Low-Temperature, Sprayed SnO_x Nanocomposite Films with Enhanced Hole Blocking for Efficient Large Area Perovskite Solar Cells

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Experimental Section

1. Electrochemical characterization of SnO_2 ETL

Cyclic voltammetry (CV) was employed to analyze the quality of SnO_2 thin film. In the 3-electrode setup, ITO and ITO coated by SnO_2 films were used as working electrode, Ag/AgCl (3M KCl) as reference electrode, and stainless steel as counter electrode. The electrolyte solution contained 0.1M $K_4Fe(CN)_6$ in H_2O. The scan rates were 50 mV/s in CVs. More details can be found in previous reports.[1] A bias potential was applied to the electrodes and current was recorded. The current generated at the electrode/solution interfaces can qualitatively reflect the compactness (pinhole density) of the SnO_2 thin film.

2. Spray coating of SnO_2 on ITO

SnO_2 films were prepared using ultrasonic spray coating with a 120 kHz ultrasonic nozzle (Sonotek) which is operated at 1 W with 2 liters per minute (LPM) flow of nitrogen gas. The nozzle is mounted on a PVA Delta 6 robotic gantry. A controlled speed of 25 mm/s was used and the nozzle height was kept at 8 cm above the substrates which were put on a hotplate. The temperature of hotplate, flow rate and spray passes were adjusted to optimize the film quality. Two precursor solutions were used to form nanocrystalline SnO_2 thin films, including SnO_2 nanoparticles (0.1wt%) in an aqueous and a mixed solution (water and isopropanol). The spray rate is ranging from 40uL/min to 60uL/min (40, 45, 50, 60uL/min) and post annealing treatment is done at different temperatures (25°C, 50 °C, 60 °C, 70 °C, 80 °C, 100 °C, 150 °C, 200 °C). The number of spray passes is from 0 to 10 layers, the raster line spacing is 0.5mm, and raster line speed is 10cm/s. After that $SnCl_2$ in isopropanol with varied concentrations (5-20 mM) was sprayed on top of SnO_2 to form nanocomposite. The optimized spray parameters for $SnCl_2$ is

flow of 50 μL/min, substrate temperature of 100° C and 2 spray passes. All ITO substrates and ITO/SnO_2 films were treated by UV-Ozone for at least 10 minutes before use in spray coating or solar cells.

3. ETL Characterizations

The nanostructures and film surface morphology were characterized using a high-resolution SEM (FEI Sirion XL30, Thermo Fisher Scientific Inc., US) and an AFM (XE-70, Park Systems, Korea) operated in tapping mode. A surface profilometer (Veeco Dektak 150, Veeco Instruments Inc., US) was used to measure the film thickness with a film edge created by masking a small region. An XPS (PHI 5000 Versaprobe, Physical Electronics Inc., US) using Al−K_α (1486 eV) X-ray source was employed for characterizing the chemical composition of the films. A Pre-sputtering was applied to remove any surface atmospheric contaminants. The crystallinity of the ETLs on glass substrates were studied using grazing angle X-ray Diffraction (X'Pert Materials Research Diffractometer, PANalytical, Inc., Netherlands) with an incident angle of 3.5 degrees, a step size of 0.02 degree, and a time per step of 0.5 s.

4. Perovskite Solar Cell Device Fabrication

A planar device structure with an n-i-p architecture (ITO glass/SnO_2/perovskite/HTL/Ag was used for perovskite solar cells. Specifically, ITO glass was cleaned with water, acetone and isopropanol, respectively. The cleaning time is at least 10 mins for each step. After UV-Ozone treatment of ITO glasses for 10 minutes, a thin SnO_2 ETL was coated on ITO by spraying a precursor solution containing 0.1 wt % SnO_2 nanoparticles in deionized H_2O (diluted from 15wt% SnO_2 aqueous dispersion). After that, $SnCl_2$ with different concentration (5mM, 10mM, 20mM) in isopropanol was sprayed on top of SnO_2 to form a nanocomposite structure. The

spray parameters used for $SnCl_2$ coating is flow of 50 μL/min, substrate temperature of 100˚ C and 2 spray passes. Then the perovskite film was fabricated on top of ITO/SnO_2 substrates. The details of preparing perovskite solution and perovskite film formation can be found in previous reports.[2] Specifically, 285.5 mg formamidinium iodide (Dyseol), 88.3 mg cesium iodide (Sigma), 686.9 mg lead iodide (TCI), and 187.2 mg of lead bromide (TCI) were dissolved in 1.6 mL of anhydrous N,N-dimethylformamide (DMF) and 0.4 mL dimethylsulfoxide (DMSO) (volume ratio =4 : 1) in a glovebox. The perovskite solution was stirred on hotplate with 60-70 ^{o}C for 1-2 hours until fully dissolved. The perovskite thin film was fabricated by one-step method, that is, 50uL of the precursor solution was spun on SnO_2/SnOx film with a two-step program (1000 rpm for 12 seconds and the second step at 6000 rpm for 30 seconds). During the last 5 seconds of the second step, 100 mL of chlorobenzene (Sigma-Aldrich) was quickly dispensed over the film. The substrates were then placed on a hot plate at 100^{o}C for 30 mins in the glovebox. The HTL solution is made from spiro-OMeTAD with different additives (LiTFSI, tert-butyl pyridine and FK209). Specially, HTL solution contains 72 mg/mL spiro-OMeTAD in chlorobenzene, with the addition of 17.5 μL LiTFSI (from a stock solution in acetonitrile with a concentration of 520 mg/mL), 28.8 μL tert-butyl pyridine or 8 μL FK209 from a stock solution in acetonitrile with concentration of 0.5 M. Afterwards, 50uL HTL solutions were spin coated on the top of the perovskite layer with a speed of 3000 rpm for 30 s. Finally, a 150 nm silver layer (the deposition rate is 0.02 nm/s for first 10 nm, and 0.1nm/s for the other 140 nm) was deposited by thermal evaporation on the HTM layer.

5. Perovskite Solar Cell Module Fabrication

Creating a monolithic, series-interconnected module requires scribing through three layers: 1) the ITO front electrode (P1); 2) the electron transport layers (ETL), hole transport layers (HTL), and perovskite (P2); and 3) the Ag back electrode (P3). Utilizing laser scribing allows for sub-millimeter wide contacts between cells, reducing the necessary dead area that takes away from the active parts of the device. The P1 scribe through the ITO utilized a belt driven fiber laser (1064 nm) at 25 W and 120 mm/s scribe speed. The P2 scribe used the same belt drive with a CO_2 source (10.6 μm) at 1W and 50 mm/s scribe speed. The P1 scribe involved two adjacent scribe marks for a total width of 180 μm. The P2 scribe involved three adjacent scribe marks for a total width of 200 μm. Rather than using a scribe for the P3, a shadow mask was used to pattern the Ag.

6. Device Characterization

Transmittance absorption spectroscopy was obtained using a spectrophotometer (Agilent Cary 6000i). Steady-state photoluminescence and time-resolved photoluminescence were measured using a Horiba FluoroLog fluorimeter. Test device architectures of glass/ETL/perovskite were excited with a 635 nm laser (Picoquant P-C-635M and PDL 800-B operating at 2.5 MHz and $8*10^{-5}$ Watts per cm^2 average intensity). A Time-Correlated Single Photon Counting (TCSPC) method was used for lifetime measurements. The perovskite solar cells were tested in ambient conditions (~ 45% RH, 25˚ C) under 1 sun, AM 1.5G illumination from a 300 W xenon lamp (Oriel) solar simulator. The lamp intensity was set based on an NREL-calibrated KG5 filtered Si reference cell. J-V curves were collected with a Keithley Model 2400 digital multimeter. The J-V scans are performed from 1.2 V to 0 V (backward) and 0V to 1.2 V (forward) with a scan rate of 0.1 V/s. The devices are kept in dark glove box at room temperature before J-V

measurements. Max Power Point (MPPT) measurements were obtained using a perturb-and-measure program with voltage steps of 5 mV and a measurement taken every 1 s.

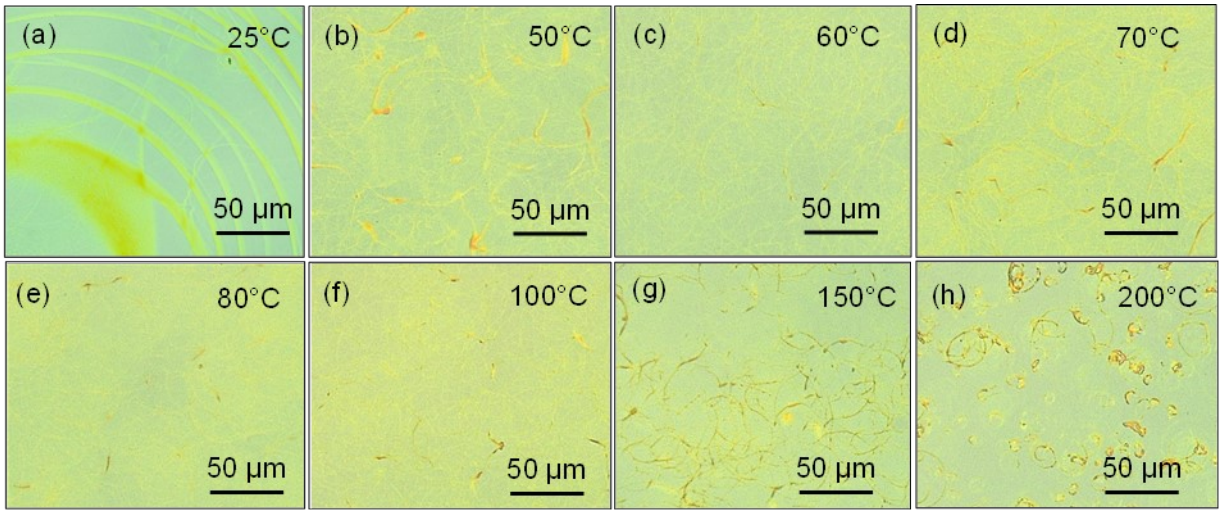


Figure S1. Temperature optimization for aqueous SnO_2 spray coating process.

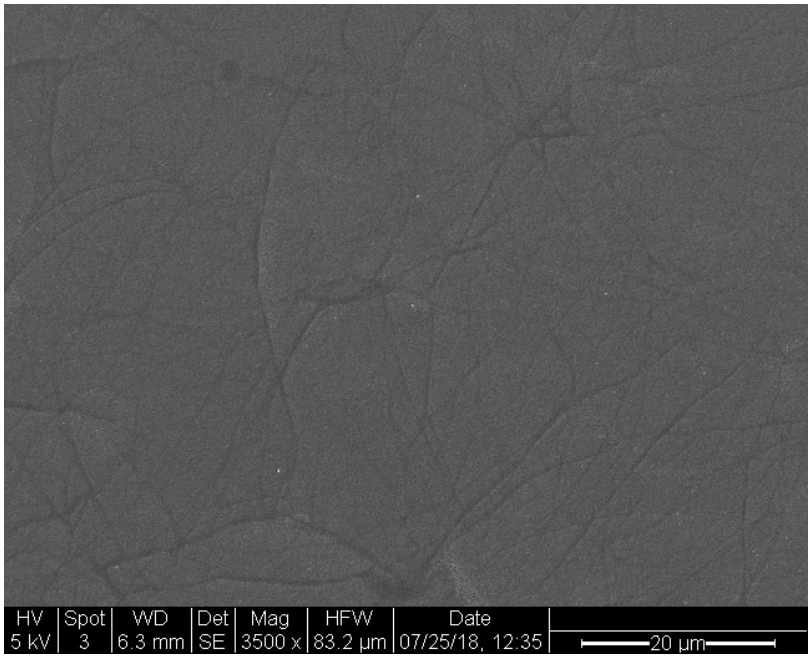


Figure S2. Top view of SEM images of sprayed a-SnO_2.

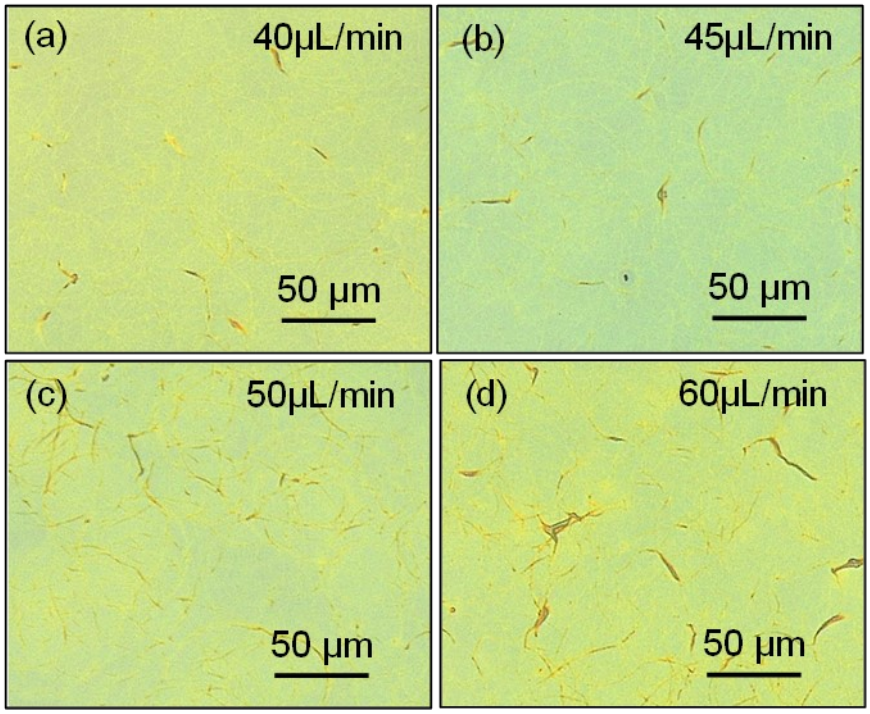


Figure S3. Solution flow optimization for aqueous SnO_2 spray coating process.

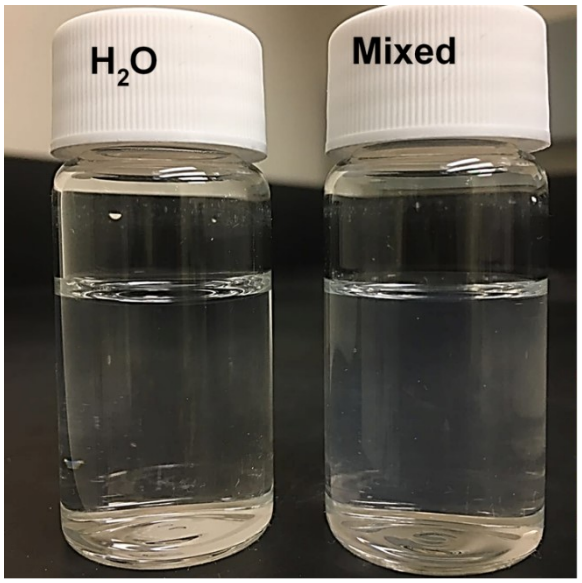


Figure S4. Images of SnO_2 precursor solution in H_2O and mixed solvents (H_2O and IPA, v:v =1:1).

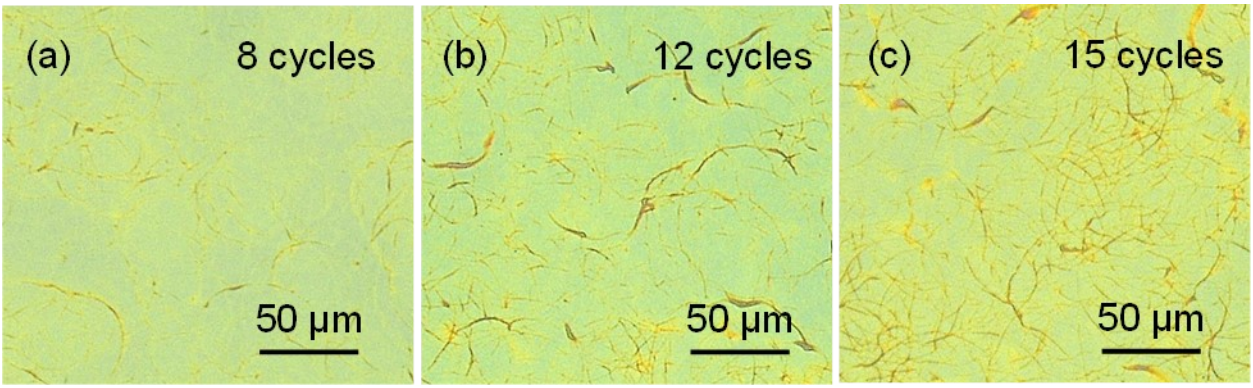


Figure S5. Solution flow optimization for aqueous SnO_2 spray coating process.

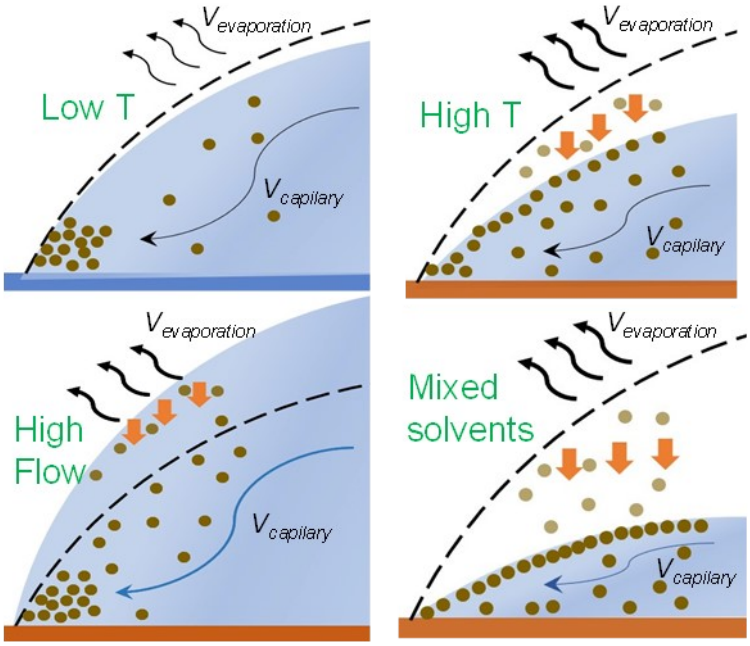


Figure S6. Solution flow optimization for aqueous SnO_2 spray coating process.

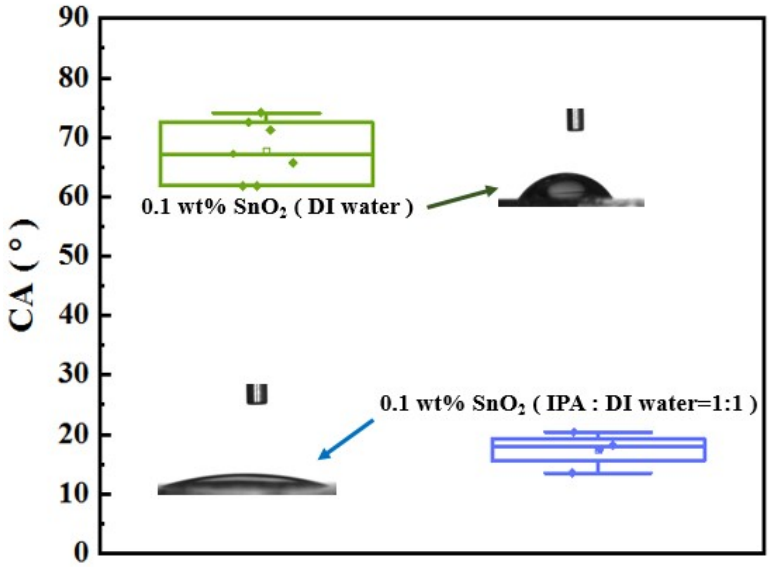


Figure S7. Contact angle of the different SnO_2 Solutions (0.1wt% in deionized water and 0.1wt% in mixture of deionized water and isopropanol with volume ratio of 1:1) on glass substrate.

Table S1. Photovoltaic parameters for champion solar cells based on sprayed SnO_2

cycles	thickness /nm	V_{oc}/ mV	J_{sc}/ mAcm^{-2}	FF	η/ %
2	14	867	19.6	0.62	10.5
4	24	905	21.3	0.61	11.7
6	37	936	21.4	0.64	12.9
8	47	957	22.2	0.62	13.1
10	50	988	21.8	0.63	13.5
mixed	-	1055	20.9	0.72	15.9

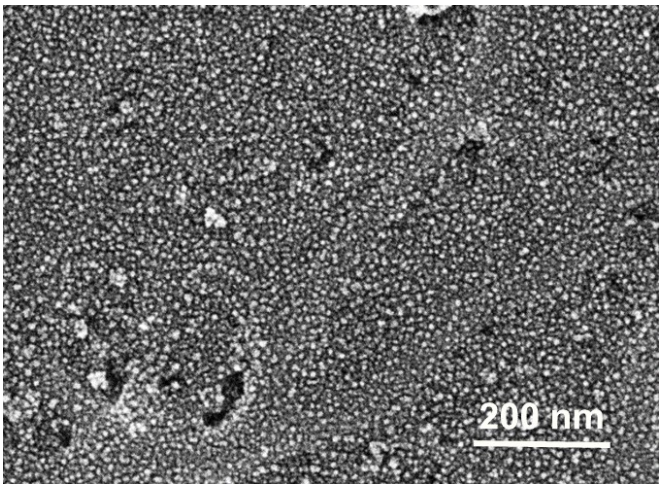


Figure S8. SEM image of bilayer SnO_2.

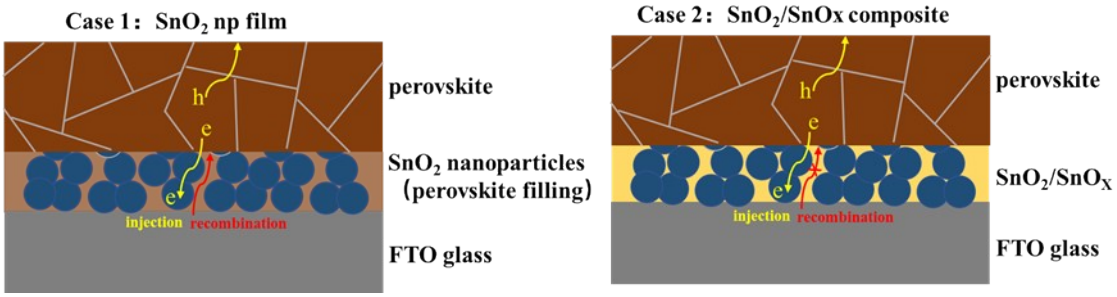


Figure S9. Charge recombination processes in devices based on SnO_2 nanoparticles and SnO_2/SnOx composite.

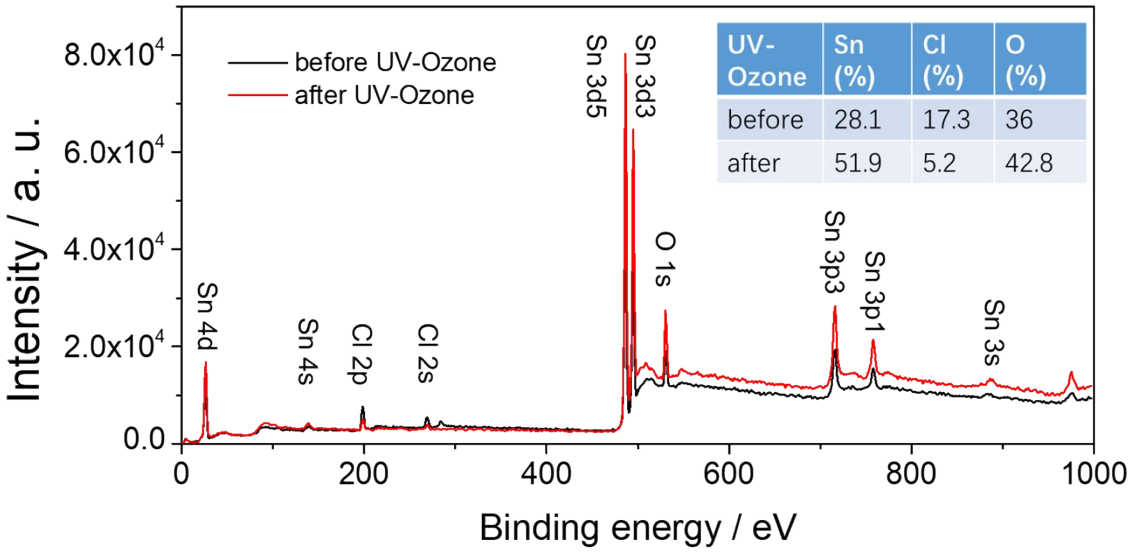


Figure S10. XPS of SnOx before and after UV-Ozone treatment.

Table S2. Photovoltaic parameters for champion solar cells based on bi-SnO_2

$SnCl_2$	V_{oc}/ mV	J_{sc}/ $mAcm^{-2}$	FF	η/ %
5mM	1066	20.5	0.76	16.5
10mM	1110	22.4	0.74	18.4
20mM	1093	21.6	0.73	17.2

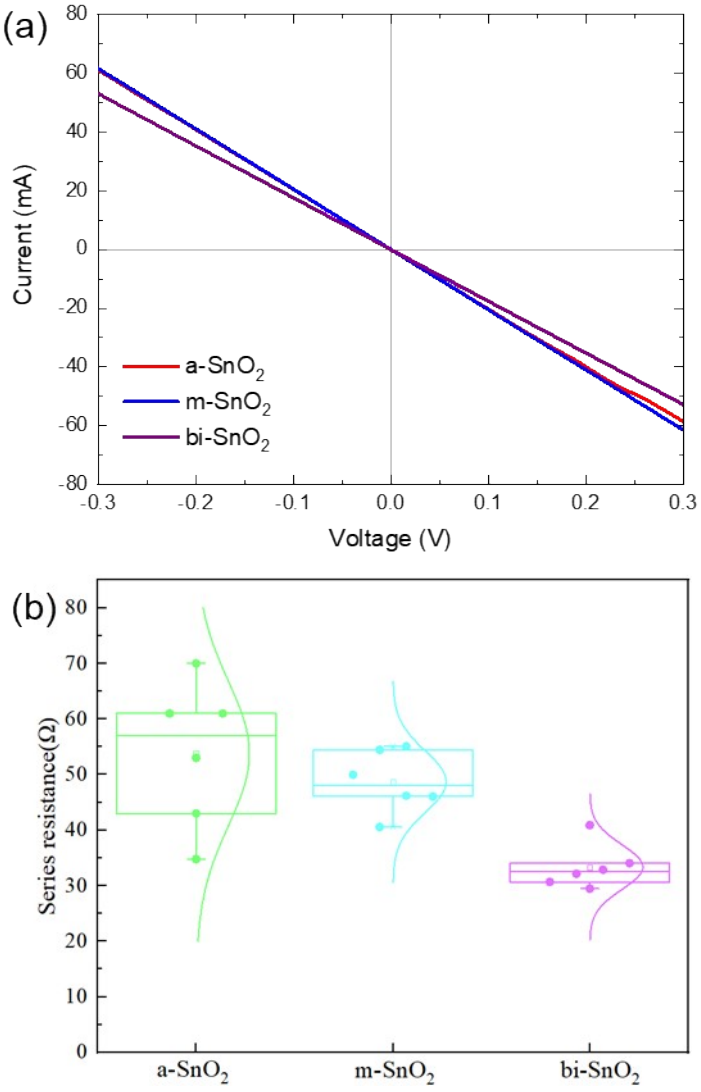


Figure S11. (a) I-V curves of ITO/ETL/Ag (ETL: a-SnO_2, m-SnO_2 and bi-SnO_2). (b) Series resistance for devices based on the optimized a-SnO_2, m-SnO_2 and bi-SnO_2.

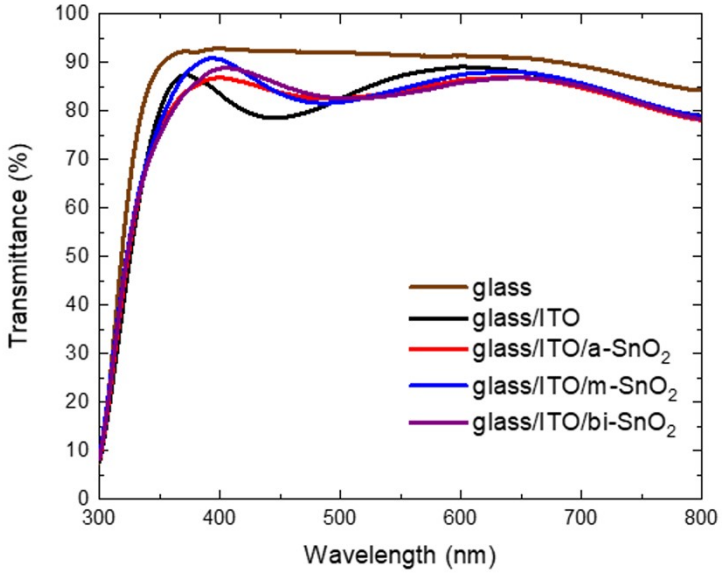
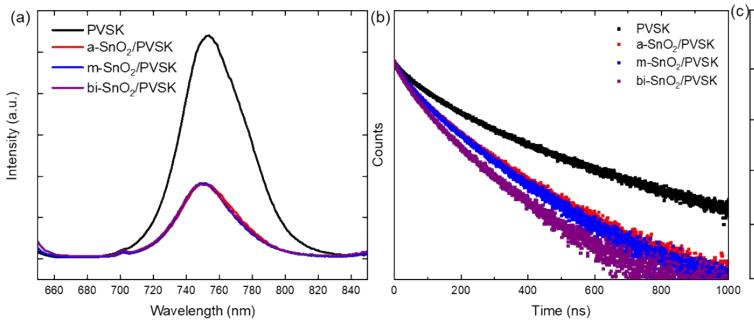


Figure S12. Transmittance spectra of three types of SnO_2 ETLs on ITO glasses.



	τ_1 (ns)	τ_2 (ns)
PVSK	38	147
a-SnO_2/PVSK	22	84
m-SnO_2/PVSK	23	81
bi-SnO_2/PVSK	21	68

Figure S13. (a) Steady-state photoluminescence (PL) and (b) time-resolved photoluminescence (TRPL) characterizations for perovskite films based on a-SnO_2, m-SnO_2, and bi-SnO_2 ETL.

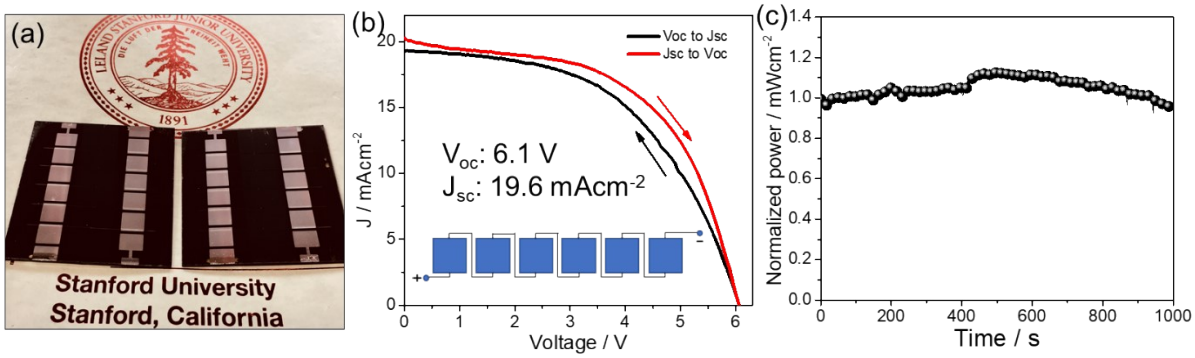


Figure S14. Perovskite solar cell modules based on sprayed SnO_2 nanocomposite. (a) Image of series-connected modules with 6 subcells on a 5x5 cm^2 ITO substrate. (b) J-V curves of the perovskite solar modules with an active area of 0.35 cm^2 per subcell. (c) Normalized power of solar modules under MPP tracking, measured under ambient without encapsulation.

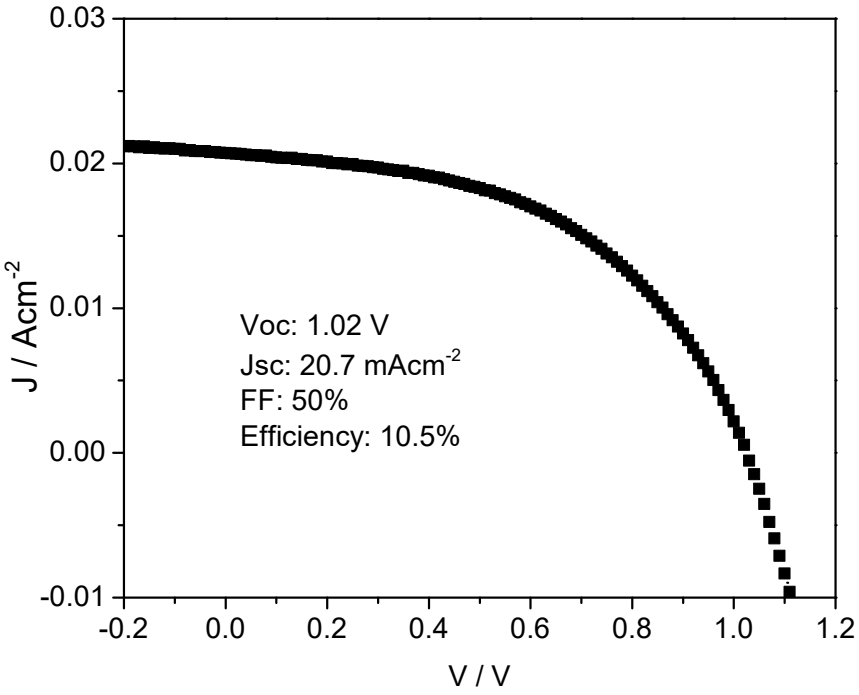


Figure S15. J-V curve of the inverted solar cell device on a 5x5 cm^2 substrate. The device structure is ITO/NiO/perovskite/C60/BCP/Ag. The perovskite is made by spin coating, and the active area for measuring is 0.23 cm^2.

References:

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(2) Chen, J. P.; Hilt, F.; Rolston, N.; Dauskardt, R. H. Scalable open-air deposition of compact ETL TiOx on perovskite for fullerene-free solar cells. *J. Mater. Chem. A,* **2020**,8, 22858-22866.