Supplementary Information

Regulating Energy Band Alignment for High-performance Broadband Perovskite Photodetectors

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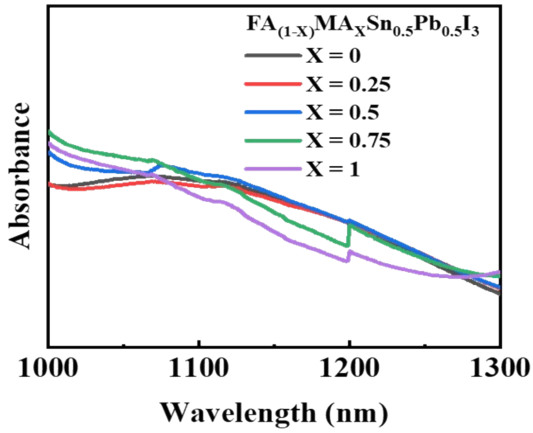

Figure S1. UV-vis-NIR absorption spectrum in the range of 1000-1300 nm

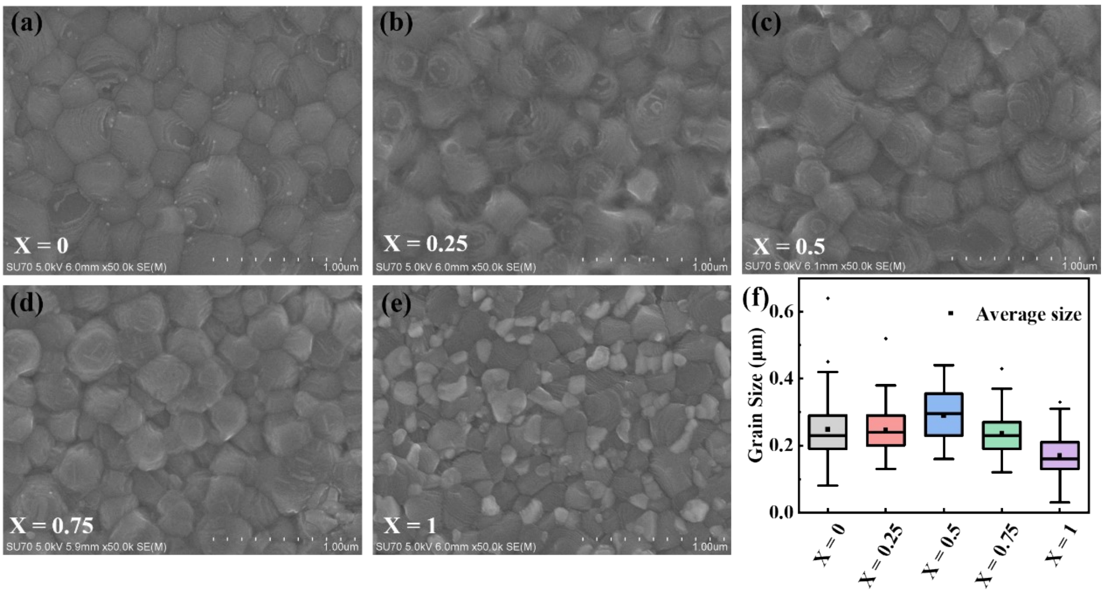

Figure S2. (a-e) SEM images of $FA_{(1-x)}MA_xSn_{0.5}Pb_{0.5}I_3$ perovskite films. (f) Statistical diagram of grain size of perovskite with different FA/MA compositions.

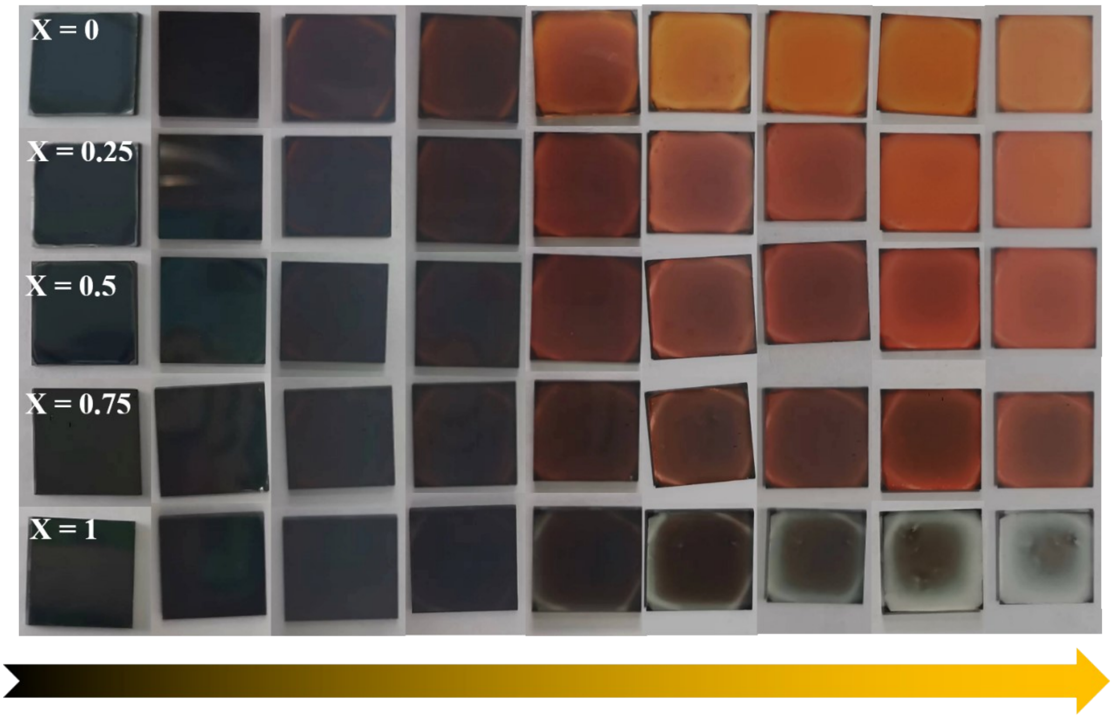

Figure S3. Degradation process of perovskite with different FA/MA components in room temperature air (25 ℃, 60% RH).

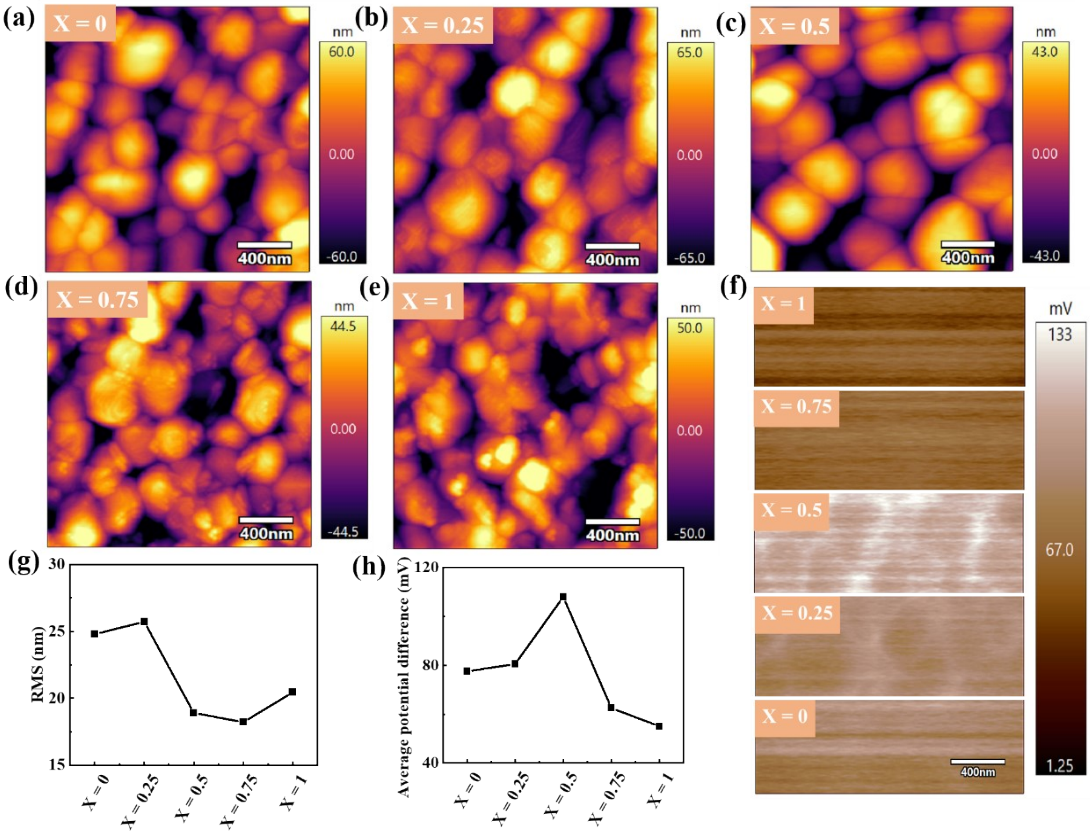

Figure S4. (a-e) AFM surface topography of $FA_{(1-x)}MA_xSn_{0.5}Pb_{0.5}I_3$ perovskite thin films. (f) KPFM diagrams, (g) Roughness comparison diagram and (h) Average potential difference comparison diagram of perovskite with various FA/MA compositions.

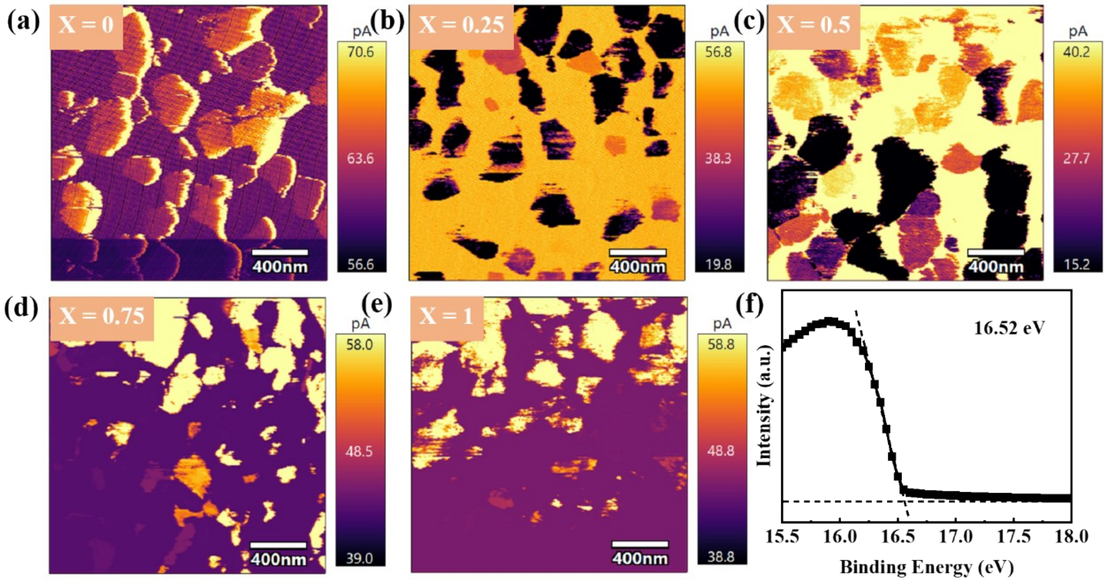

Figure S5. (a-e) C-AFM images of perovskite films with different FA/MA components. (f) UPS spectrum of ITO.

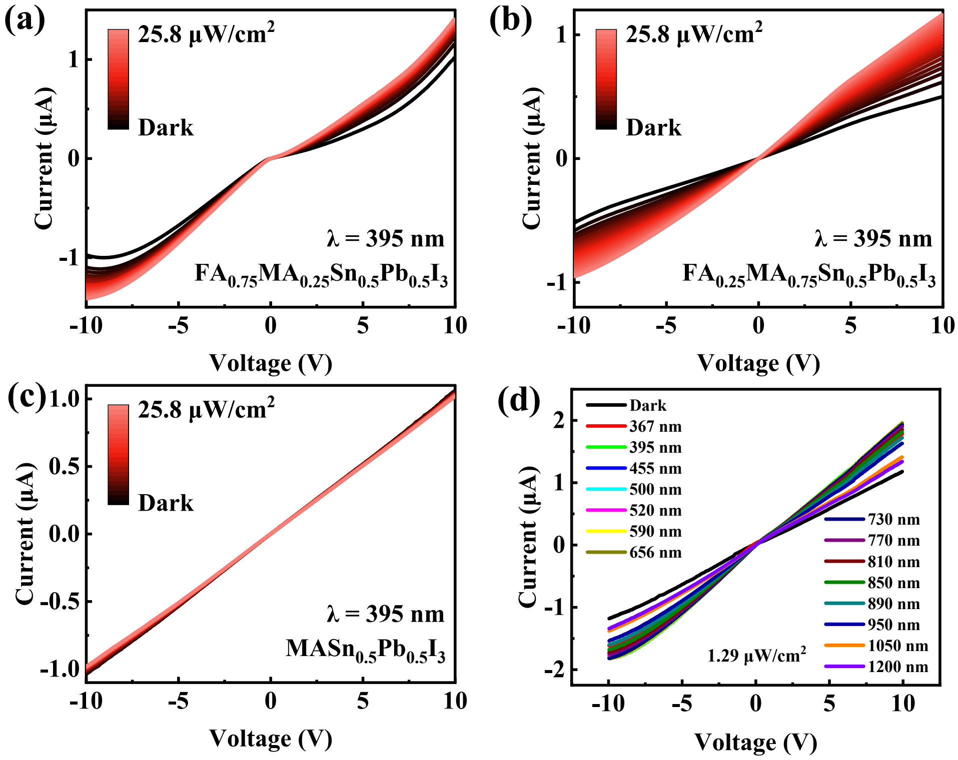

Figure S6. (a) *I-V* curves under dark and illumination for $FA_{0.75}MA_{0.25}Sn_{0.5}Pb_{0.5}I_3$ device, (b) $FA_{0.25}MA_{0.75}Sn_{0.5}Pb_{0.5}I_3$ device and (c) $MASn_{0.5}Pb_{0.5}I_3$ devices. (d) *I-V* curves of the optimized device at 367-1200 nm (1.29 μW/cm^2).

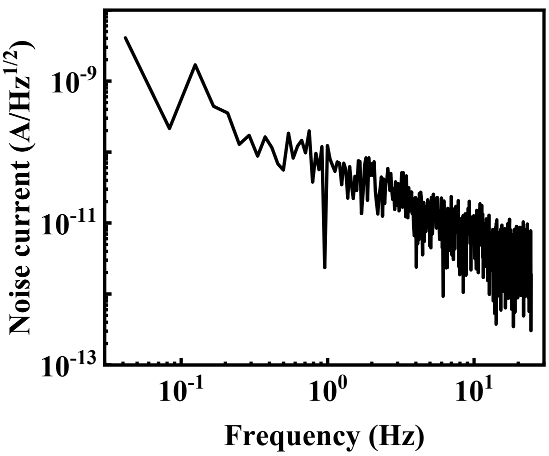

Figure S7. Noise spectral density curve.

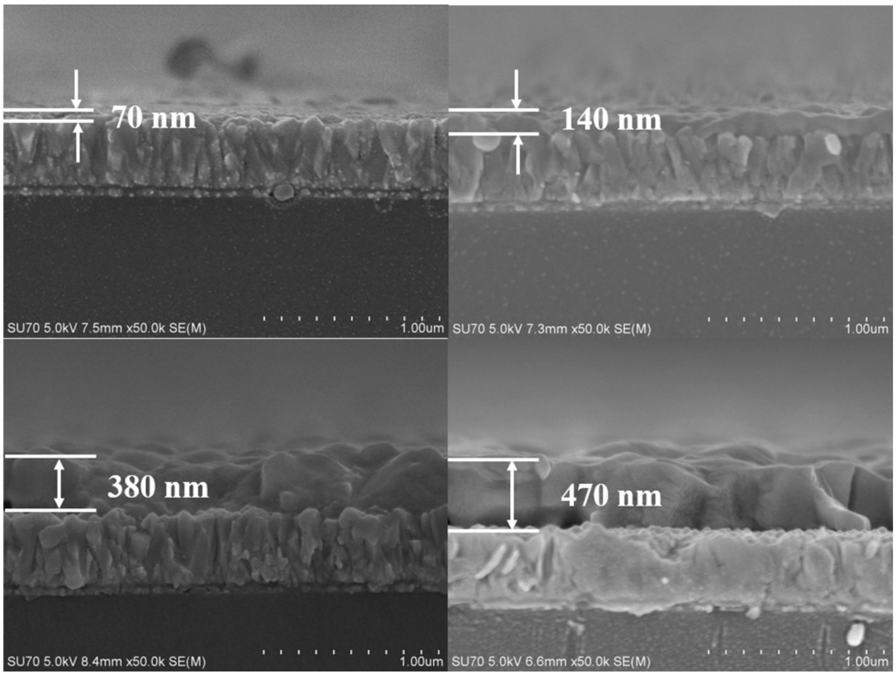

Figure S8. SEM images of the cross section of perovskites.

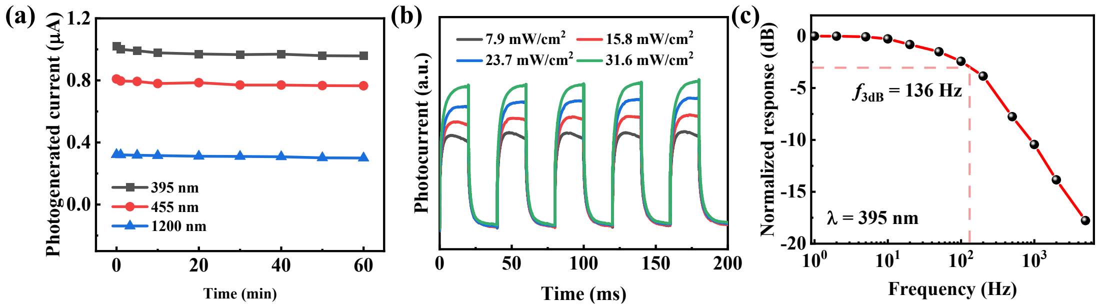

Figure S9. (a) Changes of photogenerated current under long-term irradiation with different wavelengths. (b) *I-T* curves of the photodetector under the illumination of 395 nm light. (c) Relationship between normalized light response change and frequency.

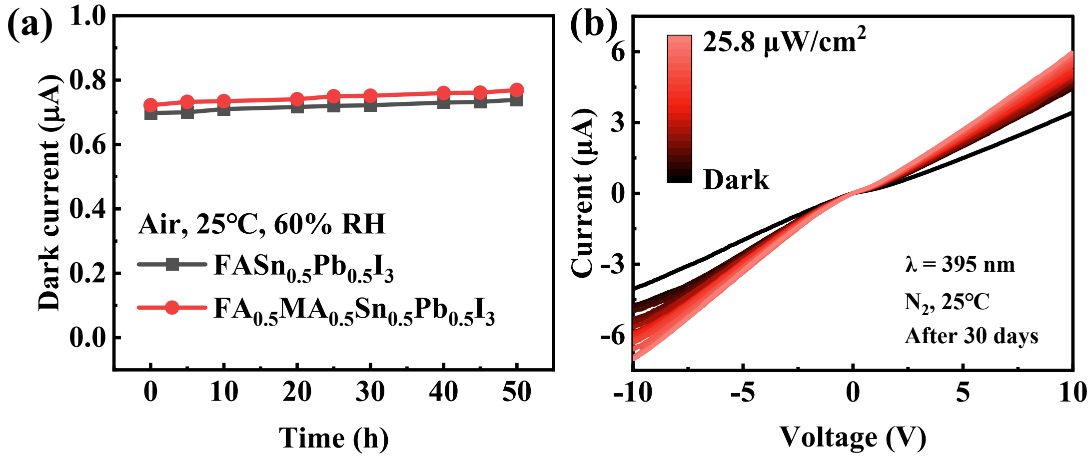

Figure S10. (a) Variation of dark current of devices with time. (b) After 30 days, the optical response curves at 395 nm.

Table S1. Comparison of perovskite photodetectors with wide spectrum response.

Perovskite (Wavelength range)	Responsivity (A/W)	Detectivity (Jones)	Linear dynamic range (dB)	Response time (t_r/t_f)	Ref.
$CsSnI_3$ nanowire (475-940 nm)	0.054 (940 nm)	3.85×10^5 [(a)] (940 nm)	—	83.8/243.4 ms	1
$(MAPbI3)_{0.2}(FASnI3)_{0.8}$ single crystals (405-1064 nm)	0.247 (405 nm) 0.012 (1064 nm)	1.12×10^{12} [(a)] (405 nm) 2.58×10^{10} [(a)] (1064 nm)	—	59/41 ms	2
$FASnI_3$ (500-850 nm)	1.1×10^5 (685 nm)	1.9×10^{12} [(b)] (685 nm)	—	8.7/57 s	3
$MAPbBr_3$ single crystals (520-1450 nm)	5.04 (520 nm)	5.37×10^{12} [(b)] (520 nm)	122	80 /110 µs	4
$(BA)_2(MA)Sn_2I_7$ single crystals (365-1064 nm)	28.4 (365 nm) 0.02 (1064 nm)	2.3×10^{10} [(a)] (365 nm) 1.8 ´ 10^7 [(a)] (1064 nm)	—	0.6 /1.2 s	5
$(FASnI_3)_{0.1}(MAPbI_3)_{0.9}$ single crystals (350-840 nm)	0.53 (800 nm)	7.09×10^{10} [(b)] (800 nm)	163.5	22.78/20.35 µs	6
$Cs_{0.05}MA_{0.45}FA_{0.5}Pb_{0.5}Sn_{0.5}I_3$ (300-1050 nm)	0.53 (910 nm)	2.07×10^{11} [(b)] (910 nm)	—	– /35.37 ns	7
$Cs_{0.05}MA_{0.45}FA_{0.5}Pb_{0.5}Sn_{0.5}I_3$ (300-1000 nm)	0.29 (720 nm) 0.2 (940 nm)	3.4×10^{12} [(a)] 1.6×10^9 [(b)]	83.6	2/2.1 µs	8
$(MA_{0.5}FA_{0.5})(Pb_{0.5}Sn_{0.5})I_3$ (370-980 nm)	1.7×10^5 (980 nm) 5.8×10^5 (760 nm) 4.6×10^4 (370 nm)	5.9×10^{13} [(b)] (980 nm) 2.0×10^{14} [(b)] (760 nm) 1.6×10^{13} [(b)] (370 nm)	—	80/ – ms	9
$FA_{0.85}Cs_{0.15}Sn_{0.5}Pb_{0.5}I_3$	0.52 (910 nm)	8.48×10^{12} [(b)] (910 nm)	213	67.5/720 ns	10

(300-1100 nm)					
$Cs_{0.15}FA_{0.85}Pb_{0.5}Sn_{0.5}I_3$ (325-980 nm)	0.52 (850 nm)	5.34×10^{12} (b) (850 nm)	224	– /39.68 ns	11
$FA_{0.8}PEA_{0.2}SnI_3$ (350-900 nm)	0.262 (780 nm)	2.3×10^{11} (b) (850 nm)	83	27.7/20.4 μs	12
$MA_{0.3}FA_{0.7}Pb_{0.5}Sn_{0.5}I_3$ (780-1100 nm)	0.16 (850 nm) 0.1 (940 nm)	6.6×10^{10} (b) (850 nm) 4.2×10^{10} (b) (940 nm)	—	—	13
$FA_{0.7}MA_{0.3}Pb_{0.5}Sn_{0.5}I_3$ (500-950 nm)	0.52 (930 nm)	7.5×10^{11} (b) (930 nm)	—	94/97 ns	14
$MASnI_3$ nanowire array (200-1000 nm)	0.47	8.8×10^{10} (a)	—	1.5/0.4 s	15
$MAPbI_3$ (400-1000 nm)	4 (800 nm)	—	—	39/1.9 μs	16
$MAPbI_3$ (400-1064 nm)	0.15 (820 nm)	—	—	120/80 ms	17
$MAPbI_3$ nanocrystal (400-980 nm)	1.42 (808 nm) 4.43×10^{-5} (980 nm)	1.7×10^{13} (a) (808 nm) 1.34×10^{8} (a) (980 nm)	—	0.28/0.34 s	18
$MAPbI_{3-x}Cl_x$ (350-1100 nm)	7.6×10^{8} (895 nm) 1.91×10^{9} (598 nm)	5.6×10^{13} (b) (895 nm)	—	—	19
$MAPbI_3$ (600-900 nm)	—	7.13×10^{11} (b) (800 nm)	—	—	20
$CsSnI_3$ (350-1000 nm)	0.257 (850 nm)	1.5×10^{11} (a) (850 nm)	—	0.35/1.6 ms	21
$FA_{0.85}Cs_{0.15}Sn_{0.5}Pb_{0.5}I_3$ (600-1000 nm)	0.53 (940 nm)	6×10^{12} (b) (940 nm)	103	58.3/860 ns	22
$(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ (300-1000 nm)	0.4 (950 nm)	1.1×10^{12} (b) (900 nm)	167	6.9/9.1 μs	23

$MA_{0.5}FA_{0.5}Pb_{0.5}Sn_{0.5}I_3$ (350-1000 nm)	> 0.2 (800-950 nm)	$> 10^{12}$ (b) (800-970 nm)	—	—	24
$MA_{0.975}Rb_{0.025}Sn_{0.65}Pb_{0.35}I_3$ (300-1100 nm)	0.4 (910 nm)	$> 10^{12}$ (b) (340-1000 nm)	110	0.04/0.468 μs	25
$MASn_xPb_{1-x}I_3$ (300-1100 nm)	0.2 (940 nm)	$> 10^{11}$ (b) (360-985 nm)	100	0.09/2.27 μs	26
$(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ (300-1000 nm)	—	$\approx 10^{11}$ (a) (850 nm)	—	19/13 ms	27
$CsPb_{0.5}Sn_{0.5}I_3$ (5% $(PEA)_2Pb_{0.5}Sn_{0.5}I_4$) (700-900 nm)	0.27(850 nm)	5.42×10^{14} (b) (850 nm)	—	—	28
$MA_{0.5}FA_{0.5}Pb_{0.5}Sn_{0.5}I_3$ (2.5% $(PEA)_2Pb_{0.5}Sn_{0.5}I_4$) (700-1000 nm)	≈ 0.1 (800 nm)	1.6×10^{12} (b) (800 nm)	—	10/10 μs	29
$FA_{0.5}MA_{0.45}Cs_{0.05}Pb_{0.5}Sn_{0.5}I_3$ (300-1050 nm)	0.35 (950 nm)	2.21×10^{11} (b) (758 nm)	185	—	30
$(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ (500-1100 nm)	0.04 (900 nm) 0.01 (1100 nm)	2.24×10^{10} (a) (900 nm)	—	20/40 ms	31
$CsSn_{0.6}Pb_{0.4}I_{2.6}Br_{0.4}$ (454-860 nm)	21 (860 nm)	3.9×10^{10} (a) (860 nm)	—	0.74/0.56 s	32
$FA_{0.5}MA_{0.5}Sn_{0.5}Pb_{0.5}I_3$ (367-1200 nm)	1.2×10^3 (395 nm) 1.1×10^3 (455 nm) 24.73 (1200 nm)	4.4×10^{13} (a) 2.02×10^{13} (b) (395 nm) 3.98×10^{13} (a) 1.52×10^{12} (b) (455 nm) 1.01×10^{12} (a) 4.16×10^{11} (b) (1200 nm)	66.5	2.4/5.4 ms	This work

(a) Calculate via $D^* = R\sqrt{\frac{A_{rea}}{2eI_{dark}}}$, (b)Calculate via $D^* = \frac{\sqrt{A_{rea}\Delta f}}{NEP}$

References

1 M. Han, J. Sun, M. Peng, N. Han, Z. Chen, D. Liu, Y. Guo, S. Zhao, C. Shan, T. Xu, X. Hao, W. Hu and Z.-x. Yang, *J. Phys. Chem. C* **2019,** *123*, 17566-17573.

2 Q. Li, S. Wang, C. Jia, H. Liu and X. Li, *J Phys Chem Lett* **2023,** *14*, 5148-5154.

3 C. K. Liu, Q. Tai, N. Wang, G. Tang, H. L. Loi and F. Yan, *Adv. Sci.* **2019,** *6*, 1900751.

4 L. Mei, K. Zhang, N. Cui, W. Yu, Y. Li, K. Gong, H. Li, N. Fu, J. Yuan, H. Mu, Z. Huang, Z. Xu, S. Lin and L. Zhu, *Small* **2023,** *19*, 2301386.

5 Y. Xu, F. Wang, J. Xu, X. Lv, G. Zhao, Z. Sun, Z. Xie and S. Zhu, *Opt. Express* **2023,** *31*, 8428-8439.

6 Z. Chang, Z. Lu, W. Deng, Y. Shi, Y. Sun, X. Zhang and J. Jie, *Nanoscale* **2023,** *15*, 5053-5062.

7 Y. Zhao, C. Li, J. Jiang, B. Wang and L. Shen, *Small* **2020,** *16*, 2070146.

8 W. Li, J. Chen, H. Lin, S. Zhou, G. Yan, Z. Zhao, C. Zhao and W. Mai, *Adv. Opt. Mater.* **2023,** *12*, 2301373.

9 H.-L. Loi, J. Cao, C.-K. Liu, Y. Xu, M. G. Li and F. Yan, *Small* **2023,** *19*, 2205976.

10 H. Liu, L. Zhu, H. Zhang, X. He, F. Yan, K. S. Wong and W. C. H. Choy, *ACS Energy Lett.* **2022,** *8*, 577-589.

11 L. He, G. Hu, J. Jiang, W. Wei, X. Xue, K. Fan, H. Huang and L. Shen, *Adv. Mater.* **2023,** *35*, 2210016.

12 M. He, Z. Xu, C. Zhao, Y. Gao, K. Ke, N. Liu, X. Yao, F. Kang, Y. Shen, L. Lin and G. Wei, *Adv. Funct. Mater.* **2023,** *33*, 2300282.

13 A. Moeini, L. Martínez-Sarti, K. P. S. Zanoni, M. Sessolo, D. Tordera and H. J. Bolink, *J. Mater. Chem. C* **2022,** *10*, 13878-13885.

14 F. Liu, K. Liu, S. Rafique, Z. Xu, W. Niu, X. Li, Y. Wang, L. Deng, J. Wang, X. Yue, T. Li, J. Wang, P. Ayala, C. Cong, Y. Qin, A. Yu, N. Chi and Y. Zhan, *Adv. Sci.* **2023,** *10*, 2205879.

15 A. Waleed, M. M. Tavakoli, L. Gu, Z. Wang, D. Zhang, A. Manikandan, Q. Zhang, R. Zhang, Y.-L. Chueh and Z. Fan, *Nano Lett.* **2017,** *17*, 523-530.

16 Y. Zhang, Y. Liu, Z. Yang and S. Liu, *J. Energy Chem.* **2018,** *27*, 722-727.

17 Q. Lin, A. Armin, P. L. Burn and P. Meredith, *Laser & Photonics Reviews* **2016,** *10*, 1047-1053.

18 C. Perumal Veeramalai, S. Yang, R. Zhi, M. Sulaman, M. I. Saleem, Y. Cui, Y. Tang, Y. Jiang, L. Tang and B. Zou, *Adv. Opt. Mater.* **2020,** *8*, 2000215.

19 C. Xie, P. You, Z. Liu, L. Li and F. Yan, *Light: Science & Applications* **2017,** *6*, e17023-e17023.

20 B. Du, W. Yang, Q. Jiang, H. Shan, D. Luo, B. Li, W. Tang, F. Lin, B. Shen, Q. Gong, X. Zhu, R. Zhu and Z. Fang, *Adv. Opt. Mater.* **2018,** *6*, 1701271.

21 F. Cao, W. Tian, M. Wang, M. Wang and L. Li, *InfoMat* **2020,** *2*, 577-584.

22 H. Liu, H. L. Zhu, Z. Wang, X. Wu, Z. Huang, M. R. Huqe, J. A. Zapien, X. Lu and W. C. H. Choy, *Adv. Funct. Mater.* **2021,** *31*, 2010532.

23 W. Wang, D. Zhao, F. Zhang, L. Li, M. Du, C. Wang, Y. Yu, Q. Huang, M. Zhang, L. Li, J. Miao, Z. Lou, G. Shen, Y. Fang and Y. Yan, *Adv. Funct. Mater.* **2017,** *27*, 1703953.

24 X. Xu, C.-C. Chueh, P. Jing, Z. Yang, X. Shi, T. Zhao, L. Y. Lin and A. K. Y. Jen, *Adv. Funct. Mater.* **2017,** *27*, 1701053.

25 H. L. Zhu, Z. Liang, Z. Huo, W. K. Ng, J. Mao, K. S. Wong, W.-J. Yin and W. C. H. Choy, *Adv. Funct. Mater.* **2018,** *28*, 1706068.

26 H. L. Zhu, H. Lin, Z. Song, Z. Wang, F. Ye, H. Zhang, W.-J. Yin, Y. Yan and W. C. H. Choy, *ACS Nano* **2019,** *13*, 11800-11808.

27 Y. Wang, C. Chen, T. Zou, L. Yan, C. Liu, X. Du, S. Zhang and H. Zhou, *Advanced Materials Technologies* **2020,** *5*, 1900752.

28 F. Cao, J. Chen, D. Yu, S. Wang, X. Xu, J. Liu, Z. Han, B. Huang, Y. Gu, K. L. Choy and H. Zeng, *Adv. Mater.* **2020,** *32*, 1905362.

29 J. Liu, Y. Zou, B. Huang, Y. Gu, Y. Yang, Z. Han, Y. Zhang, X. Xu and H. Zeng, *Nanoscale* **2020,** *12*, 20386-20395.

30 N. Ma, J. Jiang, Y. Zhao, L. He, Y. Ma, H. Wang, L. Zhang, C. Shan, L. Shen and W. Hu, *Nano Energy* **2021,** *86*, 106113.

31 L. Yan, X. Du, C. Liu, S. Zhang and H. Zhou, *Phys. Status Solidi (a)* **2019,** *216*,

1900417.

32 C. Jo, S. Lee, J. Kim, J. S. Heo, D.-W. Kang and S. K. Park, *ACS Appl. Mater. Interfaces* **2020,** *12*, 58038-58048.