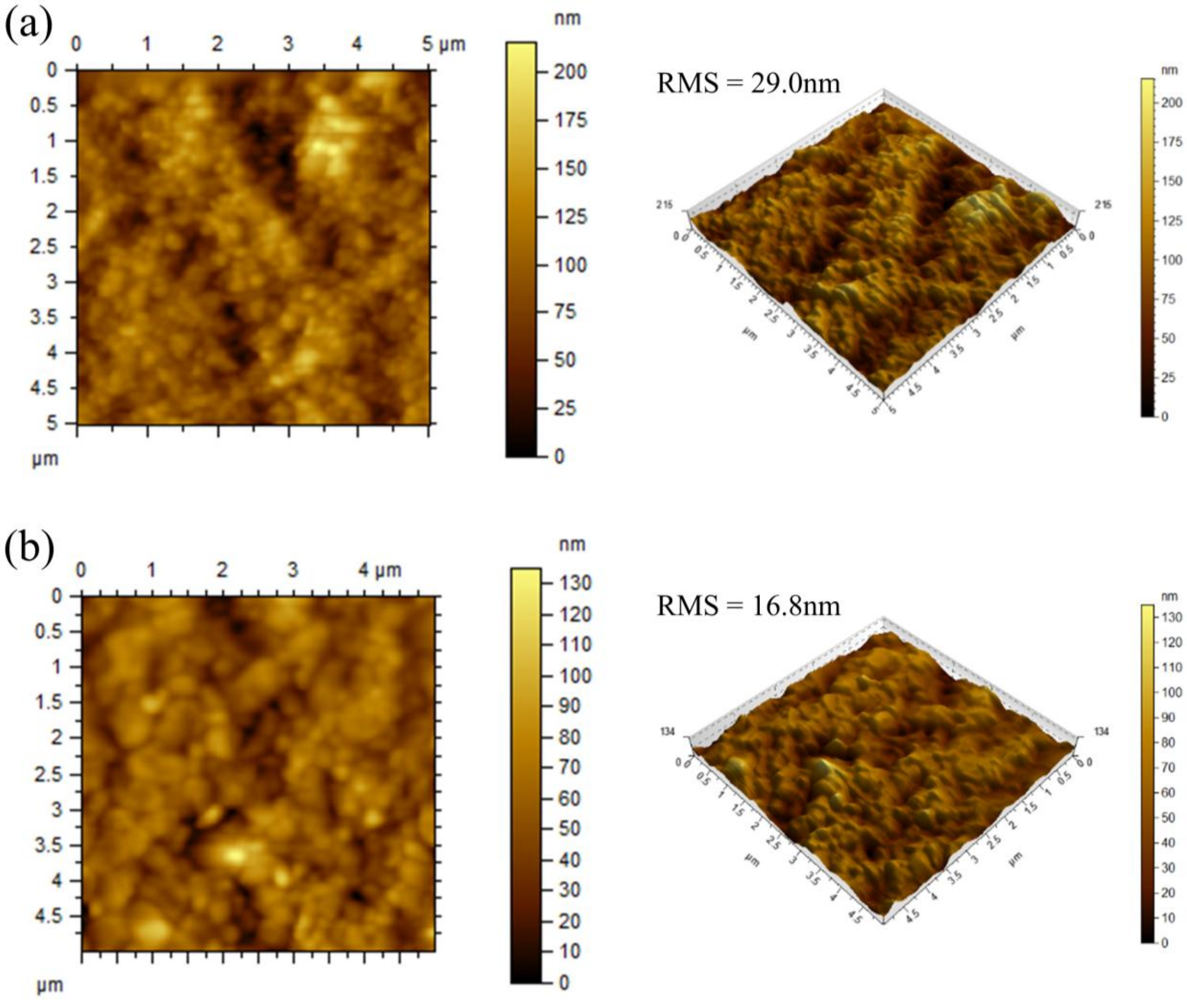


Figure S9. AFM images of perovskite films without (a) and with (b) ZIS modification.

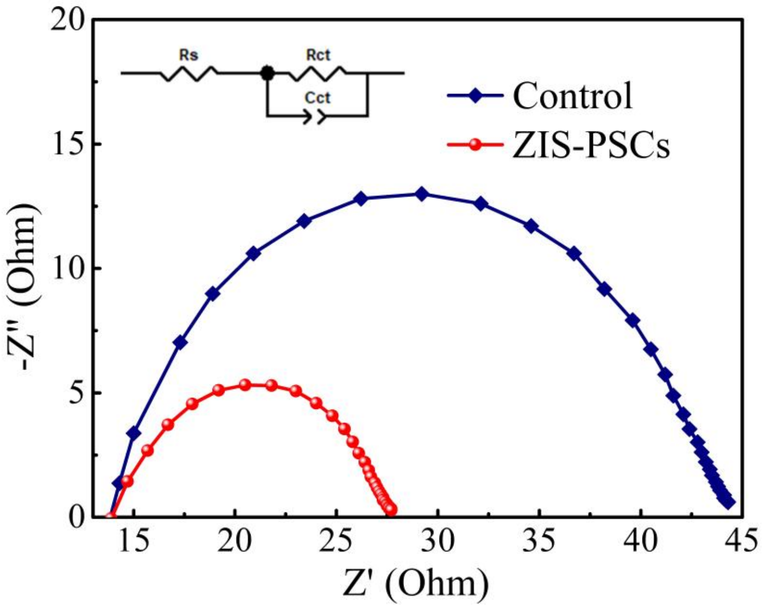


Figure S10. Nyquist plots of different PSCs devices under AM 1.5 G illumination condition.

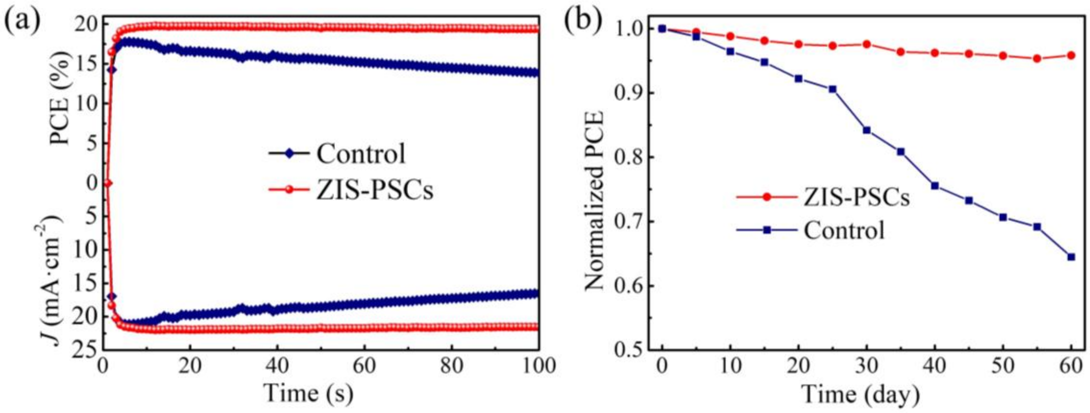


Figure S11. (a) Steady-state PCE measured under the maximum power point tracking for 100 s of the champion device, (b) long-term stability measurements of the devices without and with ZIS modification under room temperature and 15±5% RH in air for 60 days.

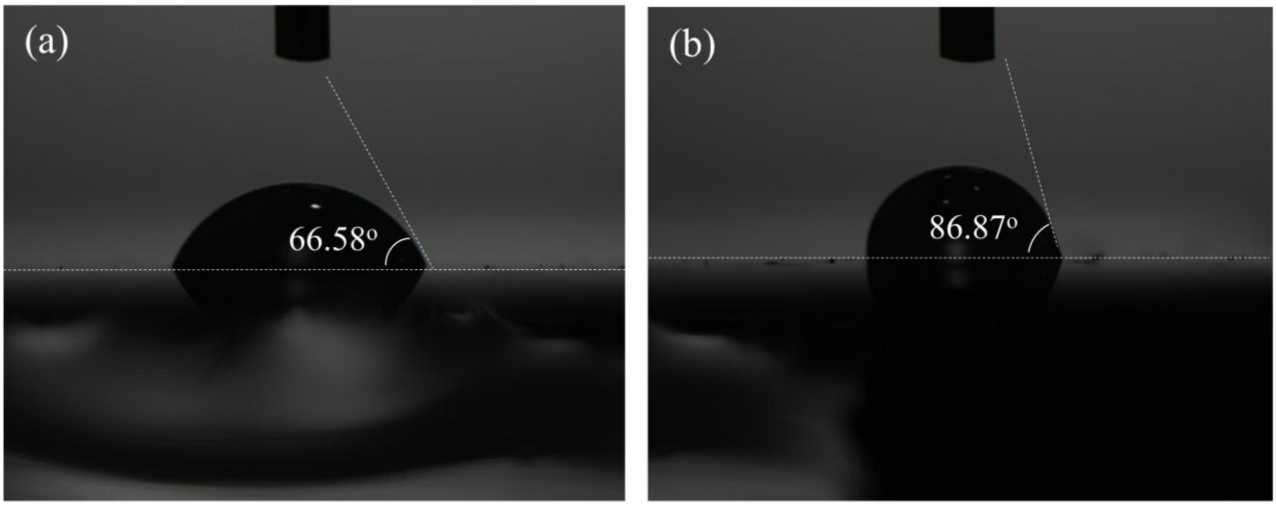


Figure S12. Contact angles of water and films: (a) control, and (b) ZIS-perovskite

Table S1. Photovoltaic parameters of the champion devices without and with ZIS modification.

Devices	**J_{SC} (mA·cm^{-2})**	**V_{OC} (V)**	**Fill Factor**	**PCE (%)**
Control	23.96	1.017	0.745	18.16
ZIS-PSCs	24.42	1.068	0.788	20.55

Table S2. Fitted data for TRPL decay based on the structure of the glass/perovskite without and with ZIS modification.

Devices	**τ_1 (ns)**	**A_1(%)**	**τ_2 (ns)**	**A_2(%)**	**τ_{ave} (ns)**
perovskite	44	5.81	327	94.19	325
ZIS-perovskite	149	2.49	759	97.51	756

Table S3. EIS data of different PSCs based on different condition.

Test	**Dark**		**Light**	
R	**R_s (Ω)**	**R_{rec} (Ω)**	**R_s (Ω)**	**R_{ct} (Ω)**
PSCs	12.7	35987	15.22	26.92
ZIS-PSCs	9.5	52948	15.19	11.34