Electronic Supplementary Material

Efficient flexible perovskite solar cells and modules using a stable SnO_2-nanocrystal isopropanol dispersion

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Experimental section

Materials: Anhydrous $SnCl_4$ was purchased from Aladdin. N-Methylpyrrolidone (NMP, 99.5%), 2-propanol (IPA 99.5%), N,N-Dimethylformamide (DMF, 99.8%), 4-tert-Butylpydrdine (98%), lithium bis (trifluoromethanesulphonyl) imide (Li-TFSI, 99.95%), chlorobenzene (anhydrous, 99.8%), and cesium iodide (99.999%) were purchased from Sigma-Aldrich. Formamidinium iodide (FAI, 99.99%) and lead chloride ($PbCl_2$,99.99%), were purchased from Xi'an Polymer Light Co., Ltd. Lead iodide (PbI_2,99.999%) and dodecyl ammonium bromide (DABr, 99%) were purchased from TCI. 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD, 99.9%) was purchased from Vizuchem Co., Ltd. The PEN/ITO was purchased from Opvtech New Energy Co. Ltd.

Synthesis of SnO_2 nanocrystals: In order to synthesize SnO_2 nanocrystals, anhydrous $SnCl_4$ was used as a tin source by a low-temperature hydrothermal method. (Ⅰ) Firstly, anhydrous $SnCl_4$ was diluted to 0.15 M in an ice bath process and reacted at 90 ℃ for 1 h to obtain a translucent colloidal solution. (Ⅱ) The obtained solution was successively added to a mixed solution of ether and isopropyl alcohol (v/v=1:1) to form a white suspension. (Ⅲ) After centrifugation at 3000 rpm for 5 min, white precipitates can be obtained at the bottom of the centrifuge tube, (Ⅳ) the precipitate was repeatedly washed with ether for three times, and then dispersed in an isopropanol solvent to obtain the SnO_2-nanocrystal isopropanol dispersion with a concentration of about 10 mg mL^{-1}. For the synthesis of glycerol-optimized SnO_2 nanocrystals, glycerol with a molar ratio of 5% was added into 0.15 M $SnCl_4$ aqueous solution, and the subsequent reaction and precipitation washing were consistent with the above.

Precursor solution preparation: The $FA_{0.83}Cs_{0.17}PbI_3$ perovskite solution was prepared by mixing 1 mmol PbI_2, 0.83 mmol FAI, 0.17 mmol CsI, 1 mmol NMP in 500 μL DMF, and 0.1 mmol $PbCl_2$ was added as the additive. The Spiro-OMeTAD solution was prepared by dissolving 91.4 mg Spiro-OMeTAD, 21 μL Li-TFSI (520 mg mL^{-1} in acetonitrile), 11.5 μL FK209-Co (III) (300 mg mL^{-1} in acetonitrile) and 35.6 μL 4-tertbutylpyridine in 1 mL chlorobenzene.

Perovskite solar cells and mini-modules fabrication: The patterned PEN/ITO substrates were obtained by chemical etching, then by ultrasonically washing with detergent, deionized water and ethanol for 1 min, respectively. After treatment by plasma for 5 min, the SnO_2 film was deposited on the PEN/ITO substrates by spin-coating the as-prepared SnO_2-nanocrystal isopropanol dispersion at 3000 rpm for 30 s, followed by annealing at 130 ℃ for 30 min. All the PEN/ITO-SnO_2 substrates were treated with UVO for 15 min before use. The perovskite precursor solution was spun on the as-prepared SnO_2 flexible substrates at 5000 rpm for 1 min and pre-annealed at 70 °C for 5 minutes in a nitrogen glove box. Then the perovskite film was annealed at 150 ℃ for 10 min under ~40% RH ambient environment to achieve dense film. After cooling down, a 15 mM DABr/IPA solution was dynamically spun on the perovskite films and further annealed at 100 °C for 5 minutes. Then the Spiro-OMeTAD solution was spin-coated as the hole transport layer and an 80 nm gold layer was vacuum deposited as the electrode. The fabrication procedures of 5 cm × 5 cm flexible solar mini-modules are similar to that of small cells, except for the scribing process to form the series connection of modules. The cross-section diagram of the flexible PSMs is shown in Fig. S10 in the ESM. P1, P2, and P3 are scribed without the use of the laser machine (Fig. S10(a) in the ESM.). First, the 5 cm × 5 cm plastic substrate is patterned by chemical etching with zinc powder and hydrochloric acid (blue line, P1=1 mm). To realize the effective connection of P2, we pre-evaporated a layer of Au (yellow line, P2=1.5 mm) at P2, and then deposited SnO_2, perovskite, Spiro-OMeTAD and DABr passivation layers in turn, which are similar to that of small cells. Before evaporation of the counter electrode, a tape with the same width as P2 is placed on the function films and gently pressed to uncover. The deposited functional layer can be peeled off together with the buried Au film to expose the ITO electrode, which can form an effective connection with the counter electrode. Then, a tape with a width of 0.5

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mm is stuck at P3 (pink line, P3=0.5 mm) before the Au counter electrode is evaporated. Finally, the flexible PSM is completed by peeling off the P3 tape. The dead width measured from P1-P2-P3 is 3 mm, therefore the calculated geometric filling factor is 57.5%. The measured active area for the *J-V* test is 11.5 cm^2.

Characterization: The SnO_2 films were characterized by field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus), atomic force microscope (AFM, Nano scope Ⅳ), and X-ray photoelectron spectroscopy (XPS, AXIS SUPRA). The perovskite films were characterized by an X-ray diffractometer (XRD, D8 Advance), a UV-Vis spectrometer (lambda 750S, PerkinElmer), time-resolved photoluminescence (TRPL, Nano LED-C2 N-485L), respectively. The photocurrent density-voltage curves of the perovskite solar cells were tested by a solar simulator (Oriel 94023 A, 300 W) and a Keithley 2400 source meter. The light intensity (100 m W cm^{-2}) was calibrated by a standard silicon solar cell (Oriel, VLSI standards). All the devices were tested under AM 1.5G 1 sun light using a black metal mask of 0.148 cm^2 (except the 5 cm × 5 cm mini-modules) with a scan rate of 100 mV/s. The EQE test was conducted by an EQE detector (PT-QEM1000, Newport).

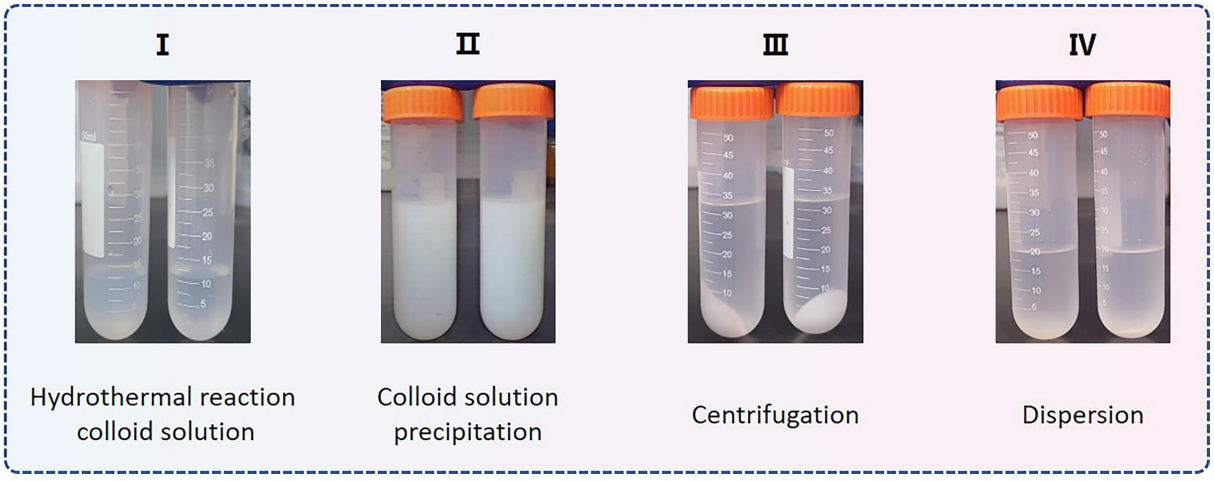

Figure S1 Flow chart for the synthesis of SnO_2 nanocrystals (The left is SnO_2-GL solution, the right is SnO_2 solution).

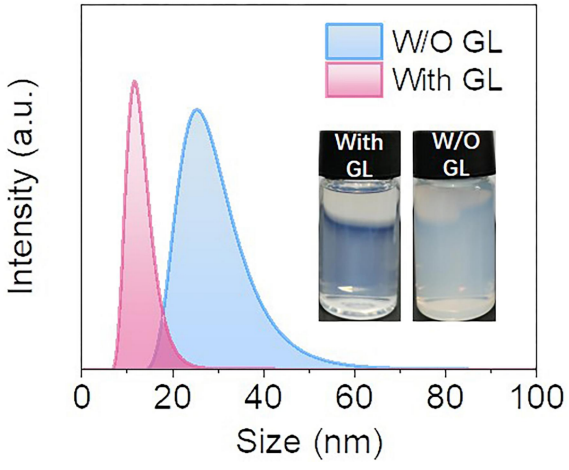

Figure S2 Dynamic light scattering spectra and photographs of the water-diluted $SnCl_4$ precursor with and without glycerol additives after hydrolysis.

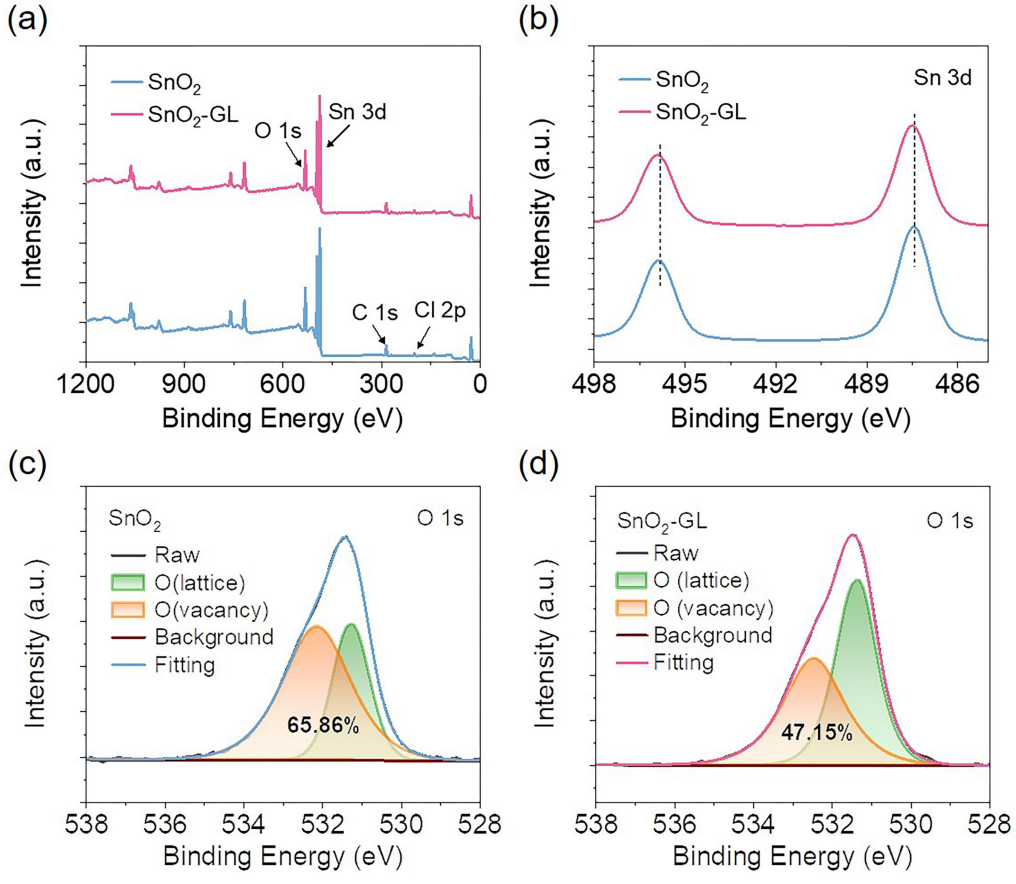

Figure S3 (a) XPS spectra (b) XPS spectra of Sn 3d core electron levels for the SnO_2 and the SnO_2-GL film. XPS spectra of O 1s core electron level for (c) the SnO_2 and (d) the SnO_2-GL film.

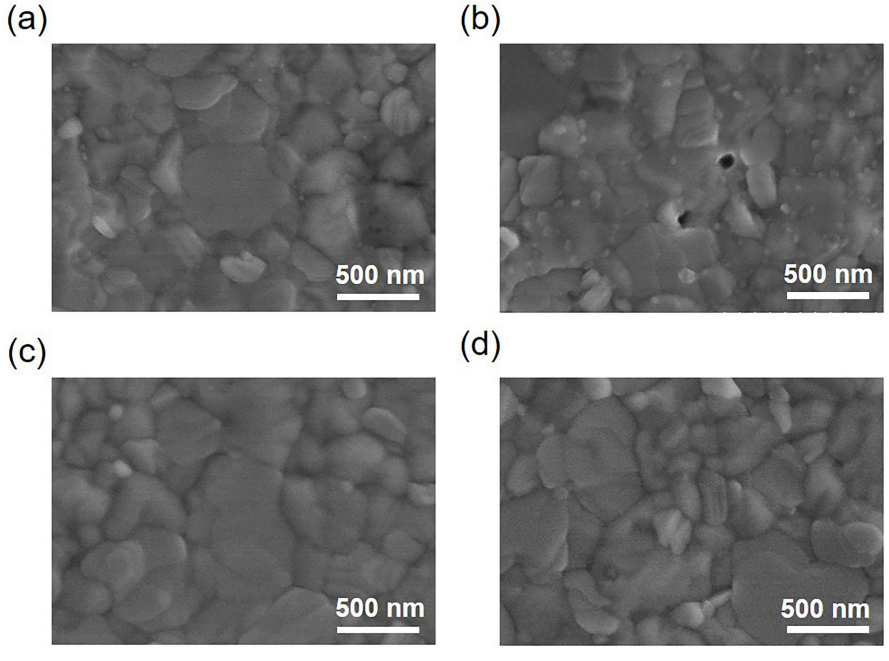

Figure S4 SEM images of perovskite films deposited on PEN/ITO substrates with the deposition of different SnO_2 films. (a) SnO_2, (b) SnO_2-aged, (c) SnO_2-GL, and (d) SnO_2-GL-aged.

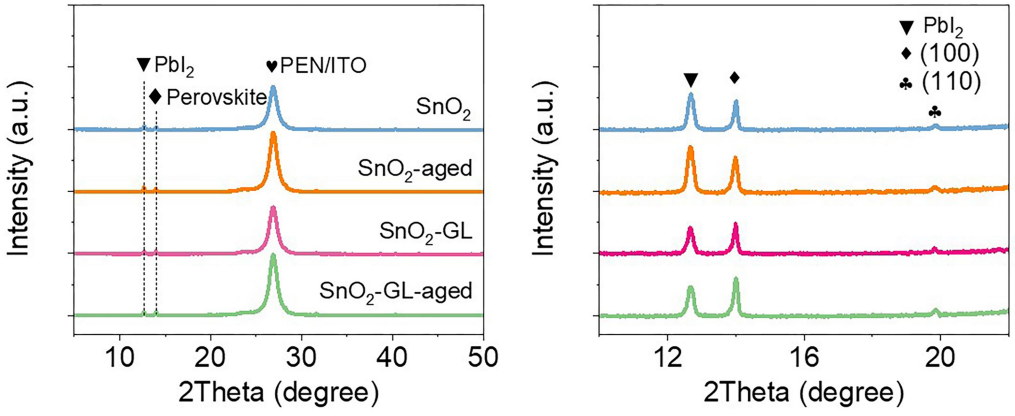

Figure S5 XRD patterns of perovskite films deposited on PEN/ITO substrates with different SnO_2 ETLs.

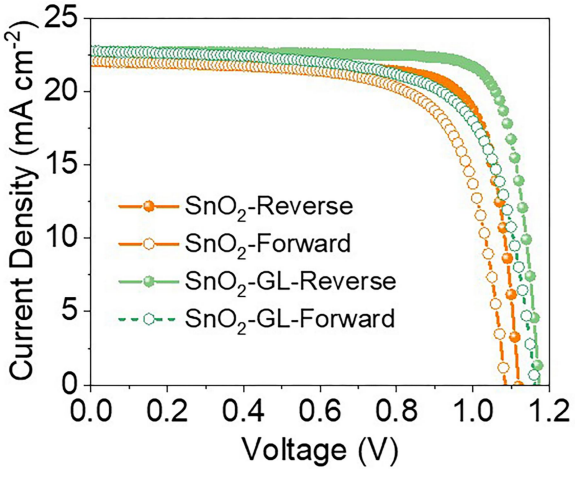

Figure S6 *J-V* curves of the different champion flexible PSCs under reverse scan and forward scan.

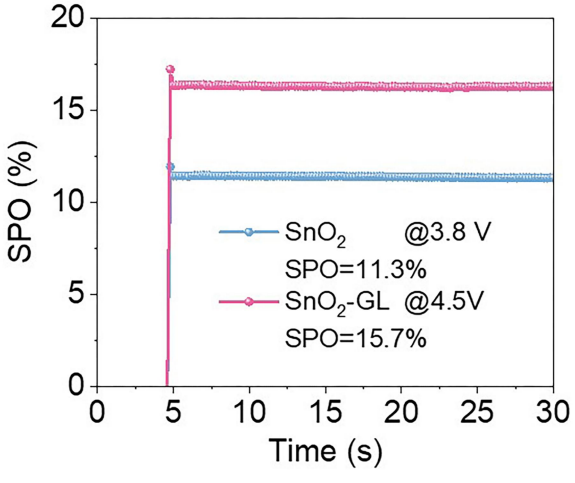

Figure S7 SPO curves of the 5 cm × 5 cm flexible-PSMs based on different SnO_2 ETLs.

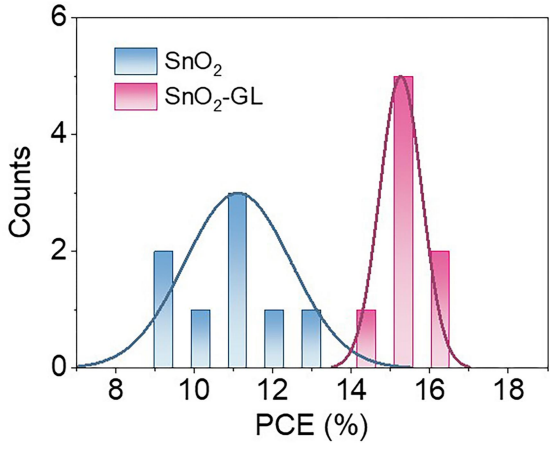

Figure S8 Statistical PCE distribution of flexible PSMs deposited on PEN/ITO substrates with different ETLs.

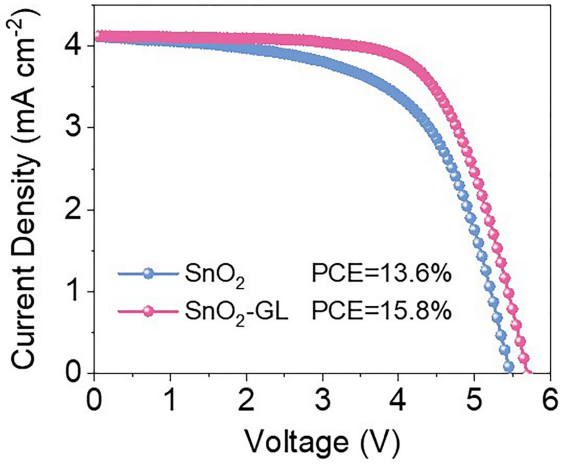

Figure S9 *J-V* curves of the 5 cm × 5 cm flexible-PSMs based on different SnO_2 ETLs used for bending stability test.

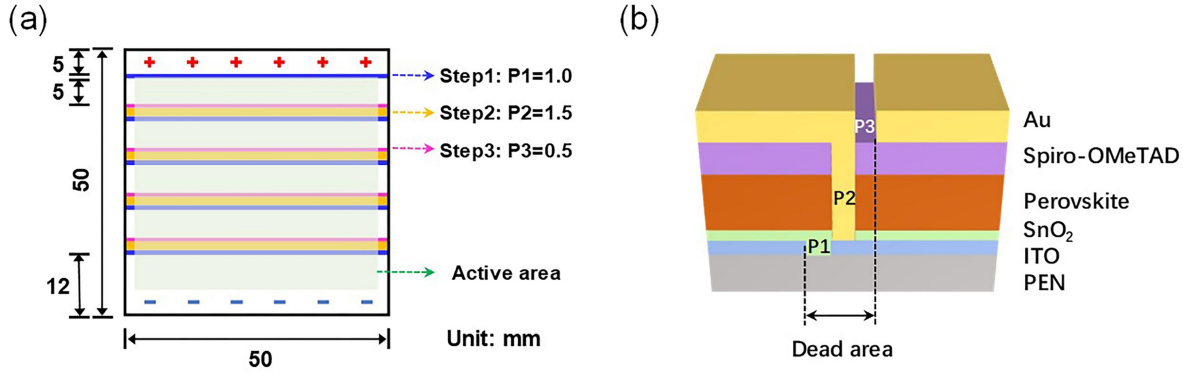

Figure S10 Design of 5 cm × 5 cm flexible perovskite mini-module. Schematic diagram of (a) the P1-P2-P3 patterning for the flexible PSMs with series connection of 5 sub-cells. (b) Flexible mini-module side view diagram of the P1-P2-P3 interconnection. P1-P2-P3 represents the dead area, the geometric filling factor (GFF) of the component is 57.5%, and the effective area = 46 mm × 5 mm × 5 sub-cells = 11.5 cm^2.

Table S1 Fitting parameters of TRPL decay spectra based on the different ETLs (The excitation light is from the Glass side)

ETL	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{ave} (ns)
SnO_2	16.16	90.16	11.56	88.44	88.46
SnO_2-aged	31.67	160.38	15.94	84.06	155.73
SnO_2-GL	18.31	84.32	14.33	85.67.11	82.01
SnO_2-GL- aged	16.18	87.82	12.09	87.91	85.95

Note: $Y=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)+A_0$, $\tau_{ave}=\Sigma A_i\ \tau_i^2/\Sigma A_i\ \tau_i$ [1].

Table S2 Fitting parameters of TRPL decay spectra based on the different ETLs (The excitation light is from the PSK side)

ETL	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{ave} (ns)
SnO_2	13.42	104.53	14.24	85.76	102.63
SnO_2-aged	10.23	90.59	19.04	80.96	88.51
SnO_2-GL	13.32	119.13	11.19	88.81	117.66
SnO_2-GL- aged	11.89	111.19	12.82	87.18	109.65

Table S3 *J-V* parameters of the champion flexible devices

Device	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
SnO_2-RS	1.120	22.05	77.7	19.18
SnO_2-FS	1.085	22.08	70.4	16.86
SnO_2-GL-RS	1.174	22.73	81.7	21.80
SnO_2-GL-FS	1.163	22.75	69.6	18.42

Table S4 *J-V* parameters of the champion F-PSMs

Device	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
SnO_2	5.594	3.82	63.9	13.66
SnO_2-GL	5.802	3.89	73.1	16.48

References

[1] Feng, J.; Yang, Z.; Yang, D.; Ren, X.; Zhu, X.; Jin, Z.; Zi, W.; Wei, Q.; Liu, S. E-beam evaporated Nb_2O_5 as an effective electron transport layer for large flexible perovskite solar cells. *Nano Energy* **2017**, *36*, 1-8.