Electronic Supporting Information (ESI)

Semiconducting Carbon Nanotubes as Crystal Growth Templates and Grain Bridges in Perovskite Solar Cells

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S.M. E-mail: maruyama@photon.t.u-tokyo.ac.jp Experimental Section

s-SWNT Dispersion Preparation. Preparation of s-SWNT dispersion was performed according to the literature.^{1,2} The SWNTs synthesized by high-pressure carbon monoxide processing (HiPco, raw soot, RO513, NanoIntegris, 1.0 - 0.3 nm in diameter) were used in this study. Dispersions of the SWNTs was prepared by dropping 1 mg mL⁻¹ of the as-prepared SWNTs in 1% SDS (99%, Sigma-Aldrich) solution and then ultrasonicating the mixture using a tip-type ultrasonic homogenizer (Sonifire 250D, Branson) for 3 h under cooling at 15 °C. The solution was then centrifuged to remove bundles and impurities (210,000 x g for 30 min at 25 °C). The resulting supernatant was collected as a dispersant of surfactant-coated SWNTs. A chromatography system (AKTA, GE Healthcare) equipped with a column packed with agarose gel beads was used for the separation of metallic and semiconducting SWNTs. After equilibration of the column with 1% SDS solution, the SWNT dispersion was applied. Metallic and semiconducting SWNTs were obtained as unbound fraction in 1% SDS and bound fraction eluted by 1% DOC, respectively. Perovskite Precursor Solution Preparation. For the MAPbI₃ Solution, CH₃NH₃I (TCI), PbI₂ (TCI), and anhydrous dimethyl sulfoxide (TCI) (molar ratio 1:1:1) were mixed in anhydrous N,Ndimethylformamide (TCI) with a concentration of 50 wt%. The solution was filtered through a 0.45 µm poly(tetrafluoroethylene) filter before use. For the water-added MAPbI₃ solution, 2 wt% pure water (Fujifilm Wako Pure Chemical Co.) was added into the prepared MAPbI₃ solution. The solution was filtered through a 0.45 µm poly(tetrafluoroethylene) filter before use. For the s-SWNT-added MAPbI₃ solution, 2 wt% semiconducting SWNT dispersion was added into the prepared MAPbI₃ solution. The solution was filtered through a 0.45 µm poly(tetrafluoroethylene) filter before use.

Perovskite Solar Cell Fabrication. ITO patterned glass substrates were cleaned and sonicated with detergent, distilled water, acetone, and isopropanol in an ultrasonic bath for 15 min, respectively. The cleaned substrates underwent the UV-ozone for enhanced wettability. Thirty millimolar SnCl₂·2H₂O (Aldrich, >99.995%) solution was prepared in ethanol (anhydrous, Fujifilm Wako Pure Chemical Co.) as a precursor solution for deposition of a compact SnO₂ layer. The solution was filtered by a 0.2 µm syringe filter, followed by spin-coating on the cleaned substrate at 3000 rpm for 30 s. The spin-coated film was annealed at 150 °C for 30 min. After cooling down to room temperature, another cycle of the spin-coating process was repeated, which was followed by annealing at 150 °C for 5 min and 180 °C for 1 h. The SnO₂-coated ITO glass was treated with UV-ozone before spin-coating of the prepared perovskite solution. Then, 25 µL of perovskite precursor solution was spin-coated onto the SnO_2 layer at 3000 rpm for 30 s, with 0.5 mL of anhydrous diethyl ether slowly dripped onto the substrate 10 s after the start of the spincoating process. Next, the film was annealed at 100 °C for 10 min to obtain a dense brown MAPbI₃ film. The spiro-MeOTAD solution was prepared by dissolving 85.8 mg of spiro-MeOTAD (Merck) in 1 mL of chlorobenzene (anhydrous, 99.8%, Sigma-Aldrich) which was mixed with 33.8 µL of 4-tert-butylpyridine (96%, Aldrich) and 19.3 µL of Li-TFSI (99.95%, Aldrich, 520 mg/mL in acetonitrile) solution. The spiro-MeOTAD solution was spin-coated on the perovskite layer at 3000 rpm for 20 s by dropping 17 μ L of the solution during the spinning. Finally, a 70nm-thick Au anode was fabricated by thermal deposition at a constant evaporation rate of 0.05 nm s^{-1}

Characterizations. The J-V curves were measured using a software-controlled source meter (Keithley 2400 Source-Meter) under dark conditions and the simulated sunlight irradiation of 1 sun (AM 1.5G; 100 mW cm⁻²) using a solar simulator (EMS- 35AAA, Ushio Spax Inc.) with an

Ushio Xe short arc lamp 500. The source meter was calibrated using a silicon diode (BS-520BK, Bunkokeiki). The SEM analysis of the perovskite films was performed using an S-4800 (Hitachi). The TEM images are taken by JEM-2010F (JEOL Ltd.) with a thermal field emission gun operated at 200 keV. The selected area electron diffraction (SAED) patterns are recorded by a charge-coupled device at a camera length of 60 cm.

Shimadzu UV-3150 was used for the UV-Vis-NIR measurement. The PL measurement for the chiral mapping and the films were obtained by a home-built micro-PL system with a supercontinuum laser as the excitation (wavelength: 450–2400 nm) and an InGaAs multiarray detector for detecting the emission (900–1600 nm in wavelength). Topography images were recorded by using an atomic force microscope (AFM) operating in tapping mode (SPI3800N, SII). The grazing-incidence XRD 2 θ scans were performed on a Jordan Valley D1 diffractometer with a copper K α 1 radiation and a parallel beam source. In the 2 θ scans, the scattering angle 2 θ between incident beam and diffracted beam changes, whereas the incident angle ω between the incident beam and the sample surface is fixed at 1°. The valence band and the Fermi levels measurements were performed using Riken Keiki PYS-A AC-2 and Kelvin probe spectroscopy in air (ESA), respectively. The photo-emission measurements were performed using XPS (PHI5000, Versa Probe) with monochromatic Al Kα radiation. Fermi levels were measured with a Riken Keiki PYS-A AC-2 photoelectron spectrometer in air. The incident photon-to-current conversion efficiency (IPCE) measurement system consisted of an MLS-1510 monochromator to scan the UV-Vis spectrum. A source measurement unit was used to record the current at each specific wavelength. Two home-made systems based on a Seki Technotron STR-250 laser Raman system (excitation wavelength of 633 nm and 785 nm) and an inVia Raman microscope (Renishaw) were used for Raman measurements. Solartron SI1287 Electrochemical Interface and Solartron 1255B

Frequency Response Analyzer were used for the Impedance Measurement. FT-IR spectra were obtained with a Nicolet Avatar 370 DTGS spectrometer which was fitted with a Smart Performer single-reflection accessory and a flat plate with a ZnSe crystal. For the TRMC measurement, thin film samples were prepared on a quartz plate. The sample was put in a resonant cavity and probed by continuous microwaves at *ca.* 9.1 GHz. The laser excitation from an optical parametric oscillator (OPO, Continuum, Panther) seeded by third-harmonic generation of a Nd:YAG laser (Continuum, Surelite II, 5–8 ns pulse duration, 10 Hz) was set at 500 nm. The photon density (I_0) varied from 1.28×10^{11} to 6.42×10^{14} photons cm⁻² pulse⁻¹. The photoconductivity transient $\Delta\sigma$ was converted to the product of the quantum efficiency of the charge-carrier generation at the pulse end (φ) and the sum of the charge carrier mobilities, $\Sigma\mu (=\mu^++\mu^-)$, by $\varphi\Sigma\mu = \Delta\sigma (eI_0F_{Light})^{-1}$, where *e* and F_{Light} are the unit charge of a single electron and a correction (or filling) factor, respectively.



Figure S1. Pictures of SWNTs without surfactants in water (left) and our s-SWNTs with DOCs dispersed in water (right).



Figure S2. A 3D graph indicating the relative abundance and chirality index (n,m) of s-SWNTs we purified.

(n,m) index	Diameter (nm)	Chiral angle (θ°)	E11 (nm)	E22 (nm)	PL Intensity (counts)	Relative Abundance (%)
(6,5)	0.76	27.00	983	570	5883	5.53
(7,5)	0.83	24.50	1022	638	9183	8.63
(7,6)	0.90	27.46	1113	642	18060	16.98
(8,3)	0.78	15.30	952	663	5875	5.52
(8,4)	0.84	19.11	1102	578	7523	7.07
(8,6)	0.97	25.28	1165	718	12026	11.31
(8,7)	1.03	27.80	1263	726	5453	5.13
(9,4)	0.92	17.48	1101	720	21780	20.48
(9,5)	0.98	20.63	1244	671	5862	5.51
(10,2)	0.88	8.948	1053	734	8731	8.21
(12,1)	0.99	3.963	1171	797	5978	5.62

Table S1. Chirality mapping table of the s-SWNT solution we purified.



Figure S3. AFM images of the drop-casted s-SWNTs on glass substrates.



Figure S4. Cross-sectional SEM images of the fabricated PSCs.



Figure S5. Current density–bias voltage (J-V) curves of the reference device (black), the wateradded PSC (blue), and the s-SWNT-added PSC (red).



Figure S6. Statistical analyses of the photovoltaic parameters of the reference devices (black), the water-added PSCs (blue), and the s-SWNT-added PSCs (red).



Figure S7. IPCE data of the reference devices (black), the water-added PSCs (blue), and the s-SWNT-added PSCs (red).



Figure S8. Maximum power point tracking of the reference devices and the s-SWNT-added PSCs.

Water additive concentration	J _{SC} (mA cm ⁻²)	<i>V</i> oc (V)	FF	<i>R</i> s (Ω cm²)	<i>R</i> _{SH} (Ω cm²)	PCE _{best} (%)	PCE _{average} (%)
1wt%	23.1	1.06	0.74	51.1	1.15x10⁴	18.2	17.9 ±0.3
2wt%	22.9	1.08	0.76	58.5	1.94x10⁵	18.7	18.3 ±0.4
3wt%	21.8	1.07	0.75	43.2	5.64x10⁵	17.5	17.2 ±0.3
5wt%	22.8	1.10	0.74	63.1	2.46x10⁵	18.3	18.1 ±0.4
10wt%	22.4	1.09	0.73	70.9	2.95x10⁵	17.9	17.3 ±0.4

Table S2. Photovoltaic performance of the water-added PSCs with varying water concentrations.



Figure S9. TEM images of (a), (c) the reference perovskite films and (b), (d) the s-SWNT-added perovskite films.



Figure S10. ESEM images of the reference MAPbI₃ films, the water-added MAPbI₃ films, and the s-SWNT-added MAPbI₃ films as we anneal the environmental temperature *in situ*.



Figure S11. DFT calculation modelling of interaction between Pb²⁺ and the Lewis donors.

	DMSO	H₂O	MA	DOC
Energy	-50.2	-14.2	-37.1	-392
Energy next to Pb ²⁺	-51.3	-15.2	-39.1	-393
Interaction energy (eV)	-0.506	-0.388	-1.331	-0.525

Table S3. DFT calculation of interaction between Pb^{2+} and the Lewis donors.



Figure S12. (a) XRD spectra of the reference MAPbI₃ films (black), the water-added MAPbI₃ films (red), and the s-SWNT-added MAPbI₃ films (blue). (b) Normalized (110) peak showing the FWHM trend.

Table S4. XRD peak characterizations and information for the reference MAPbI₃ films, the wateradded MAPbI₃ films, and the s-SWNT-added MAPbI₃ films.

Sample	Peak	Position (°)	Intensity	Peak Area	FWHM	Peak Ratio
Deneuslyite (ref.)	<110>	14.0	1242.87	604.41	0.456	1.97
Pelovskile (rel.)	<220>	28.2	905.02	517.53	0.548	1.37
Perovskite + Water	<110>	14.0	1799.25	900.18	0.469	1.04
	<220>	28.2	1456.85	860.55	0.571	1.24
	<110>	14.0	1799.25	492.46	0.448	1 50
Pelovskile + S-SWINT	<220>	28.3	1456.85	374.86	0.539	1.50



Figure S13. (a) Normalized (110) peak showing the FWHM trend of perovskite films with the increase in the s-SWNT concentration. (b) Magnified PbI_2 peaks of the perovskite films with the increase in the s-SWNT concentration.



Figure S14. XRD spectra of perovskite films with the increase in the s-SWNT concentration.

Table S5.	XRD peak characterizations and information for the s-SWNT-added MAPbI ₃ film	m with
varying s-S	SWNT _(aq) concentrations.	

Sample	Peak	Position (°)	Intensity	Peak Area	FWHM	Peak Ratio
Perovskite +	<110>	14.1	374653	39607	0.401	0.10
1wt% s-SWNT	<220>	28.4	320750	15818	0.388	2.18
Perovskite +	<110>	14.1	501915	37888	0.398	0.16
2wt% s-SWNT	<220>	28.4	451442	15172	0.402	2.10
Perovskite +	<110>	14.1	637150	39691	0.392	0.10
3wt% s-SWNT	<220>	28.4	582173	15736	0.403	2.19
Perovskite +	<110>	14.1	813492	51066	0.388	2.24
5wt% s-SWNT	<220>	28.4	734450	20489	0.386	2.24
Perovskite +	<110>	14.1	948474	39449	0.391	0.10
10wt% s-SWNT	<220>	28.4	894635	16531	0.385	2.13



Figure S15. (a),(c) Raw and (b),(d) their normalized PL spectra with the different excitation wavelength of the reference MAPbI₃ films (black), the water-added MAPbI₃ films (blue), and the s-SWNT-added MAPbI₃ films (red).



Figure S16. Time-resolved PL spectra of the reference MAPbI₃ films (black), the water-added MAPbI₃ films (blue), and the s-SWNT-added MAPbI₃ films (red).



Figure S17. Cross-sectional illustration of MAPbI3 films (above) and the s-SWNT-added MAPbI3 films (below).

DOC concentration	J _{SC} (mA cm ⁻²)	$V_{\rm oc}$ (V)	FF	$R_{\rm S}(\Omega \ {\rm cm^2})$	PCE _{best} (%)	PCE _{average} (%)
0.1 wt%	9.82	1.02	0.33	567	3.38	2.85 ±0.37
1.00 wt%	8.72	0.95	0.27	671	2.21	1.77 ±0.32

 Table S6. Photovoltaic performance of the DOC-added PSCs.



Figure S18. Conductive AFM images of the water-added MAPbI₃ films (left), and the s-SWNT-added MAPbI₃ films (right).

Table S7. EIS parameters for the PSCs of the reference MAPbI₃, the water-added MAPbI₃, and the s-SWNT added MAPbI₃.

Sample	Rs (Ω)	Rct (Ω)
Perovskite (ref.)	24.3	248.3
Perovskite + Water	82.1	121.2
Perovskite + s-SWNT	45.3	95.8

 m-SWNT concentration
 J_{SC} (mA cm⁻²)
 V_{OC} (V)
 FF
 R_S (Ω cm²)
 PCE_{best} (%)
 PCE_{average} (%)

 2 wt%
 15.28
 0.91
 0.47
 44.4
 1.43x10²
 6.6

 Table S8. Photovoltaic performance of the m-SWNT-added PSCs.

References

- 1. T. Tanaka, Y. Urabe, D. Nishide, H. Kataura, Appl. Phys. Express, 2009, 2, 125002.
- 2. T. Tanaka, Y. Urabe, D. Nishide, H. Liu, S. Asano, S. Nishiyama, H. Kataura, Phys. Status

Solidi B, 2010, **247**, 2867–2870.