

Electronic Supplementary Information

Point Defects-Reduced Colloidal SnO₂ 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 minutes¹. The colloidal SnO₂ (C-SnO₂) layer was spin-coated (4000 rpm for 30 s) on the cleaned ITO/glass substrate, using a diluted solution of colloidal SnO₂ nanoparticles in hexane (20 mg/ml). The SnO₂ film was prepared through the sol-gel method (S-SnO₂): the precursor solution of 0.2 M SnCl₂·2H₂O in 1-butanol 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 [CsPbI₃]_{0.05}[(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}]_{0.95}) by dissolving corresponding amounts of PbI₂, FAI, PbBr₂, 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 SnO₂ films were measured using a D8 Discover instrument with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The crystal lattice and the size of the C-SnO₂ 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 (Quantaaurus-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/cm²) 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 cm² during the measurements.

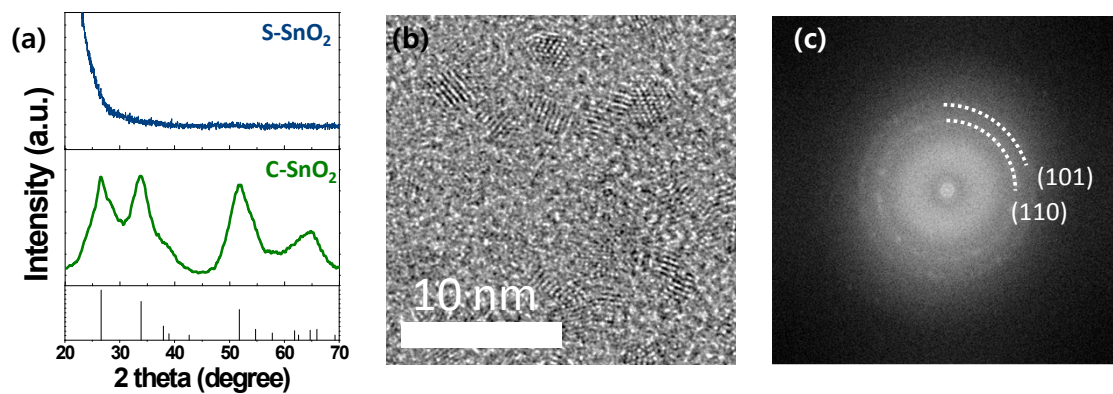


Fig. S1. (a) X-ray diffraction (XRD) patterns for S-SnO₂ and C-SnO₂; (b) high-resolution transmission electron microscopy (TEM) image of C-SnO₂; (c) reduced Fourier-transform pattern of C-SnO₂.

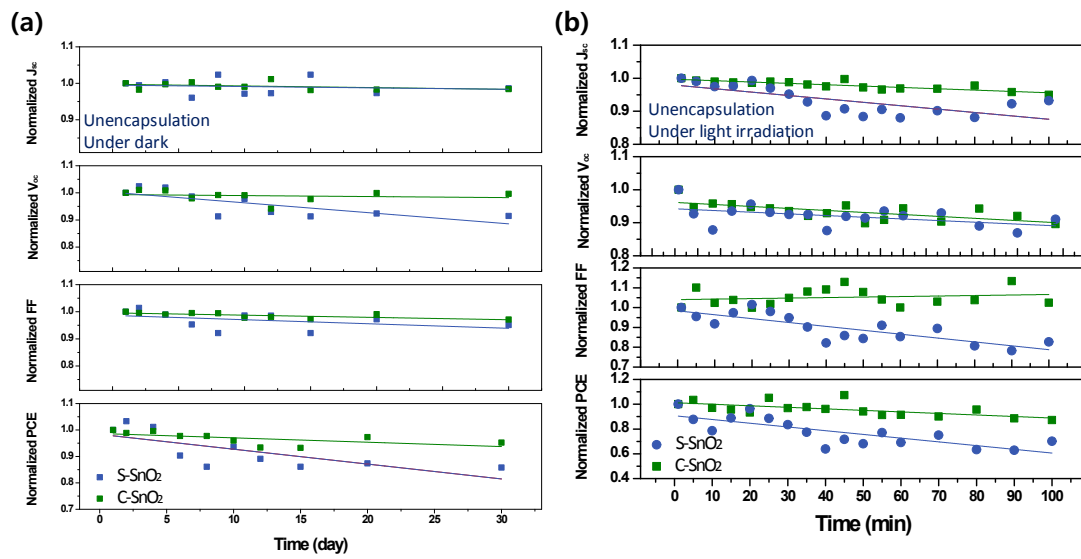


Fig. S2. Change in normalized J_{sc} , V_{oc} , FF, and power conversion efficiency (PCE) of S-SnO₂- and C-SnO₂-based perovskite solar cells (a) under dark condition and (b) under light soaking condition (AM 1.5G) in below 20% humidity and 25 °C ambient air.

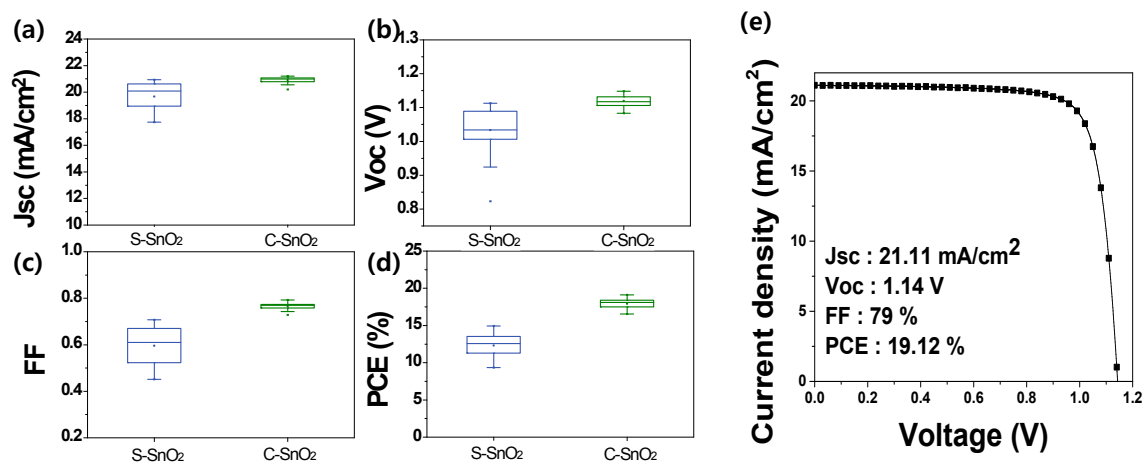


Fig. S3. Statistical photovoltaic parameters of (a) J_{sc}, (b) V_{oc}, (c) FF, and (d) PCE obtained from the S-SnO₂- and C-SnO₂- based PSCs; (e) J-V curves for the champion device based on the C-SnO₂ electron transport layer.

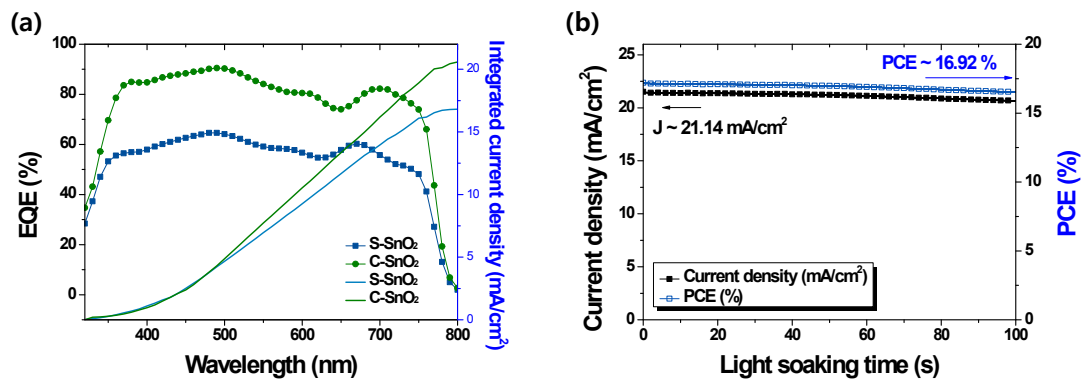


Fig. S4. (a) External Quantum efficiency (EQE) and integrated current density of devices with S-SnO₂ and C-SnO₂ ETLs, (b) Steady-state current and efficiency of PSCs employing C-SnO₂ ETL measured at forward bias 800 mV and stabilized power output under simulated AM 1.5G sunlight 100 mW cm⁻²

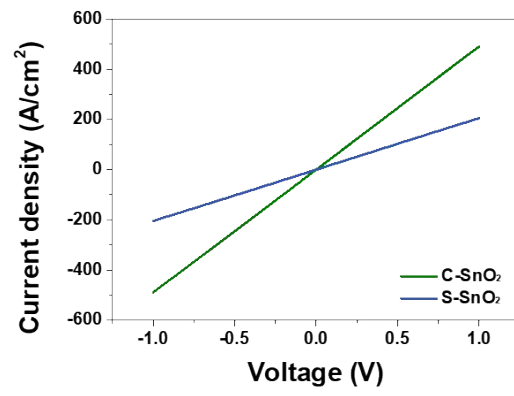


Fig. S5. J-V curves for S-SnO₂ and C-SnO₂ thin films obtained under dark condition.

Table S1. Parameters of the perovskite solar cells.

		Voc [V]	Jsc [mA cm ⁻²]	FF [%]	PCE(Max.) [%]	Rs [Ω]	Rsh [kΩ]
S-SnO ₂	Reverse	1.08	20.76	76	16.45 (16.96)	31.46	21.60
	Forward	1.06	20.48	63	13.69		
C-SnO ₂	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.