## Dark-blue mirror-like perovskite dense films for efficient organic-inorganic hybrid solar cells

**Supporting Information** 

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## **Experimental procedures:**

**Synthesis of TiO<sub>2</sub> paste**. 10~20 nm anatase-TiO<sub>2</sub> nanoparticles were synthesized via a hydrothermal approach reported elsewhere with some modifications.<sup>1-2</sup> Typically, 19.9 g titanium (IV) isopropoxide was mixed with 4.2 g acetic acid and stirred at room temperature for 15 min. Then the mixed solution was poured into 101 mL deionized water and stirred for 60 min at room temperature with a rate of 1000 rpm. Next, 1.4 mL 65% nitric acid (HNO<sub>3</sub>) was added to the solution and stirred for 40 min, followed by reflux at 80 °C for further 60 min. 20 mL deionized water was then added, before transferring all of the solution to Teflon reactors in an oven held at 250 °C for 12 h. After cooling to room temperature, 0.84 mL 65% HNO<sub>3</sub> was added, followed treated with a 40 W ultrasonic probe at frequency of 60 pulses every 2 s. The resultant solution was centrifuged at 7500 rpm and rinsed with water for three

times. Centrifugation and rinsing were repeated three more times with ethanol before a white precipitate containing 40 wt%  $TiO_2$  in absolute ethanol was obtained. 0.72 g ethyl cellulose, 0.14 g lauric acid, and 7.2 g terpineol were added into the 3.75 g 40 wt% ethanol solution of  $TiO_2$  particles, and then the ethanol was removed from the solution employing a rotary evaporator to prepare viscous  $TiO_2$  pastes.

**Synthesis of TiO<sub>2</sub>-coated FTO substrates.** FTO-coated glass substrates were etched with Zn powder and 37% HCl to obtain the required pattern. The etched FTO substrates were then cleaned by hellmanex detergent, deionized water, acetone, isopropanol and ethanol respectively, followed by drying with N<sub>2</sub> blow. The clean FTO substrates were coated with a TiO<sub>2</sub> blocking layer through spin-coating a 0.15 M titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol) in 1-butanol at 2000 rpm for 40 s, followed by heating at 125 °C for 5 min. After cooling to room temperature, a diluted TiO<sub>2</sub> paste solution (0.12 g TiO<sub>2</sub> paste in 1 mL ethanol) was spin-coated on the TiO<sub>2</sub> blocking layer at 2000 rpm for 10 s, and dried at 120 °C for 10 min. After that, the resultant substrates were annealed at 550 °C for 30 min, providing a thickness of 130~150 nm (Fig. S1). The mesoporous TiO<sub>2</sub> films were immersed in a 0.04 M aqueous TiCl<sub>4</sub> solution at 90 °C for 10 min. After washing with deionized water, the films were annealed at 550 °C for 20 min to obtain the TiO<sub>2</sub>-coated FTO substrates for perovskite deposition.



Fig. S1 Linear surface profile of the  $TiO_2$ -coated FTO substrate monitored by thickness profiler (a) and the enlarged pattern (b).

Synthesis of organometal halide perovskite precursor solution. Perovskite precursors were prepared according to the reported procedure with some modifications.<sup>3-4</sup> Typically, 36 mL methylamine (CH<sub>3</sub>NH<sub>2</sub>) (33 wt% in absolute ethanol) was reacted with 15 mL hydroiodic acid (HI) (57 wt % in water) with stirring at 0 °C for about 2 h to synthesize methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I). Crystallization of CH<sub>3</sub>NH<sub>3</sub>I was achieved using a rotary evaporator at 60 °C for 2~3 h. The obtained CH<sub>3</sub>NH<sub>3</sub>I powder was washed with diethyl ether and dried in a vacuum oven at 50~60 °C for 24 h. Pbl<sub>2</sub> was prepared as yellow precipitate by mixing solutions of 0.05 mole (16.56 g) Pb(NO<sub>3</sub>)<sub>2</sub> and 0.1 mole (16.6 g) KI, followed by drying in a vacuum oven at 50~60 °C for 24 h. 1.6 M clear perovskite precursor solution was obtained by mixing 3.688 g Pbl<sub>2</sub> and 1.272 g CH<sub>3</sub>NH<sub>3</sub>I in a mixed solvent containing 5 mL DMF and 600 µL DMSO at room temperature with stirring for 15~30 min.

Dark-blue mirror-like perovskite thin film fabrication. Dark-blue mirror-like perovskite films were prepared by the solvent-treated two-step spin-coating method. First, 100 µL clear perovskite solution (1.6 M) was spin-coated on the surface of the  $TiO_2$ -coated FTO substrate (active area 1\*1.5 cm<sup>2</sup>) at 2000 rpm for 15 s (the first-step process). After the substrate was completely frozen, 1.5 mL nonpolar solvent (e.g. diethyl ether, toluene, chloroform, dichloromethane, chlorobenzene, and n-butanol, typically diethyl ether for the best device performance and reproducibility) was immediately spread over the substrate to wash the as-prepared film within 3~5 s. Then the substrate was accelerated again to get rid of the excess solvent left in the nonpolar solvent scouring process and spun at 5000 rpm for 20 s, resulting in a transparent film formed on the substrate (the second-step process). The resultant film was heated at 100 °C for 2 min to synthesize dark-blue mirror-like perovskite film. The procedure of the spin-coater is summarized in Fig. S2. Dark-blue mirror-like perovskite films with different thicknesses were obtained by employing different rotation speeds (4000, 5000, and 6000 rpm) in the second-step spin-coating process to investigate the effect of the film thickness on the absorption and the photovoltaic

3



Fig. S2 Procedure of the spin-coater in the solvent-treated two-step spin-coating method.

**Dark-brown perovskite thin film fabrication.** Dark-brown perovskite films were prepared by the conventional solvent engineering one-step spin-coating process, where the nonpolar solvent is added to the substrate while spinning.<sup>5-7</sup> Typically, 100  $\mu$ L perovskite solution was dropped onto the TiO<sub>2</sub>-coated FTO substrate (active area 1\*1.5 cm<sup>2</sup>). The substrate was then spun at 5000 rpm for 35 s and 1.5 mL diethyl ether was quickly dropped onto the center of the spinning substrate within 5 s. Darkbrown perovskite film was prepared by heating the resultant film at 100 °C for 2 min. The procedure of the spin-coater is summarized in Fig. S3. Dark-brown perovskite films with different thicknesses were obtained by employing different rotation speeds (3000, 4000, and 5000 rpm) in the spin-coating process to investigate the effect of the film thickness on the absorption and the photovoltaic performances.



Fig. S3 Procedure of the spin-coater in the solvent-treated one-step spin-coating method.

**Solar cell fabrication**. The as-prepared perovskite films were spin-coated with a 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD) solution at 4000 rpm for 20 s, which was obtained by dissolving 73 mg spiro-MeOTAD in 1 mL chlorobenzene, 29  $\mu$ L 4-tert-butyl pyridine (TBP) and 18  $\mu$ L lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) (520 mg LI-TSFI in 1 mL acetonitrile) solution. Finally, a 100~150 nm Au layer was thermally evaporated on the spiro-MeOTAD layer as counter electrode.

**Characterizations**. The morphologies of the synthesized perovskite films were characterized by a field emission scanning electron microscope (Zeiss Supra-55) operated at 10 kV and an optical microscope (Olympus BX51). Statistical histograms of the pinhole sizes were summarized from the optical microscopic images with magnification of 50 X. AFM characterizations were performed using a Bruker Innova in tapping mode. The AFM images were measured by scanning over a range of 15\*15  $\mu$ m<sup>2</sup> at a resolution of 256\*256 data points. The thicknesses of the TiO<sub>2</sub> films and the

synthesized perovskite films were characterized by a Stylus Profiler (Bruker Dektak XT) and confirmed by cross-sectional SEM images. X-ray diffraction (XRD) patterns of the samples were obtained using a diffractometer (Rigaku RINT2000 X-Ray) with Cu K $\alpha$  radiation at a scan rate of 4° min<sup>-1</sup> under operation condition of 50 kV and 80 mA. Ultraviolet-visible diffuse absorption spectra were recorded on a spectrophotometer (Hitachi U3900) in 450~850 nm wavelength at room temperature. Photoluminescence (PL) spectra were obtained by an optical spectrometer system (Horiba HR Evolution) with a 50 mW laser ( $\lambda$  = 532 nm) as excitation source. Fabricated photovoltaic cells were characterized by incident photon-to-current conversion efficiency (IPCE) and current-voltage (J-V) tests in air. The IPCE values were measured by an EQE system (Oriel IQE200) under DC mode, where a 300 W Xenon lamp was used as the light source for generating monochromatic beam. The J-V curves of the photovoltaic cells were measured under AM 1.5 G one sun illumination (100 mW cm<sup>-2</sup>) with a solar simulator (Newport 94021A), a source meter (Keithley 4200), and a calibrated Si-reference cell certified by NREL. The J-V curves were recorded by forward (from short-circuit to open-circuit) and reverse (from open-circuit to short-circuit) modes with a scan rate of 10 mV s<sup>-1</sup> and a delay time of 40 ms. All devices were measured by masking the active area with a shadow mask  $(0.196 \text{ cm}^2 \text{ in area})$  and placed in the dark prior to the start of the measurement without any voltage applied both for the reverse and forward scans.

## **Reference:**

- 1. S. Ito et al., *Thin Solid Films*, 2008, **516**, 4613.
- 2. J. A. Chang et al., Nano lett., 2010, 10, 2609.
- 3. H. S. Kim et al., *Sci. Rep.*, 2012, **2**, 591.
- 4. A. Kojima et al., J. Am. Chem. Soc., 2009, 131, 6050.
- 5. N. J. Jeon et al., Nat. Mater., 2014, **13**, 89.
- 6. N. Ahn et al., J. Am. Chem. Soc., 2015, 137, 8696.
- 7. M. Xiao et al., Angew. Chem. Int. Ed., 2014, 53, 9898.



**Fig. S4**. Optical microscopic (a) and SEM (b) images of the perovskite film prepared by the solvent-treated two-step spin-coating approach with inappropriate nonpolar solvent treatment (dropwise dripping).



**Fig. S5**. Optical microscopic images of perovskite films prepared by the solventtreated two-step spin-coating approach, where diethyl ether (a), toluene (b), chloroform (c), dichloromethane (d), chlorobenzene (e), and n-butanol (f) were employed as the nonpolar solvent added between the first- and the second-step spin-coating processes.



Fig. S6. Statistical histograms of the pinhole sizes summarized from the optical microscopic images shown in Fig. S5.



Fig. S7. SEM images of perovskite films prepared by the solvent-treated two-step spin-coating approach, where diethyl ether (a), toluene (b), chloroform (c), dichloromethane (d), chlorobenzene (e), and n-butanol (f) were employed as the nonpolar solvent added between the first- and the second-step spin-coating processes.



**Fig. S8**. Diffuse absorbance spectra for perovskite films prepared by the solventtreated two-step spin-coating approach with treatment of different nonpolar

solvents.



**Fig. S9** Full-width at half-maximum (FWHM) of the 110 XRD peaks for perovskite films prepared by different solvent-treated spin-coating processes.



Fig. S10. (a-c) Cross-sectional SEM images of dark-brown perovskite films on TiO<sub>2</sub>-coated FTO substrates prepared by the one-step spin-coating approach with different rotation speeds. (d-i) Linear surface profiles of perovskite films monitored by thickness profiler (d-f) and their enlarged patterns (g-i). Rotation speed for sample (a, d, g), (b, e, h) and (c, f, i) is 5000, 4000, and 3000 rpm, respectively. Since there is a TiO<sub>2</sub> layer with thickness of ~150 nm on the FTO, the calculated thickness is about 350, 400, and 480 nm for the sample (a, d, g), (b, e, h) and (c, f, i), respectively.



Fig. S11 Photograph of dark-brown perovskite films prepared by the one-step spin-

coating approach with different rotation speeds.





rotation speeds.



Fig. S13 Cross-sectional SEM image of the dark-brown perovskite film-based solar

cell and the device schematic illustration.



Fig. S14 (a-c) Cross-sectional SEM images of dark-blue perovskite films on TiO<sub>2</sub>- coated FTO substrates prepared by the two-step spin-coating approach with different rotation speeds in the second-step spin-coating process. (d-i) Linear surface profiles of perovskite films monitored by thickness profiler (d-f) and their enlarged patterns (g-i). Rotation speed in the second-step spin-coating process for sample (a, d, g), (b, e, h) and (c, f, i) is 6000, 5000, and 4000 rpm, respectively. Since there is a TiO<sub>2</sub> layer with thickness of ~150 nm on the FTO, the calculated thickness is about 300, 350, and 450 nm for the sample (a, d, g), (b, e, h) and (c, f, i), respectively.







**Fig. S16** *J-V* curves for the best-performing solar cells based on dark-blue mirror-like perovskite films with different thicknesses. The curves were performed by reverse mode (from open-circuit to short-circuit) with a scan rate of 10 mV s<sup>-1</sup> and a delay time of 40 ms under AM 1.5 G illumination. The data is summarized from 30 samples for ~350 nm film and 5 samples for others.



**Fig. S17** *J-V* curves for the best-performing solar cells based on dark-brown perovskite films with different thicknesses. The curves were performed by reverse mode (from open-circuit to short-circuit) with a scan rate of 10 mV s<sup>-1</sup> and a delay time of 40 ms under AM 1.5 G illumination. The data is summarized from 30 samples for ~350 nm film and 5 samples for others.

Perovskite film	Film thickness	J <sub>sc</sub> (mA cm <sup>-</sup>	Voc	FF	PCE
	(nm)	<sup>2</sup> )	(V)		(%)
Dark-blue mirror-like	~300	20.92	0.96	0.682	13.7
film	~350	23.13	0.96	0.723	16.1
	~450	22.35	0.97	0.665	14.4
Dark-brown film	~350	21.12	0.97	0.699	14.3
	~400	21.32	0.97	0.647	13.4
	~480	20.27	0.96	0.646	12.6

**Table S1** Photovoltaic properties of the best-performing solar cells based onperovskite films fabricated by solvent-treated spin-coating processes



**Fig. S18** Comparison of histograms of photovoltaic parameters for solar cells based on ~350 nm dark-blue mirror-like perovskite films (a, c, e, g) and ~ 350 nm darkbrown perovskite films (b, d, f, h).