Electronic Supplementary Information

**Point Defects-Reduced Colloidal SnO$_2$ Electron Transport Layers for Stable and Hysteresis Less Perovskite Solar Cells**

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Experimental section

Materials

Dimethylformamide (DMF, 99.8 %), Dimethyl sulfoxide (DMSO, 99.9 %), Chlorobenzene (CB, 99.8 %), Acetonitrile (99.8 %), 4-tert-butylpyridine (tBP, 96 %), Lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI) and Cesium iodide (CsI) were purchased from Sigma-Aldrich. Also, all reagents for colloid SnO₂ synthesis and sol-gel SnO₂ ETL preparation were purchased from Sigma-Aldrich. Anhydrous 1-butanol (99 %) was purchased from Tokyo Chemical Industry Corporation. Lead iodide (PbI₂) and Lead bromide (PbBr₂) were purchased from Alfa Aesar. Formamidinium iodide (FAI) and Methylammonium bromide (MABr) were purchased from Xi’an Polymer Light Technology Corporation. 2,29,7,79-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-MeOTAD) was purchased from the Luminescence Technology Corp.

Synthesis of C-SnO₂ nanocrystals

Colloidal SnO₂ (C-SnO₂) nanocrystals were synthesized by the inverse micelle-water injection method according to previous methods.¹ In typical synthetic process, 1 mmol of tin acetate (Sn(CH₃CO₂)₄), 10 mmol of oleylamine and 10 mmol of oleic acid were dissolved in 30 ml of xylene. The mixture was heated to 110 °C and kept the same temperature for 30 minutes under stirring to eliminate the water, and then cooled to 90 °C. Then, the 1ml of deionized water in the syringe was injected swiftly into the mixture solution at 90 °C. We further refluxed the cloudy solution at the same temperature until the solution became transparent, and the reaction solution was cooled to room temperature. The as-synthesized C-SnO₂ nanocrystals were purified by washing them with ethanol and subsequently centrifuging. The C-SnO₂ were redispersed in hexane.
**Solar cell fabrication**

We cleaned the laser-etched ITO/glass substrates with acetone, distilled water, and ethanol in an ultrasonic bath for 15 min. Hexane was drop-casted during the spin-coating process for coating uniformity and annealed at 90 °C for 15 minutes. The colloidal SnO$_2$ (C-SnO$_2$) layer was spin-coated (4000 rpm for 30 s) on the cleaned ITO/glass substrate, using a diluted solution of colloidal SnO$_2$ nanoparticles in hexane (20 mg/ml). The SnO$_2$ film was prepared through the sol-gel method (S-SnO$_2$): the precursor solution of 0.2 M SnCl$_2$·2H$_2$O in 1-buthanol was spin-coated on the same ITO/glass substrate, at 3000 rpm for 30 s and annealed at 180 °C for 30 min. We prepared the perovskite precursor solutions (1.3M [CsPbI$_3$]$_{0.05}$[(FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$]$_{0.95}$) by dissolving corresponding amounts of PbI$_2$, FAI, PbBr$_2$, MABr, CsI in a DMSO/DMF (7:3 v/v) mixed solvent. After exposure to UV-Ozone irradiation for 20 min, we spin-coated the perovskite precursor solution on top of the deposited electron transfer layer with a 30 nm thickness (5000 rpm for 25 s); additionally, 0.5 ml of Anisole were dropped on the rotating substrate at 20 s. We heated sequentially the spin-coated substrates at 150 °C for 10 min. The thickness of resultant perovskite layer was around 580 nm. A hole transport layer solution consists of 36 mg spiro-OMeTAD, 14.4 μl 4-tert-butylpyridine, and 8.8 μl LiTF-SI solution (360 mg mL$^{-1}$ in acetonitrile) dissolved in 0.5 ml CB. 25 μl hole transport layer solution was coated by spin coating at 4000 rpm for 30s onto the perovskite thin film. A hole transport layer was obtained 130 nm thickness. The Ag electrode was deposited on the prepared samples using a thermal evaporation system, under a pressure of 10$^{-6}$ Torr.

**Characterization**
The X-ray diffraction (XRD) patterns of the SnO$_2$ films were measured using a D8 Discover instrument with Cu-Kα radiation ($\lambda = 1.5418$ Å). The crystal lattice and the size of the C-SnO$_2$ sample were characterized using a high-resolution transmission electron microscope (HRTEM, JEM-3010, JEOL). Fourier-transform infrared spectra were obtained using an FT-IR, Nicolet 6700, Thermo Scientific: 32 scans were done at a resolution of 8, in the range of 600 and 4000 cm$^{-1}$. X-ray photoelectron spectroscopy (XPS, ESCA-LAB250Xi, Thermo UK) was used to determine the chemical states on the substrate surfaces. The steady-state and time-resolved photoluminescence were observed with a fluorescence lifetime spectrometer (Quantaurus-Tau C11367-12, HAMAMATSU) using a 464-nm laser (PLP-10, HAMAMATSU) for photoexcitation. We measured the absorbance spectrum of perovskite film on colloidal and sol-gel by ultraviolet visible (UV–Vis) spectroscopy (Perkin Elmer, Lamda 35). The current density-voltage (J-V) and the current density-time (J-T) characteristics under illumination at AM 1.5G (1.00 mA/cm$^2$) were performed using a solar simulator (Newport Oriel Solar 3A class AAA, 64023A) and a potentiostat (CH instruments, CHI 660D). We adjusted the light intensity using a standard Si-solar cell (Oriel, VLSI standards) and a light sensor current controller (Newport Oriel, 68945). We covered all devices with a thin metal mask, which had an active area of 0.14 cm$^2$ during the measurements.
Fig. S1. (a) X-ray diffraction (XRD) patterns for S-SnO$_2$ and C-SnO$_2$; (b) high-resolution transmission electron microscopy (TEM) image of C-SnO$_2$; (c) reduced Fourier-transform pattern of C-SnO$_2$. 
Fig. S2. Change in normalized $J_{sc}$, $V_{oc}$, FF, and power conversion efficiency (PCE) of S-SnO$_2$- and C-SnO$_2$-based perovskite solar cells (a) under dark condition and (b) under light soaking condition (AM 1.5G) in below 20% humidity and 25 °C ambient air.
**Fig. S3.** Statistical photovoltaic parameters of (a) $J_{SC}$, (b) $V_{OC}$, (c) FF, and (d) PCE obtained from the S-SnO$_2$- and C-SnO$_2$- based PSCs; (e) J-V curves for the champion device based on the C-SnO$_2$ electron transport layer.
Fig. S4. (a) External Quantum efficiency (EQE) and integrated current density of devices with S-SnO$_2$ and C-SnO$_2$ ETLs, (b) Steady-state current and efficiency of PSCs employing C-SnO$_2$ ETL measured at forward bias 800 mV and stabilized power output under simulated AM 1.5G sunlight 100 mW cm$^{-2}$
**Fig. S5.** J-V curves for S-SnO$_2$ and C-SnO$_2$ thin films obtained under dark condition.
Table S1. Parameters of the perovskite solar cells.

| Material | Mode  | Voc [V] | Jsc [mA cm⁻²] | FF [%] | PCE(Max.) [%] | Rs [Ω] | Rsh [kΩ] |
|----------|-------|---------|---------------|--------|---------------|--------|----------|
| S-SnO₂   | Reverse | 1.08    | 20.76         | 76     | 16.45 (16.96) | 31.46  | 21.60    |
|          | Forward | 1.06    | 20.48         | 63     | 13.69         |        |          |
| C-SnO₂   | Reverse | 1.12    | 21.10         | 78     | 18.34 (19.12) | 29.10  | 33.18    |
|          | forward | 1.11    | 21.42         | 76     | 18.17         |        |          |
Reference

1. S. Y. Park, M. Y. Baek, Y. Ju, D. H. Kim, C. S. Moon, J. H. Noh and H. S. Jung, *The journal of physical chemistry letters*, 2018, **9**, 5460-5467.