

## Supporting Information

### Hexagonal Mesoporous Silica Islands to Enhance Both Transmittance and Efficiency of Planar Perovskite Solar Cells

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### Experiments

#### Synthesis of the mesoporous SiO<sub>2</sub> nanoparticles (HMS)

The HMS was prepared by exploiting dodecylamine (DDA) as the template [1]. 6.54 mL of DDA was dissolved in 50 mL of ethanol. Then, 50 mL of DW was added to above solution under vigorous stirring. Subsequently, 22.4 mL of tetraethylorthosilicate (TEOS) was added drop-wise at stirring until homogeneous dispersion. After aging at RT for 18 h, the wormhole-like HMS was obtained by filtration, washing, drying at 80 °C overnight, and calcination in air at 550 °C for 6 h.

#### Perpared of the mesoporous SiO<sub>2</sub> pastes

According to the reported [2], the pastes used for fabricating porous films were prepared by mixing 1 g SiO<sub>2</sub>, 0.5 g ethyl cellulose (EC), 3.5 g terpeneol and 25 g ethanol together. After ball milling for 3 h, the mixture was concentrated using a rotary evaporator to obtain viscous pastes.

#### Fabrication of the perovskite solar cells

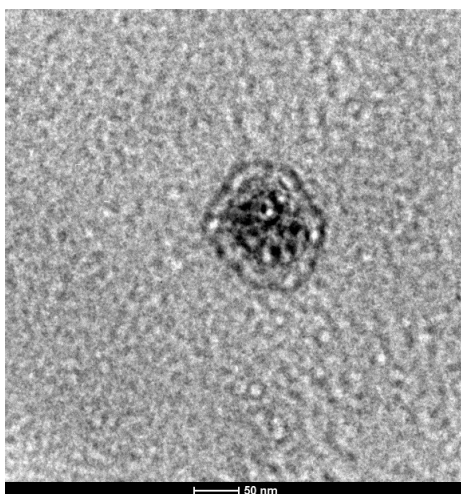
Chemically etched FTO glass (Nippon Sheet Glass) was cleaned with detergent solution, acetone, and isopropanol. To form a 20 to 25 nm thick TiO<sub>2</sub> blocking layer, diluted titanium diisopropoxide

bis(acetylacetonate) (TAA) solution (Sigma-Aldrich) in ethanol (0.2 ml of TAA in 6 ml of anhydrous ethanol) was sprayed at 450 °C. A mesoporous SiO<sub>2</sub> was coated on the substrate by spin coating at a speed of 2000 rpm for 10 s with a ramp-up of 1000 rpm s<sup>-1</sup> from SiO<sub>2</sub> paste in ethanol; the weight ratio of SiO<sub>2</sub> paste to ethanol is 15:1. After spin coating, the substrate was immediately dried on a hotplate at 80°C, and the substrates were then sintered at 500°C for 20 min before the deposition of the perovskite layer. MAPbI<sub>3</sub> precursor solution was prepared by mixing 1.2 M of PbI<sub>2</sub> and MAI in DMSO. And then, perovskite solutions are spin-coated on the substrates at 1000 rpm for 10 s and 5000 rpm for 30 s, respectively. 100 µL of chlorobenzene was dropped in 10 s at 5000 rpm. MAPbI<sub>3</sub> films were annealed at 100 °C for 20 min. The HTM solution was prepared by dissolving 91 mg of Spiro-OMeTAD (Merck) with additives in 1 mL of chlorobenzene. As additives, 21 µL of Li-bis(trifluoromethanesulfonyl) imide from the stock solution (520 mg in 1 mL of acetonitrile), 16 µL of FK209 [tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (375 mg in 1 mL of acetonitrile) and 36 µL of 4-tertbutylpyridine were added. The HTM layer was formed by spin-coating the solution at 4000 rpm for 20 s, and followed by the deposition of the 80 nm thick Au electrode by a thermal evaporation. All the preparative work to deposit perovskite and Spiro-OMeTAD was done inside the glove box filled with nitrogen to minimize the influence of moisture.

### **Characterization**

The **ultraviolet-visible absorption and transmission** was measured with PerkinElmer lambda 850 with 150 mm InGaAs integration sphere. Samples were illuminated with by a 450 W Xe lamp filtered through a double monochromator (5 nm landpass) directed onto the sample.

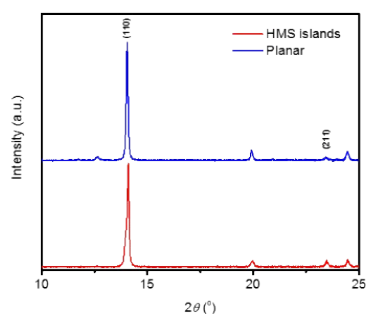
### **Transmission Electron Microscopy**



**Figure S1.** TEM images of HMS particles.

Samples for transmission electron microscopy (TEM) were prepared by drop-casting of dilute paste of the HMS on the holy-carbon TEM grids as support. Bright-field TEM images were acquired digitally on an 11 Megapixel Gatan ORIUS CCD camera.

**Wide angle X-ray diffraction** was performed using a D8 Advance diffractometer (Bruker AXS) model in an angle range of  $2\theta = 5^\circ - 40^\circ$  or  $10^\circ - 30^\circ$  (Bruker Corporation, Billerica, MA, USA).

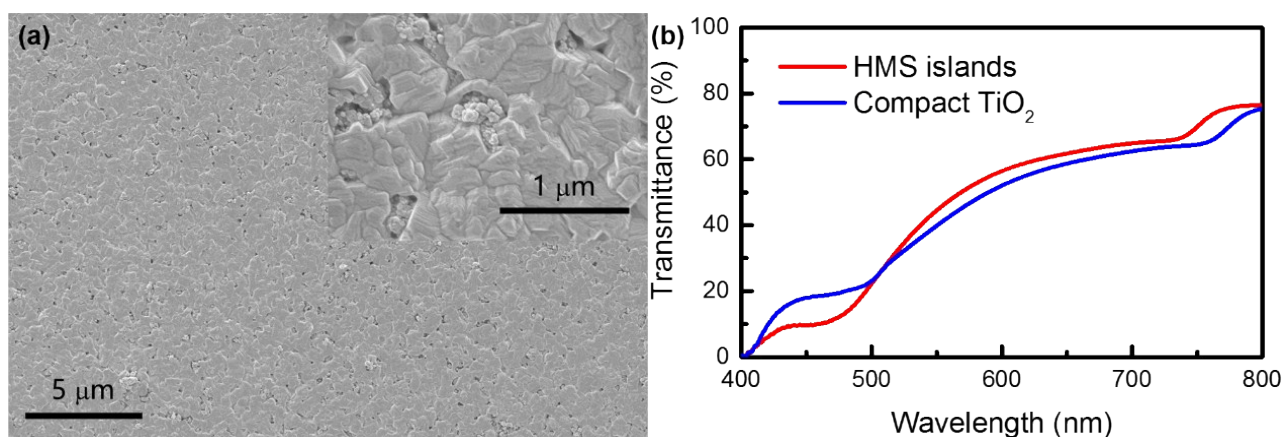


	Diffraction	Intensity	FWHM
Planar	(110)	84.78	<b>0.10939</b>
	(211)	1.585	0.16617
	Ratio ( $I_{(211)}/I_{(110)}$ )	<b>0.019</b>	
HMS islands	(110)	65.15	<b>0.13831</b>
	(211)	4.157	0.14382
	Ratio ( $I_{(211)}/I_{(110)}$ )	<b>0.064</b>	

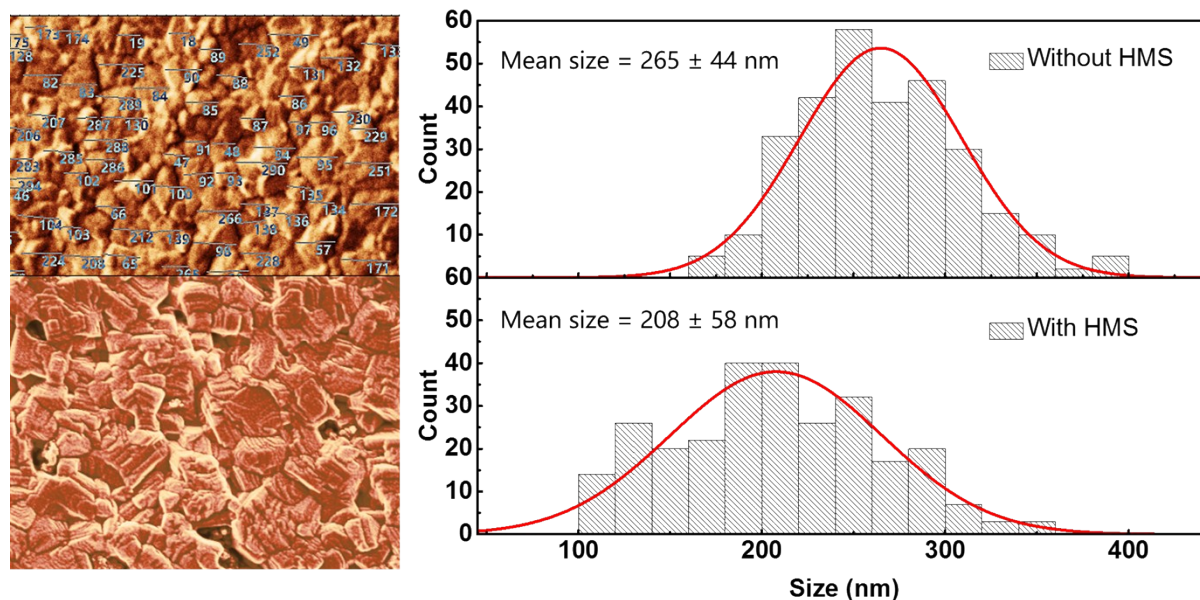
**Figure S2.** Comparison of two characteristic diffractions in the two perovskite films

### Scanning Electron Microscope

The morphology of the films was characterized using a high-resolution scanning electron microscope (SEM, ZEISS Merlin).



**Figure S3.** HMS islands in the perovskite layer and transmittance of two different perovskite films



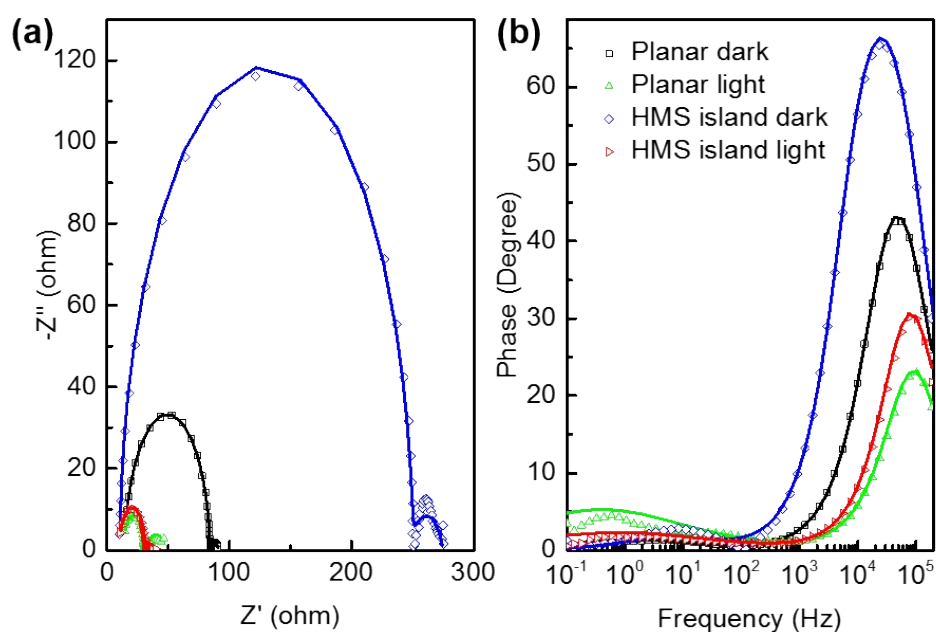
**Figure S4.** SEM images and grain size distribution histograms of the two different perovskite films for the statistics of grain size with high contrast color mode. Statistics of grain size distribution were conducted by transfer SEM images to a high contrast color mode by software of “wyddion”. These size bars were manually marked for each grain, and the grain size data was collected by software “wyddion”. The grains have irregular shapes. In order to get accurate size distribution, all the size bars were aligned in the same direction, and all grains in the images were included in the statistics without selection.

**Time-resolved PL experiments** were performed with the Fluorolog using a pulsed source either at 406 nm (NanoLED 402-LH from Horiba, pulse width < 200 ps, 11 pJ/pulse, approx. 1 mm<sup>2</sup> spot size)

or at 460 nm (Ps diode lasers BDS-SM, pulse with  $< 100$  ps, from Photonic Solutions, 0.2 pJ/pulse, approx. 1 mm<sup>2</sup> spot size) and the signal was recorded at 770 nm by the Time Correlated Single Photon Counting (TCSPC) technique. The samples were excited from the mesoporous SiO<sub>2</sub> side under ambient conditions. A mono-exponential fitting was used to analyze the background-corrected PL decay signal. The fitting lifetimes and the relative amplitudes for the as-prepared films are shown in the Figure.

### Impedance Measurements.

The impedance measurements were performed using a Bio-Logic SP200 potentiostat. A dc potential bias was applied and overlaid by a sinusoidal ac potential perturbation of 15 mV over a frequency range of 1 MHz to 300 MHz. The applied dc potential bias was changed by  $\sim 100$  mV steps from 0 to 1000 mV. The resulting impedance spectra were fitted using the ZView software (Scribner Associates Inc.).



**Figure S5.** (a) Nyquist plots of c-TiO<sub>2</sub>/HMS island/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Spiro-OMeTAD/Au and c-TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Spiro-OMeTAD/Au devices in the dark and illumination with bias at 1.0 V over the frequency range of 1 MHz to 300 MHz, and (b) the Bode plot for the device.

Samples	$R_s$ ( $\Omega$ )	$R_1$ ( $\Omega$ )	$Y_{02}$ ( $S \cdot sec^n/cm^2$ )	$n_2$	$R_2$ ( $\Omega$ )	$\tau_1$ (s)	$\tau_2$ (s)
Dark planar	14.48	69.39	0.02327	0.6366	7.124	0.06	3.52E-6
Light planar	12.75	17.43	0.04155	0.4283	21.05	0.41	1.75E-6
Dark HMS	10.47	238.9	0.003159	0.7262	25.26	0.02	6.68E-6
Light HMS	9.986	20.79	0.06733	0.3977	8.701	0.19	1.98E-6

**Table S1.** EIS results of the devices with and without HMS islands

**Device Measurement:** Current–voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400). The light source was a 450 W xenon lamp (Oriol) equipped with a SchottK113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cutoff filter (KG-3, Schott). IPCE spectra were recorded as functions of wavelength under a constant white light bias of  $\approx 10 \text{ mW cm}^{-2}$  supplied by an array of white light emitting diodes. The excitation beam coming from a 300 W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) and chopped at  $\approx 2 \text{ Hz}$ . The signal was recorded using a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems). All measurements were conducted using a nonreflective metal aperture of  $0.16 \text{ cm}^2$  to define the active area of the device and avoid light scattering through the sides.

**Table S2.** Photovoltaic parameter of short-circuit photocurrent density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor ( $FF$ ) and power conversion efficiency ( $PCE$ ) of 30 sample with and without HMS islands. Temperature and relative humidity were about  $20 \sim 30 \text{ }^\circ\text{C}$  and  $25 \sim 30\%$ .

Planar + HMS islands	$J_{sc}$	$V_{oc}$	$FF$	$PCE$	$R_s$	Planar Junction	$J_{sc}$	$V_{oc}$ (V)	$FF$	$PCE$ (%)	$R_s$
	( $\text{mA}/\text{cm}^2$ )	(V)		(%)	( $\Omega$ )		( $\text{mA}/\text{cm}^2$ )				( $\Omega$ )
	21.15	1.086	0.747	17.16	1.11		21.13	1.081	0.723	16.52	1.05
	21.58	1.069	0.742	17.11	1.15		19.8	1.071	0.742	15.73	1.6
	22.11	1.07	0.724	17.14	1.11		19.78	1.07	0.745	15.77	1.4

	21.95	1.09	0.758	18.08	0.847		20.62	1.052	0.7	15.19	1.26
	21.61	1.1	0.772	18.37	0.881		20.83	1.052	0.719	15.74	1.15
	20.87	1.11	0.774	17.94	0.998		19.83	1.074	0.746	15.85	1.34
	22.27	1.07	0.737	17.52	1.2		19.91	1.069	0.735	15.65	1.07
	20.69	1.11	0.769	17.62	1.14		19.83	1.071	0.743	15.78	1.19
	21.41	1.09	0.755	17.57	1.12		19.77	1.089	0.742	15.97	1.05
	21.65	1.07	0.742	17.24	1.21		20.05	1.091	0.725	15.86	1.11
	21.68	1.11	0.765	18.39	0.903		20.01	1.093	0.734	16.06	1.07
	21.09	1.09	0.766	17.53	1.12		19.89	1.072	0.745	15.88	1.1
	22.29	1.1	0.76	18.61	0.882		19.93	1.072	0.74	15.82	1.3
	21.98	1.07	0.752	17.62	1.22		19.98	1.073	0.738	15.83	1.31
	21.24	1.09	0.742	17.21	1.19		19.97	1.074	0.743	15.92	1.21
	22.35	1.08	0.724	17.43	1.23		20.05	1.075	0.747	16.09	1.03
	21.97	1.1	0.75	18.05	1.01		19.97	1.075	0.746	16.01	1.04
	21.73	1.09	0.743	17.53	1.23		19.97	1.075	0.742	15.93	1.1
	21.49	1.09	0.746	17.54	1.3		20.6	1.08	0.749	16.68	0.983
	22.11	1.08	0.73	17.35	1.25		20.59	1.083	0.746	16.63	1.01
	20.15	1.09	0.78	17.05	1.33		20.65	1.084	0.751	16.81	0.988
	21.14	1.08	0.748	17.15	1.41		19.29	1.079	0.746	15.52	1.3
	22.41	1.07	0.761	18.33	0.922		19.36	1.079	0.748	15.63	1.31
	20.43	1.1	0.769	17.35	1.23		21.59	1.055	0.678	15.44	1.2
	21.8	1.08	0.741	17.35	1.3		21.62	1.055	0.684	15.61	1.15
	21.77	1.08	0.749	17.67	1.18		21.54	1.057	0.646	14.71	2.72
	21.47	1.09	0.751	17.53	1.24		19.25	1.08	0.745	15.48	1.55
	21.03	1.08	0.749	17.08	1.33		19.41	1.082	0.748	15.71	1.6
	21.6	1.1	0.705	16.72	1.54		19.48	1.085	0.744	15.72	1.52
	21.58	1.09	0.749	17.59	1.41		19.73	1.088	0.741	15.91	1.41
Average	21.55 ± 0.56	1.09 ± 0.01	0.75 ± 0.02	17.56 ± 0.45	1.17		20.15 ± 0.66	1.07 ± 0.01	0.73 ± 0.02	15.85 ± 0.42	1.27

[1] P.T. Tanev, T.J. Pinnavaia, A neutral templating route to mesoporous molecular sieves. Science, 1995, 267, 865–867

[2] Y. Zhang, et al. Preparation of Dye Sensitized Solar Cells with high photocurrent and photovoltage

by using mesoporous TiO<sub>2</sub> particles as photoanode material. Nano Research, 2015, 8(12), 3830–3841