

## Supporting Information

### Chemical Management for Colourful, Efficient, and Stable Inorganic-Organic Hybrid Nanostructured Solar Cells

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#### Experimental Section

**Solar cell fabrication.** A 60-nm-thick dense blocking  $\text{TiO}_2$  (bl- $\text{TiO}_2$ ) was deposited onto a F-doped  $\text{SnO}_2$  (FTO, Pilkington, TEC8) substrate by a spray pyrolysis deposition with a 20 mM titanium diisopropoxide bis(acetylacetonate) (Aldrich) solution at 450 °C to prevent direct contact between FTO and the hole-conducting layer. A 600-nm-thick mesoporous  $\text{TiO}_2$  (mp- $\text{TiO}_2$ ) films were screen-printed onto the bl- $\text{TiO}_2$ /FTO substrate using the paste, which was prepared according to a reported method,<sup>1</sup> and the films were calcined at 500 °C for 1 h to remove the organic part. The films were then immersed in a 40 mM  $\text{TiCl}_4$  aqueous solution at 60 °C for 1 h and then were heat-treated at 500 °C for 30 min to improve interfacial contact with the nanocrystalline  $\text{TiO}_2$ .  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{CH}_3\text{NH}_3\text{Br}$  were synthesized from 30 mL hydroiodic acid (57% in water, Aldrich) or 44 mL hydrobromide acid (48% in water, Aldrich), respectively, by reacting 27.86 mL methylamine (40% in methanol, Junsei Chemical Co., Ltd.) in a 250-mL round-bottomed flask at 0 °C for 2 h with stirring. The precipitates were recovered by evaporation at 50 °C for 1 h. The products were dissolved in ethanol, recrystallized from diethyl ether, and finally dried at 60 °C in a vacuum oven for 24 h. The  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution of 40 wt% was made by reacting the synthesized  $\text{CH}_3\text{NH}_3\text{I}$  powder and  $\text{PbI}_2$  (Aldrich) at a 1:1 mol ratio in  $\gamma$ -butyrolactone at 60 °C for 12 h. The  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  solution of 28.5 wt% was made by reacting the synthesized  $\text{CH}_3\text{NH}_3\text{Br}$  powder and  $\text{PbBr}_2$  (Aldrich) at a 1:1 mol ratio in dimethylformamide at 60 °C for 12 h. The desired  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$  solutions were made by stoichiometric mixing of synthesized

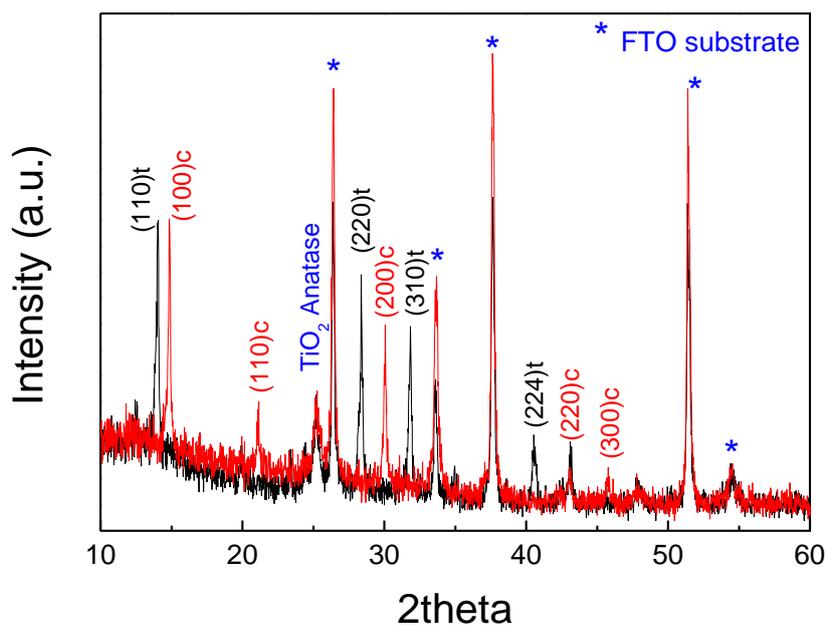
CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> solutions at 60 °C for 1 h. The CH<sub>3</sub>NH<sub>3</sub>Pb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> solution was then coated onto the mp-TiO<sub>2</sub>/bl-TiO<sub>2</sub>/FTO substrate by consecutive spin coating at 2000 rpm for 60 s and at 3000 rpm for 60 s and then dried on a hot plate at 100 °C for 5 min. A poly-triarylamine (PTAA) (EM index, Mw = 17,500 g/mol)/toluene (15 mg/1ml) solution with an additive of 13.6 µl Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (28.3 mg/1 ml) and 6.8 µl 4-*tert*-butylpyridine (TBP) was spin-coated on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/mp-TiO<sub>2</sub>/bl-TiO<sub>2</sub>/FTO substrate at 3000 rpm for 30 s. Finally, an Au counterelectrode was deposited by thermal evaporation. The active area was fixed at 0.16 cm<sup>2</sup>.

**Materials characterization.** The morphology of the mp-TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> bilayer nanocomposites was observed with a field-emission scanning electron microscopy (FESEM, Tescan Mira 3 LMU FEG). The structure analysis of CH<sub>3</sub>NH<sub>3</sub>Pb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> deposited on mp-TiO<sub>2</sub> was conducted by X-ray diffraction (XRD, Rigaku D/Max II X-ray diffractometer) using Cu K $\alpha$  radiation ( $\lambda=0.1542$  nm). The absorption spectra of the mp-TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> bilayer nanocomposites were measured using a UV-Vis spectrometer (Hitachi U-3300) with an integrated sphere.

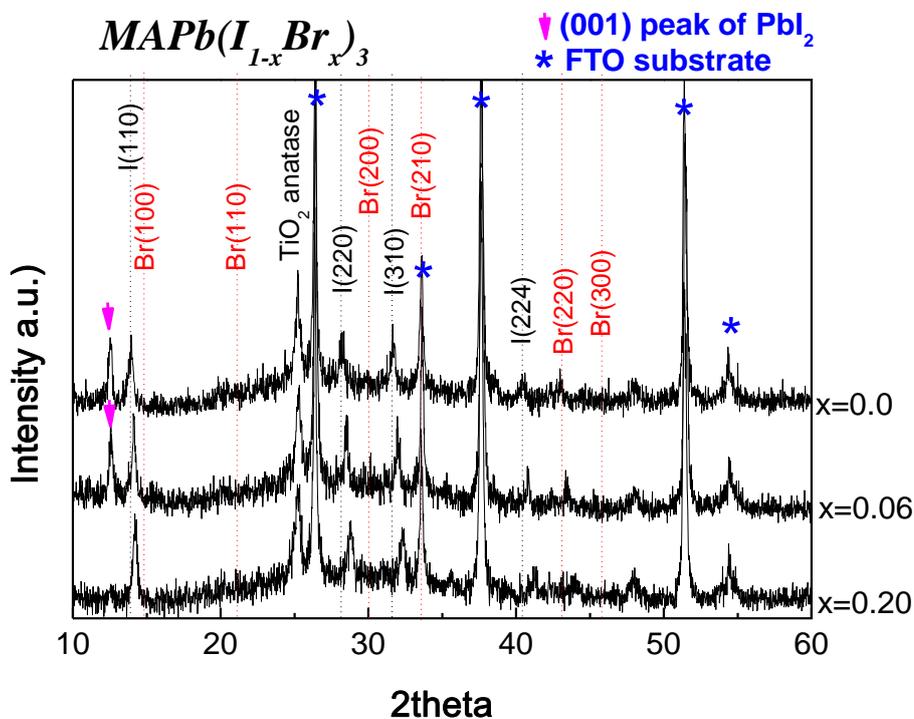
**Device characterization.** The IPCE was measured by a power source (Newport 300W Xenon lamp, 66920) with a monochromator (Newport Cornerstone 260) and a multimeter (Keithley 2001). The current density-voltage (*J-V*) curves were measured by a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) at 100 mA cm<sup>-2</sup> illumination AM 1.5G and a calibrated Si-reference cell certificated by NREL. The *J-V* curves of all devices were measured by masking the active area with a metal mask of 0.096 cm<sup>2</sup>.

## Reference

- (1) Chang, J. A.; Rhee, J. H.; Im, S. H.; Lee, Y. H.; Kim, H.; Seok, S. I.; Nazeeruddin, Md. K.; Grätzel, M. *Nano Lett.* **2010**, *10*, 2609–2612.

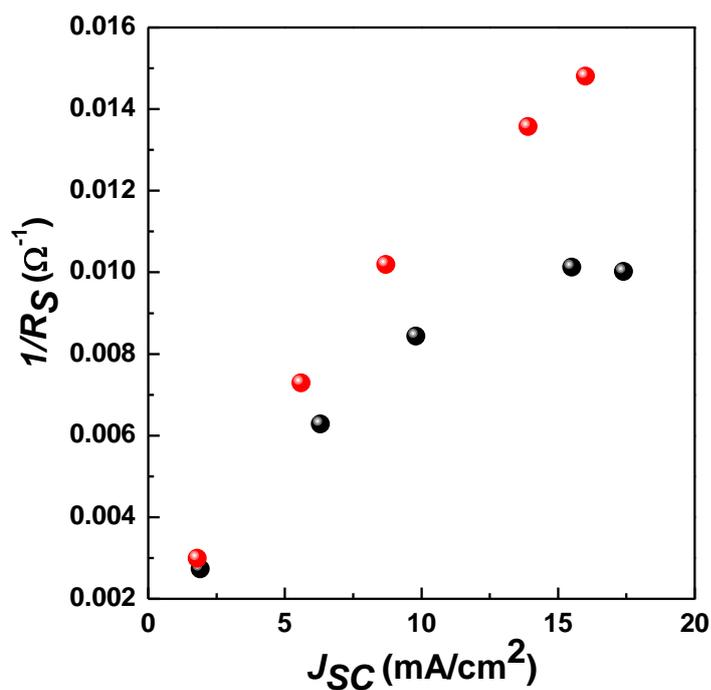


**Figure S1.** XRD patterns of MAPbI<sub>3</sub> (black line) and MAPbBr<sub>3</sub> (red line) deposited on mp-TiO<sub>2</sub>/FTO glass substrate.  $(hkl)_t$  and  $Br(hkl)_c$  indicate diffraction peak for  $(hkl)$  plane of tetragonal MAPbI<sub>3</sub> and cubic MAPbBr<sub>3</sub>, respectively.



**Figure S2.** XRD patterns of MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> ( $x = 0, 0.06, \text{ and } 0.20$ ) deposited on mp-

TiO<sub>2</sub>/FTO glass substrate after exposure to 55% humidity for 1 day. The peak around 12.5° at x=0 and 0.06 appeared after the exposure which is indexed by (001) peak of PbI<sub>2</sub>.  $I(hkl)$  and  $Br(hkl)$  indicate diffraction peak for  $(hkl)$  plane of MAPbI<sub>3</sub> and MAPbBr<sub>3</sub>, respectively.



**Figure S3.** The relationship between reciprocal series resistance and short circuit current density ( $J_{sc}$ ) for the cells fabricated from MAPbI<sub>3</sub> and MAPb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub> as light harvesters.  $J_{sc}$  was obtained as a function of light intensity.