Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Laminar $MAPbBr_3/MAPbBr_{3-x}I_x$ graded heterojunction single crystal for enhancing charge extraction and optoelectronic performance

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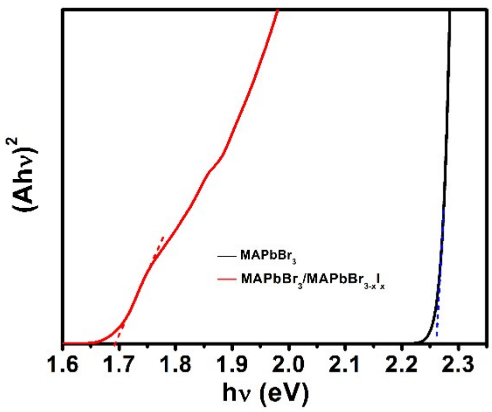

Fig. S1 Tauc plots of the laminar $MAPbBr_3$ SC and $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC.

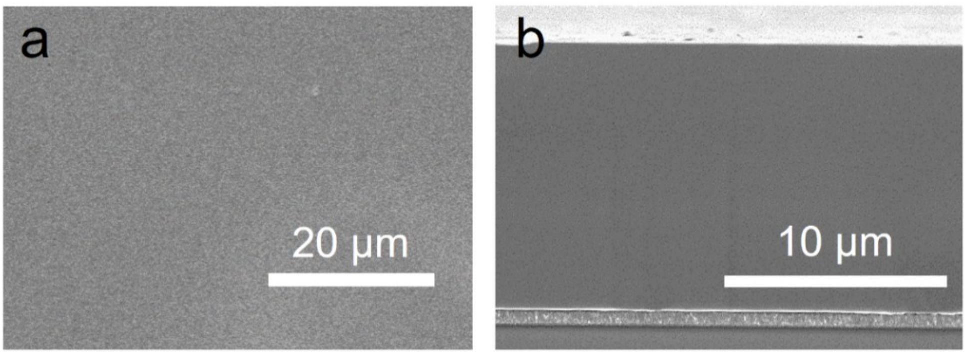

Fig. S2 (a) The surface and (b) cross-sectional SEM images of the laminar $MAPbBr_3$ SC.

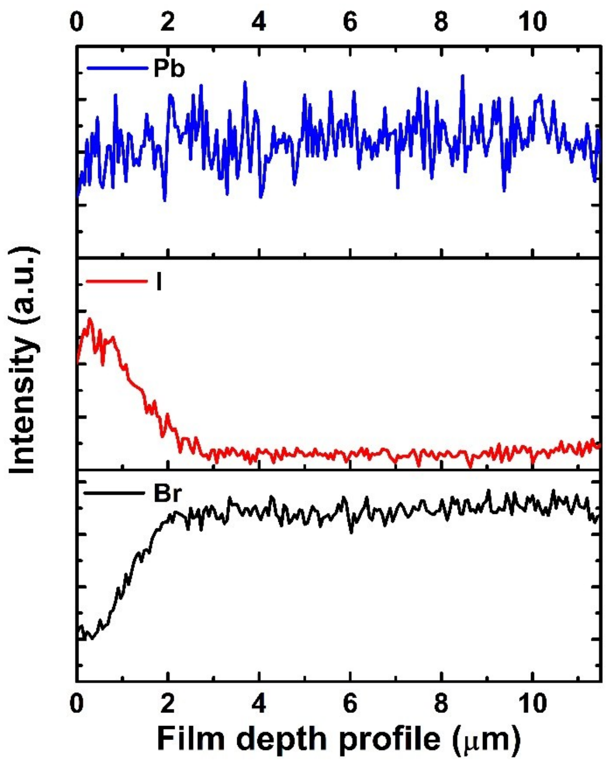

Fig. S3 The cross-sectional EDX linescan of the laminar $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC.

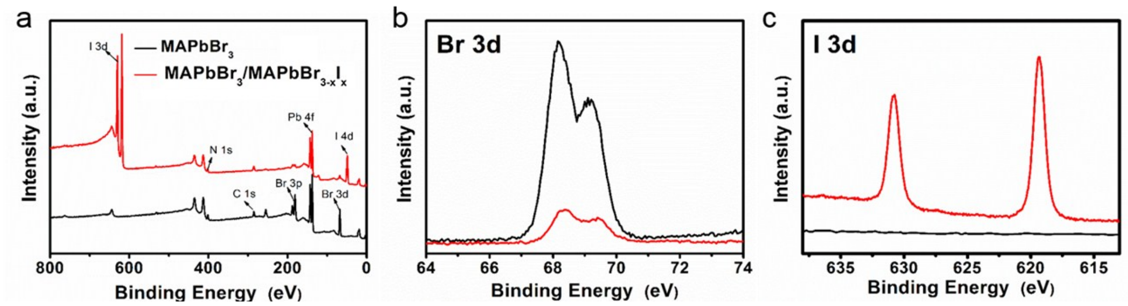

Fig. S4 (a) XPS spectra of the laminar $MAPbBr_3$ SC and $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC, (b) Br 3d peak and (c) I 3d peak.

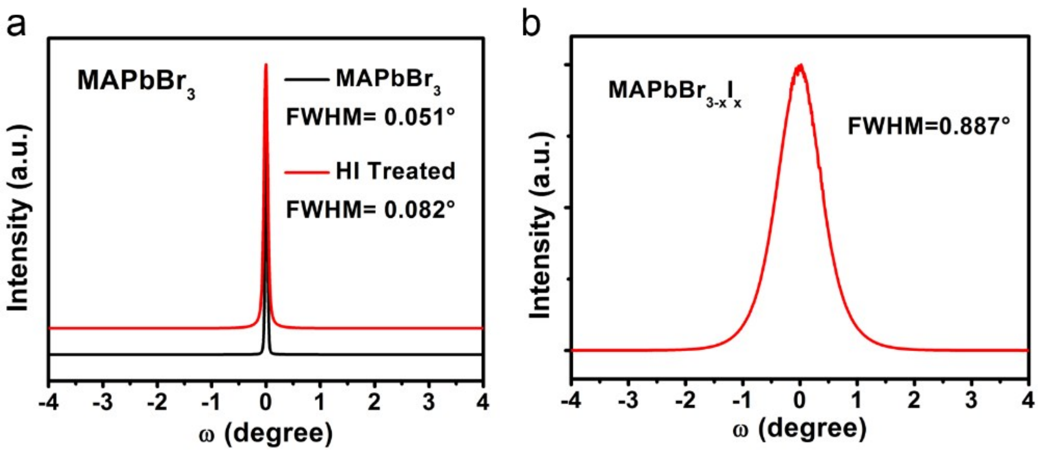

Fig. S5 High-resolution X-ray diffraction analysis on laminar $MAPbBr_3$ SC and $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC: rocking curve of (a) the 14.97° peak of $MAPbBr_3$ and (b) the 14.26° peak of $MAPbBr_{3-x}I_x$.

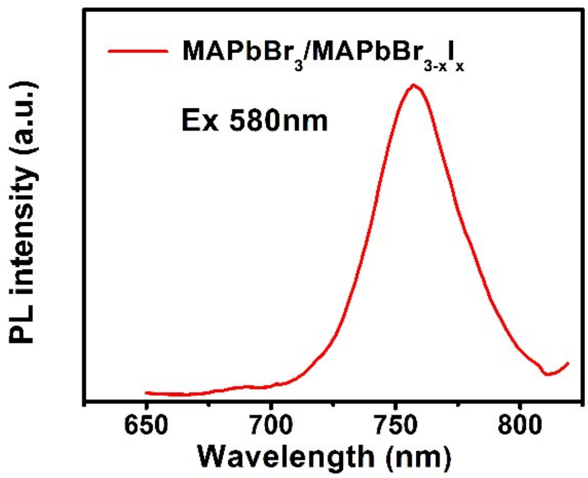

Fig. S6 The PL spectrum of the laminar $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC under 580 nm excitation from the glass side.

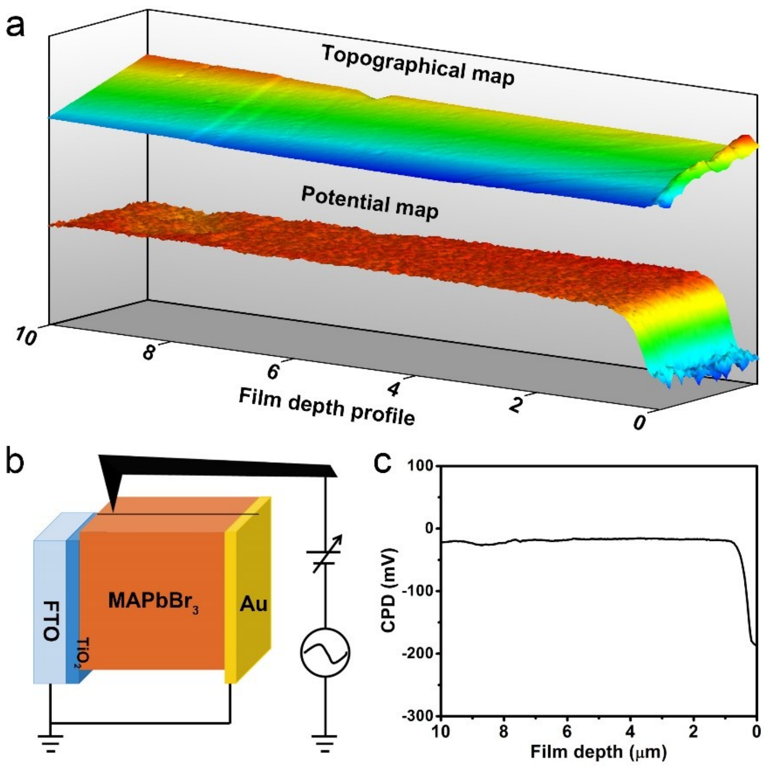

Fig. S7 (a) AFM topography and the corresponding KPFM CPD map across the cross-section of the laminar $MAPbBr_3$ SC on TiO_2/FTO substrate. (b) Schematic of cross-sectional KPFM measurement setup in short-circuit mode. 100 nm gold film was deposited on the single crystal surface and the FTO substrate by sputtering to both make well grounding. (c) CPD depth profile averaged from (a) along the lateral direction of the cross-section.

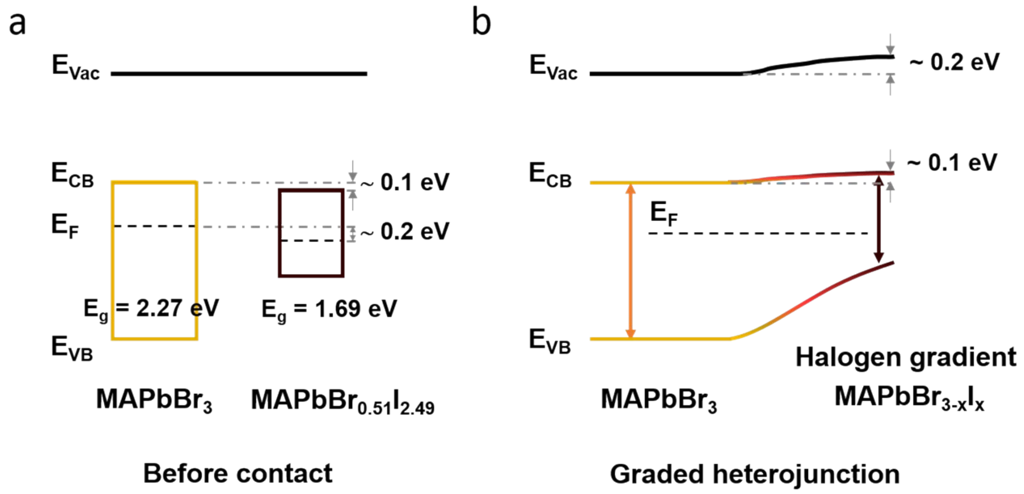

Fig. S8 (a) The relative energy band position between the pure $MAPbBr_3$ and the iodine-rich $MAPbBr_{3-x}I_x$ component deduced from the KPFM result and the previous reports. (b) The proposed band alignment of the $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC.

The KPFM result of the $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC reveals that the iodine-rich $MAPbBr_{3-x}I_x$ region possesses about 0.2 eV larger work function than the pure $MAPbBr_3$ region. Since the conduction band minimum (CBM) of $MAPbI_3$ is approximately 0.1 eV lower than that of $MAPbBr_3$ according to the literatures,[1,2] the up-shift of vacuum level may gradually bend up the conduction band in the halogen gradient $MAPbBr_{3-x}I_x$ region in the range of ≈0.1 eV when the Fermi levels are aligned in an equilibrium condition.

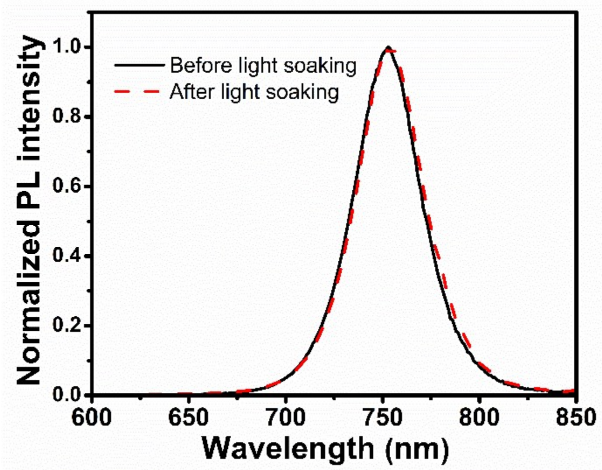

Fig. S9 PL spectra of the laminar $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC (excited from PVK side) before and after light soaking (100 mW cm^{-2} from white LED) for 30 min.

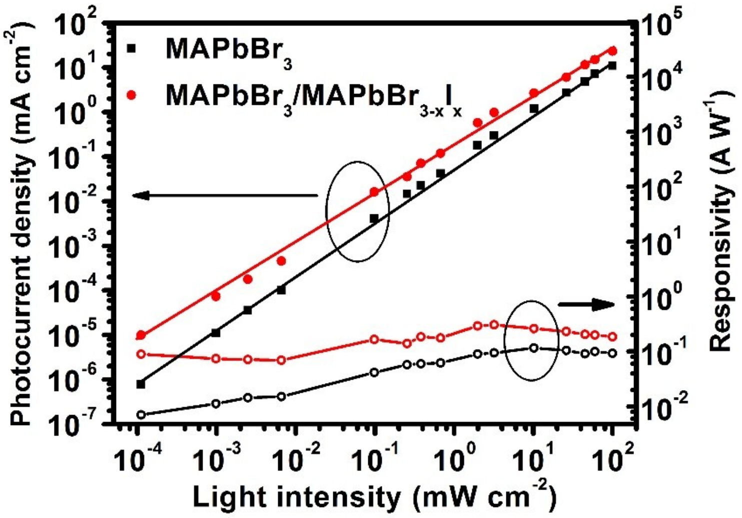

Fig. S10 Linear dynamic range of the photodetectors based on the laminar $MAPbBr_3$ SC and the $MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC at 0 V bias. The corresponding responsivity are shown in the figure with Y axis on the right.

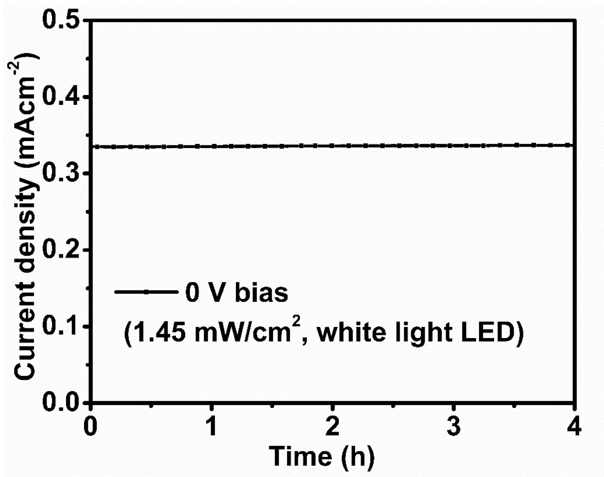

Fig. S11 The photocurrent evolution of the $MAPbBr_3$/$MAPbBr_{3-x}I_x$ GHSC photodetector at 0 V bias under continuous white LED illumination of 1.45 mW cm^{-2}.

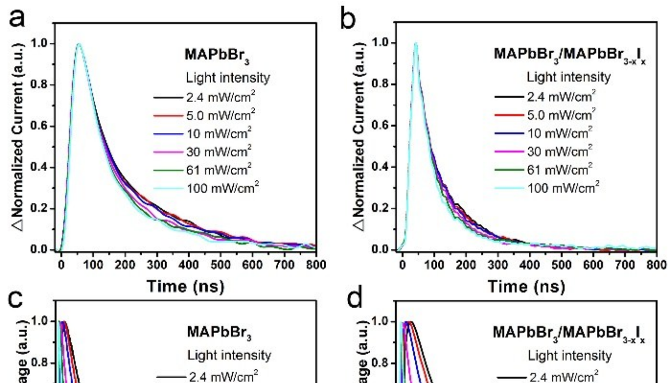

Fig. S12 The TPC (a, b) and TPV (c, d) curves of the $MAPbBr_3$ SC and $MAPbBr_3$/$MAPbBr_{3-x}I_x$ GHSC devices

Table S1 The detailed biexponential fitting parameters from the TRPL spectra in Fig. 2c and d.

Excitation direction	Sample	τ_1 [ns]	%	τ_2 [ns]	%	τ_{total} [ns]
PVK side	$MAPbBr_3$	14.0	17.4	139.2	82.6	117.4
PVK side	$MAPbBr_3/MAPbBr_{3-x}I_x$	5.7	12.1	229.0	87.9	201.9
Glass side	$MAPbBr_3$	8.8	35.4	31.2	64.6	23.3
Glass side	$MAPbBr_3/MAPbBr_{3-x}I_x$	0.5	21.7	5.5	78.3	4.4

Table S2 Summary of the performance of single crystal photodetectors.

Sample	Thickness [μm]	EQE [%]	Responsivity [A/W]	Response time [μs]	3dB bandwidth [Hz]	Reference
$MAPbBr_3$ SC	11	25(0 V); 120(-2V)	0.1 (0 V, 2.4 mW cm^{-2})	0.67	1.3×10^6	This work
$MAPbBr_3/MAPbBr_{3-x}I_x$ GHSC	11	40(0 V); 170(-2V)	0.27 (0 V, 2.4 mW cm^{-2})	0.56	3.0×10^6	This work
$MAPbBr_3$ SC	100	20(-1 V) 80(-2 V)	-	120	1.0×10^5	*Adv. Mater.*, 2017, **29**, 1602639.
$MAPbBr_3$ SC	0.38	-	-	930	1.4×10^3	*Adv. Mater.*, 2018, **30**, 1704333.
$MAPbBr_3$ SC	1000	-	-	216	-	*Nat. Photonics*, 2016, **10**, 333.

References

[1] X. Zhou, W. Ye, X. Li, W. Zheng, R. Lin, F. Huang and D. Zhong, *Appl. Phys. Lett.* 2016, **109**, 233906.

[2] I. Karimata, Y. Kobori and T. Tachikawa, *J. Phys. Chem. Lett.* 2017, **8**, 1724-1728.