

Experimental Procedures

Materials and Reagents

All materials and reagents such as PbBr_2 (Aladdin; >99.0%), CsBr (Aladdin; > 99.9%) were purchased from Aladdin and used without further purification. TiO_2 colloid, NiO_x , SnS and ZnS nanoparticles were synthesized according to previous reports.¹⁻³

Synthesis of the TiO_2 Colloid: Under vigorous agitation at 25 °C, 10 mL of titanium tetrabutolate was dropwise into 100 mL of deionized water, which was further agitated for 30 min. After filtration, 10 mL of acetic acid and 0.8 mL of nitric acid were added into these filter powders. After agitating for 15 min at 80 °C, 160 mL of deionized water was added. When the reactant solution became semi-transparency, the obtained solution was undergone hydrothermal treatment at 200 °C for 12 h. Subsequently, 0.4 g of commercial P25 was added and sonicated for 30 min and then heated at 200 °C for another 12 h. The resultant colloid was finally mixed with 0.8 g of poly(ethylene glycol) ($M_w = 20,000$) and 1 mL of OP emulsifier and then concentrated to 40 mL at 80 °C.

Synthesis of the NiO_x Nanoparticles: 0.25 mol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dropwise into 50 mL of deionized water under continuous magnetic stirring to obtain a dark green solution. Subsequently, the pH of the solution was adjusted to 10 by dropwise adding 1.0 M NaOH aqueous solution. After agitating for 15 min, the green filter colloidal precipitation was rinsed with deionized water twice, and dried at 80 °C for 6 h. Next, these precipitations were grinded to finer powder using an agate mortar and then calcined at 270 °C for 2 h to obtain a black powder. Finally, these black powders were dispersed into chlorobenzene to obtain 0.5 M solution.

Synthesis of the SnS and ZnS Nanoparticles: 76 mg of SnCl_2 was added to 20 mL of ethylene glycol under vigorous agitation. Subsequently, 4 mL of triethanolamine was slowly dripped into the above solution. The SnS nanoparticles were rinsed by ultrasonication-centrifugation process continuously in ethanol three times. Afterward, the SnS nanoparticles were uniformly dispersed in tertiary butanol by ultrasonication for 5 min. The ZnS nanoparticles were prepared according to similar procedures without triethanolamine. And the zinc source changed to $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$.

Preparation of TiO_2 Photoanodes

FTO glass was etched by Zn powders and HCl for a slender strip pattern, and rinsed with ethanol and deionized water. A layer of compact TiO_2 (*c*- TiO_2) was deposited onto FTO glass by spin-coating an ethanol solution of 0.5 M titanium isopropoxide and 0.5 M diethanol amine at 7000 rpm for 30 s and annealing in air at 500 °C for 2 h. The mesoscopic TiO_2 (*m*- TiO_2) layer was then deposited by spin-coating the TiO_2 colloid at 2000 rpm for 30 s and annealed in air at 450 °C for 30 min. Then the substrate was immersed in an aqueous solution of 0.04 M TiCl_4 at 70 °C for 30 min, rinsed with deionized water and anhydrous ethanol, and finally annealed at 450 °C for another 30 min.

Assembly of Solar Cells⁴

A dimethyl formamide (DMF) solution of 1.0 M PbBr_2 was spin-coated onto the pre-heated *m*- TiO_2 layer at 2000 rpm for 30 s, followed by drying at 80 °C for 30 min. Subsequently, a mixture from 3 mol% TbCl_3 and PbBr_2 in DMF was spin-coated onto the pre-heated *m*- TiO_2 layer at 2000 rpm for 30 s and drying at 80 °C for 30 min. Then, 90 μL of 0.07 M CsBr methanol solution was coated onto FTO/*c*- TiO_2 /*m*- TiO_2 / PbBr_2 or FTO/*c*- TiO_2 /*m*- TiO_2 / $\text{Pb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ at 2000 rpm for 30 s, following heated to 250 °C for 5 min on a hotplate. This step was repeatedly performed for four times to form a dense $\text{Pb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ layer. The CsPbBr_3 layer was also prepared according to similar procedures without doping TbCl_3 .

The solution of $\text{SnS}:\text{ZnS}$ in tert-butyl alcohol was spin-coated at perovskite film at a speed of 2000 rpm for 30 s, followed by drying at 100 °C for 5 min to fabricate compact $\text{SnS}:\text{ZnS}$ layer. A NiO_x film was prepared onto the above $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3/\text{SnS}:\text{ZnS}$ or CsPbBr_3 film at 2000 rpm for 30 s. Finally, a carbon back-electrode with an average area of 0.09 cm^2 was used to cover PSC device by coating conductive carbon ink onto FTO/*c*- TiO_2 /*m*- TiO_2 / $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3/\text{SnS}:\text{ZnS}/\text{NiO}_x$ structure and heated at 70 °C for 60 min.

Photovoltaic Measurements and Characterizations

The photocurrent density-voltage (*J*-*V*) curves of solar cells were recorded on a CHI660E electrochemical workstation under irradiation of simulated solar light intensity controlled at AM 1.5 (100 mW cm^{-2}). UV-vis spectra were obtained with a MATASH ultraviolet-visible spectrometer. The morphologies of the films and device were characterized by a field-emission scanning electron microscopy (FESEM, Japan Hitachi field emission S4800). The crystal structures of the halides were assessed by an X-ray diffraction (PHILIPSPW1800 diffractometer with Cu-K α radiation). The steady-state photoluminescence was obtained at room temperature by FLS920 all functional fluorescence spectrometer.

The incident-photo-to-current conversion efficiency (IPCE) spectra were characterized by a power source (Newport 300 W xenon lamp, 66920) with a monochromator (Newport Cornerstone 260) in the 300-800 nm wavelength range at room temperature. The time-resolved PL measurement was performed using time-resolved fluorescence (Horiba JobinYvon, FL). Main Text Paragraph.

Supporting Figures

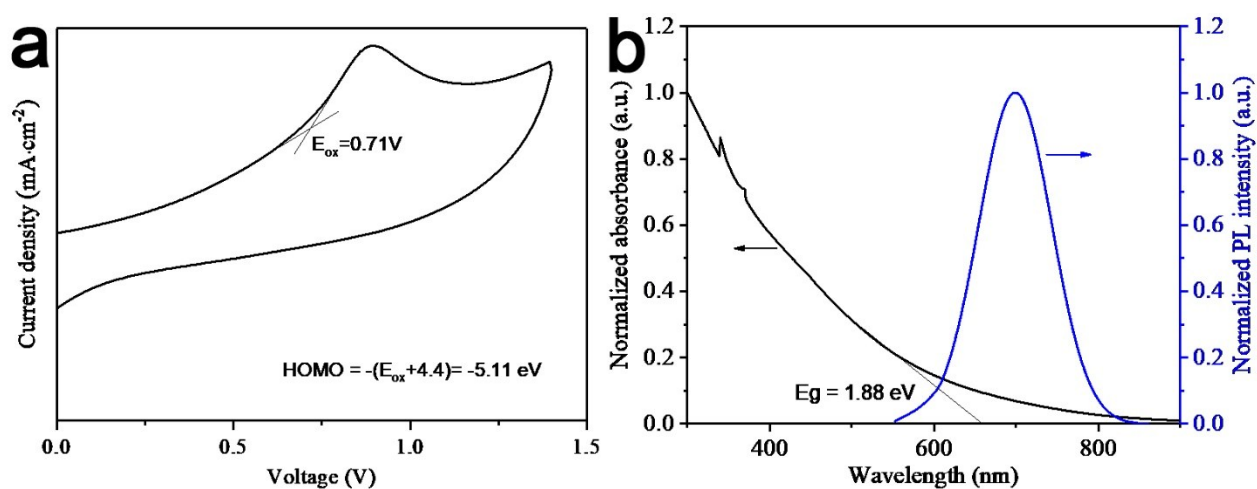


Figure S1. (a) CV curve of SnS on platinum electrode. (b) UV-vis absorption spectra and PL emission spectra of SnS nanoparticles.

Cyclic voltammetry (CV) was carried out to estimate the HOMO energy levels of SnS according to previous report.⁵ CV was carried out on a standard three-electrodes system: the working electrode coated with SnS; the counter electrode; and the Ag/AgCl reference electrode. The supporting electrolyte was constituted of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6, Aldrich) acetonitrile solution. The scanning speed was controlled at 0.01 V s⁻¹. Finally, the E_{ox} was determined to be 0.71 V, and corresponding HOMO levels were -5.11 eV. LUMO levels was calculated to be -3.23 eV according to $CB = VB + BG$.

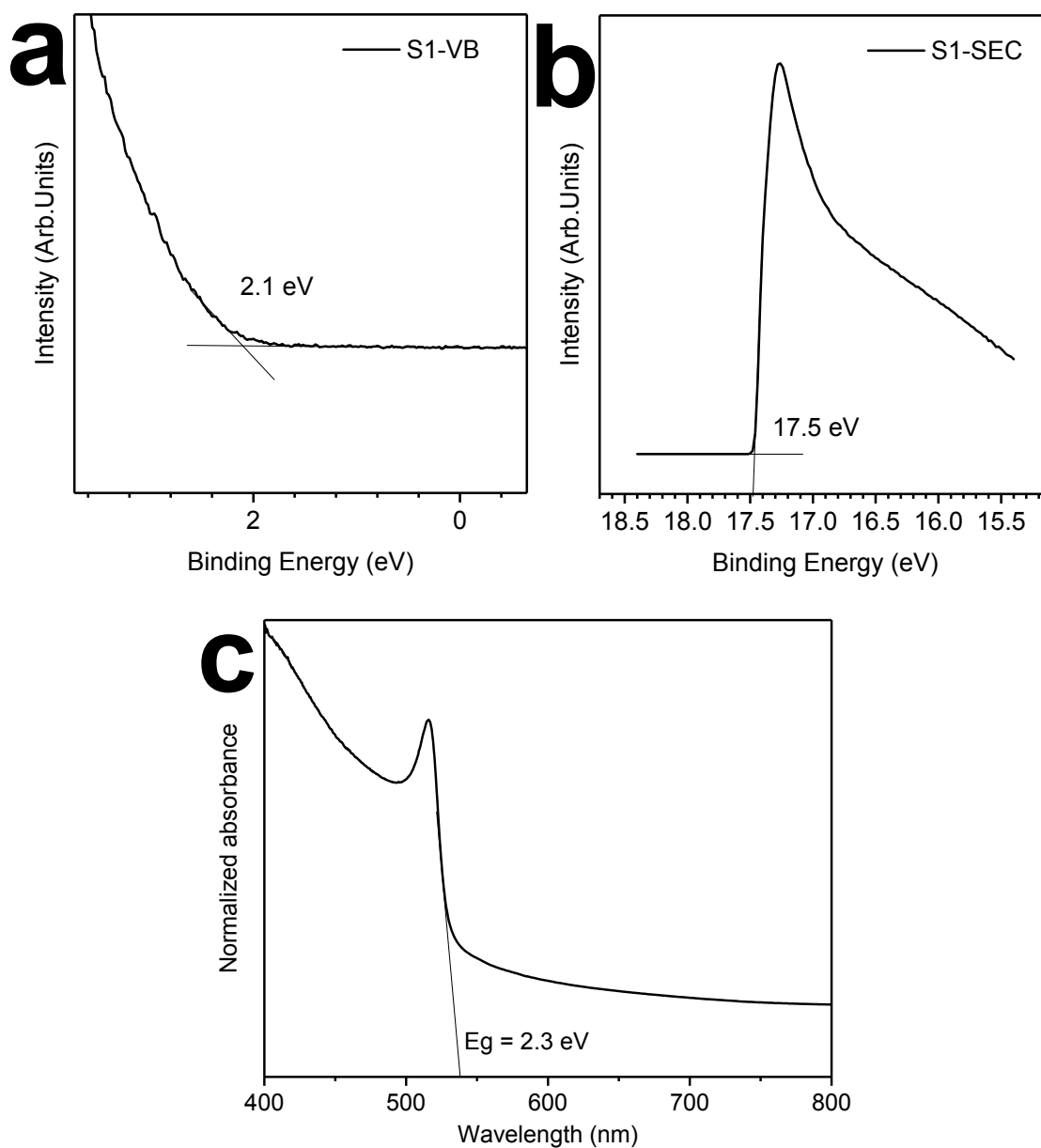


Figure S2. (a) Valence band and (b) secondary electron cutoff UPS spectrum of $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ film. (c) UV-vis absorption spectra of $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ film.

The spectrometer work function of the UPS instrument used in this work is 3.7 eV. The valence band maximum (VBM) of $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ was determined by taking a linear extrapolation and was estimated to be 5.8 eV, as shown in Figure S2. Besides, Figures S2c indicate the optical bandgap of $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ is 2.3 eV. Thus, the conduction band minimum (CBM) of $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ film was calculated to be 3.5 eV.

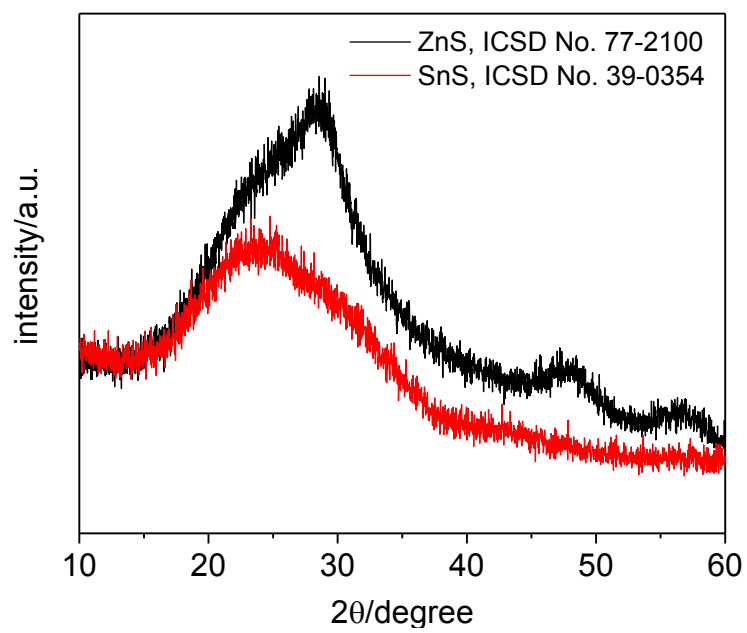


Figure S3. XRD patterns for SnS and ZnS nanoparticles.

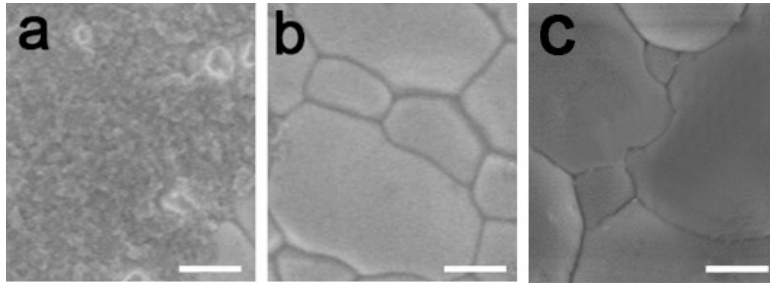


Figure S4. SEM photographs of $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ films (a) with or (b) without SnS:ZnS PAL. (c) SEM image of the $\text{CsPb}_{0.97}\text{Tb}_{0.03}\text{Br}_3$ film treated by tert-butyl alcohol disposed. The scale label is 1 μm .

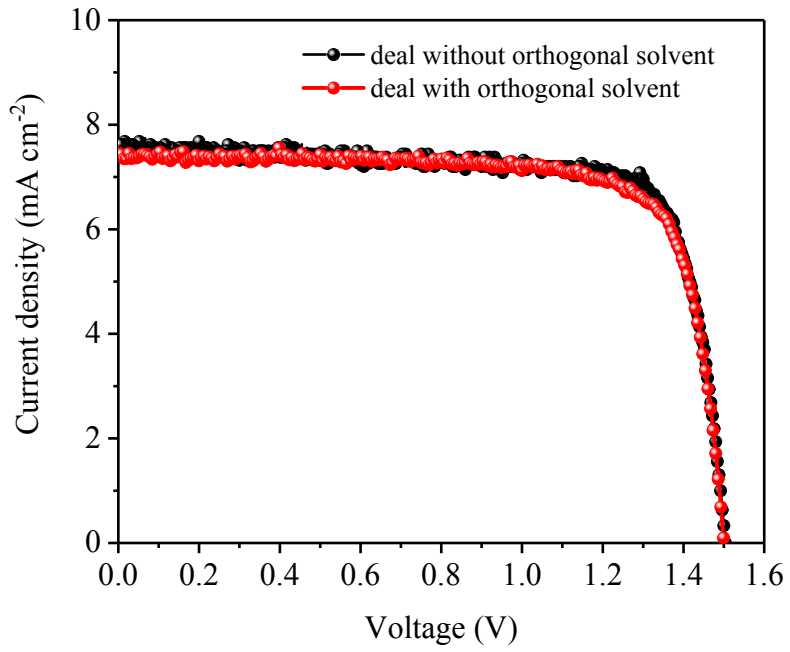


Figure S5. *J-V* curves of CsPb_{0.97}Tb_{0.03}Br₃ based PSCs dealt with or without orthogonal solvent (tert-butyl alcohol).

As shown in SEM images of perovskite film deal (**Figure S4b**) without or (**Figure S4c**) with tert-butyl alcohol and corresponding *J-V* curves (**Figure S5**). It indicates that orthogonal solvent (tert-butyl alcohol) does not have negative effect on the morphology of perovskite and corresponding photovoltaic performances.

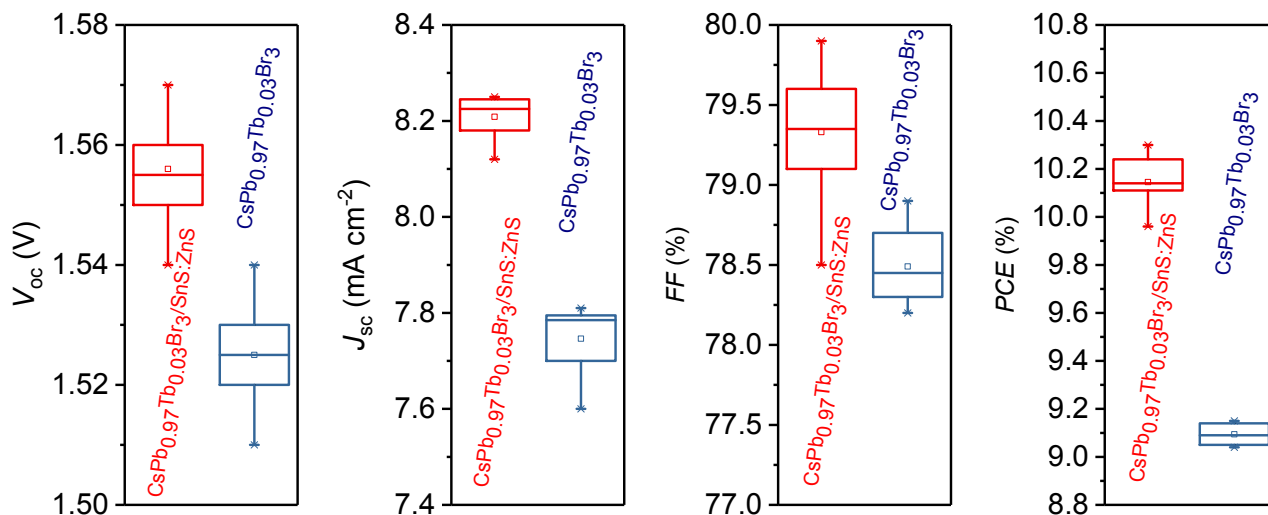


Figure S6. The random photovoltaic parameters for various PSCs.

References

1. J. H. Han, X. W. Yin, H. Nan, Y. Zhou, Z. B. Yao, J. B. Li, D. Oron, H. Lin, *Small* 2017, 13, 1700953.
2. Y. Duan, Q. Tang, Z. Chen, B. He, H. Chen, *J. Mater. Chem. A* 2014, 2, 12459-12465.
3. Q. Q. He, K. Yao, X. F. Wang, X. F. Xia, S. F. Leng, F. Li, *ACS Appl. Mater. Interfaces* 2017, 9, 41887-41897.
4. J. L. Duan, Y. Y. Zhao, B. L. He and Q. W. Tang, *Angew. Chem. Int. Edit.* 2018, 57, 3787-3791.
5. V. Gupta, N. Chaudhary, R. Srivastava, G. D. Sharma, R. Bhardwaj, S. Chand, *J. Am. Chem. Soc.* 2011, 133, 9960-9963.