Supporting Information

Enhanced Light Harvesting in Lead-Free $Cs_2AgBiBr_6$ Double Perovskite Solar Cells with Plasmonic Ag Nanoparticles

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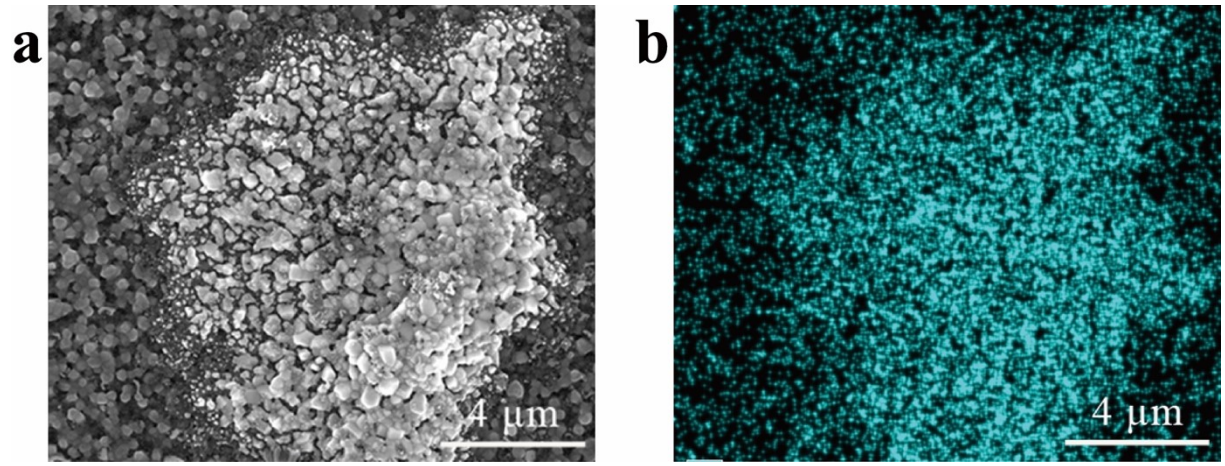

Fig. S1 (a) SEM image and (b) EDS mapping of perovskite film treated with a higher Ag concentration (30 mg/L).

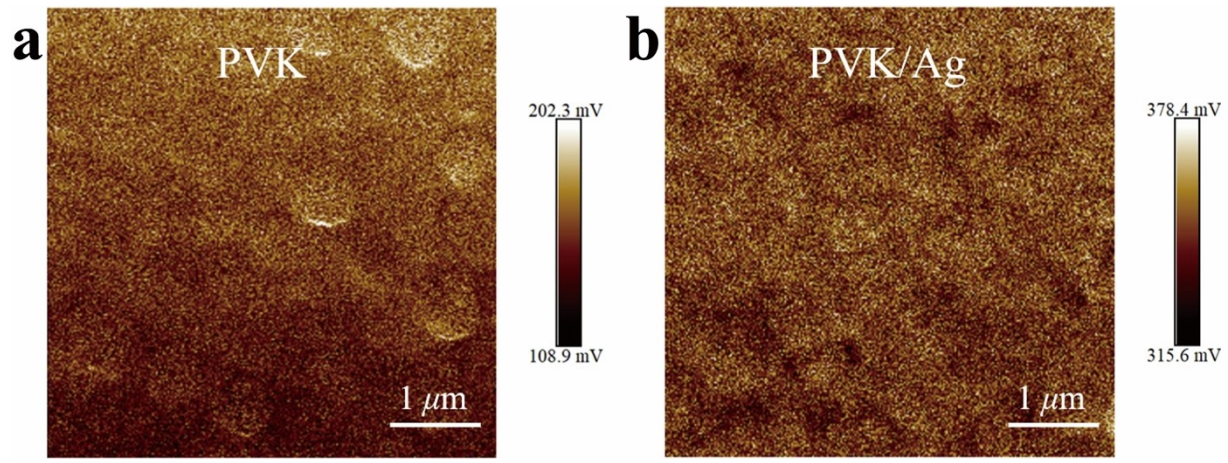

Fig. S2 Surface potential of perovskite films (a) without and (b) with Ag NPs.

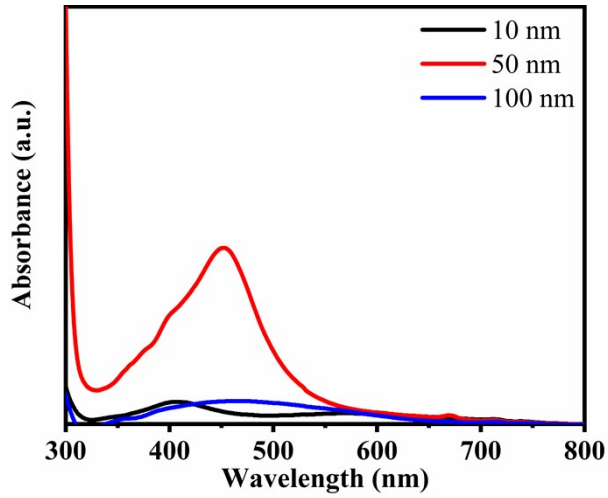

Fig. S3 UV-vis absorption spectra of Ag NPs with different sizes.

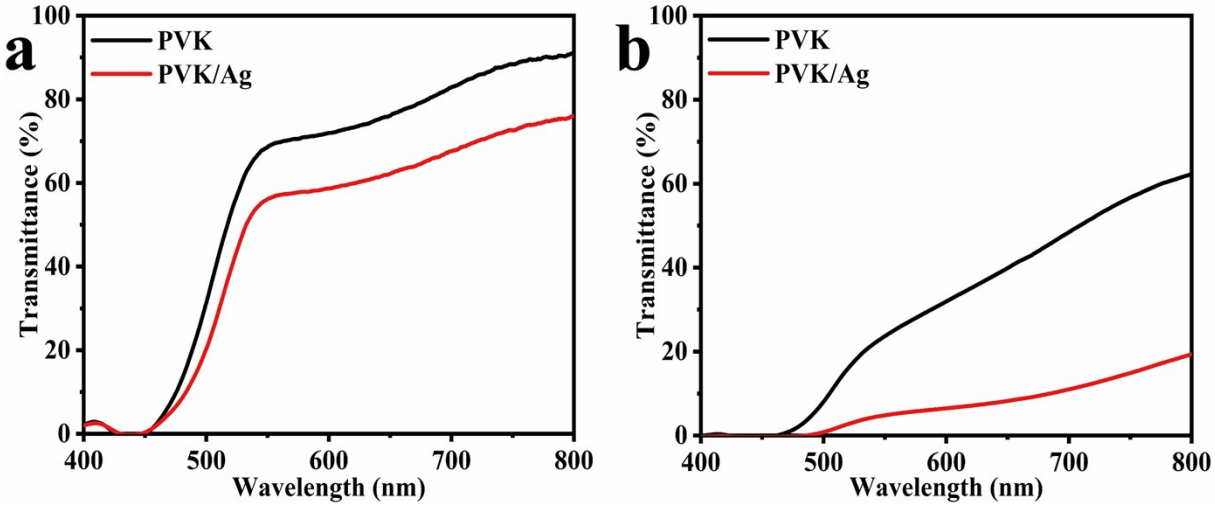

Fig. S4 (a) TT and (b) VT spectra of perovskite films without and with Ag NPs.

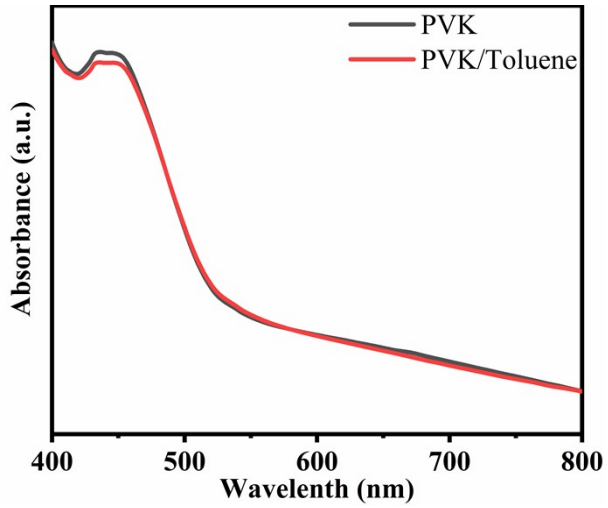

Fig. S5 UV-vis absorption spectra of perovskite films without and with toluene modification.

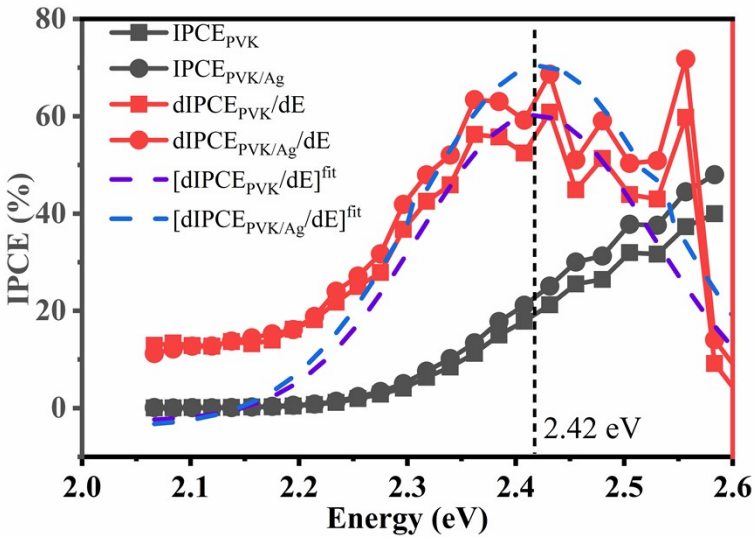

Fig. S6 Band gap calculation of different perovskite films based on IPCE spectra.

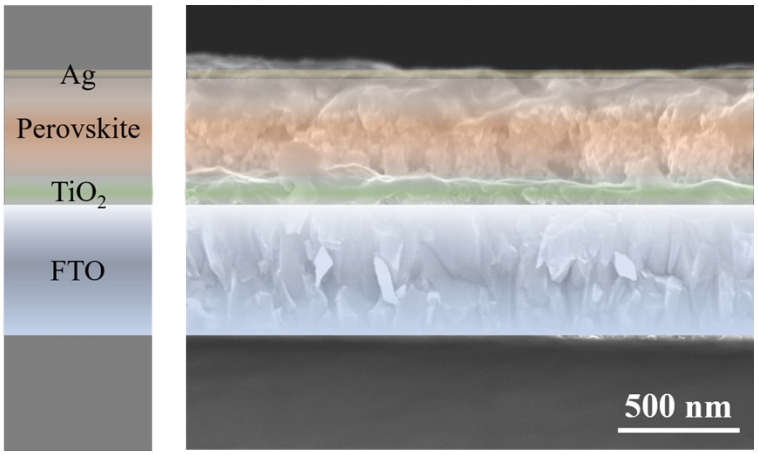

Fig. S7 Cross-sectional SEM image of PSC device.

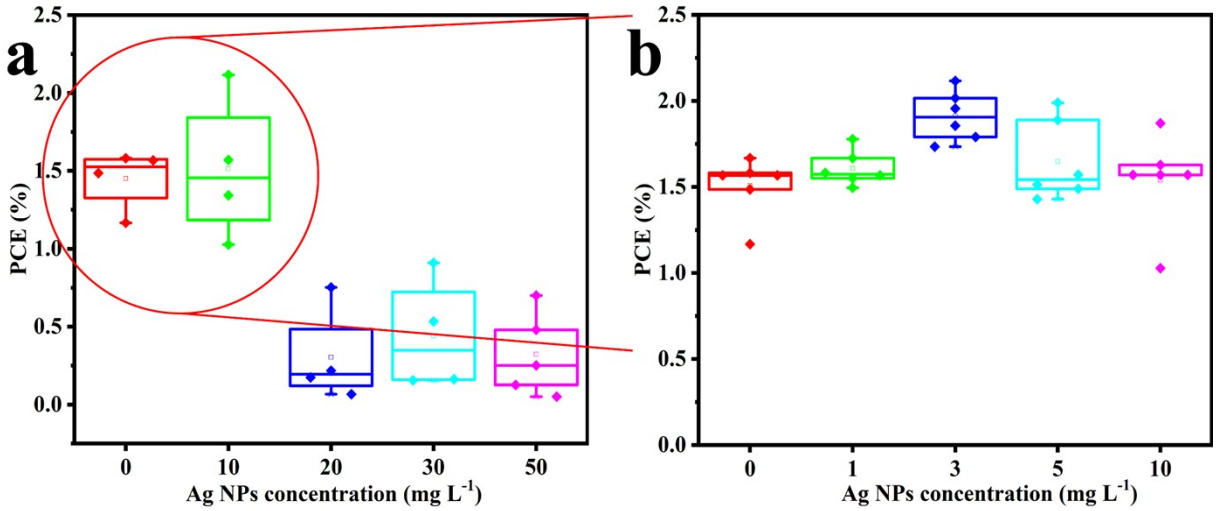

Fig. S8 PCEs of devices with different concentrations of Ag NPs.

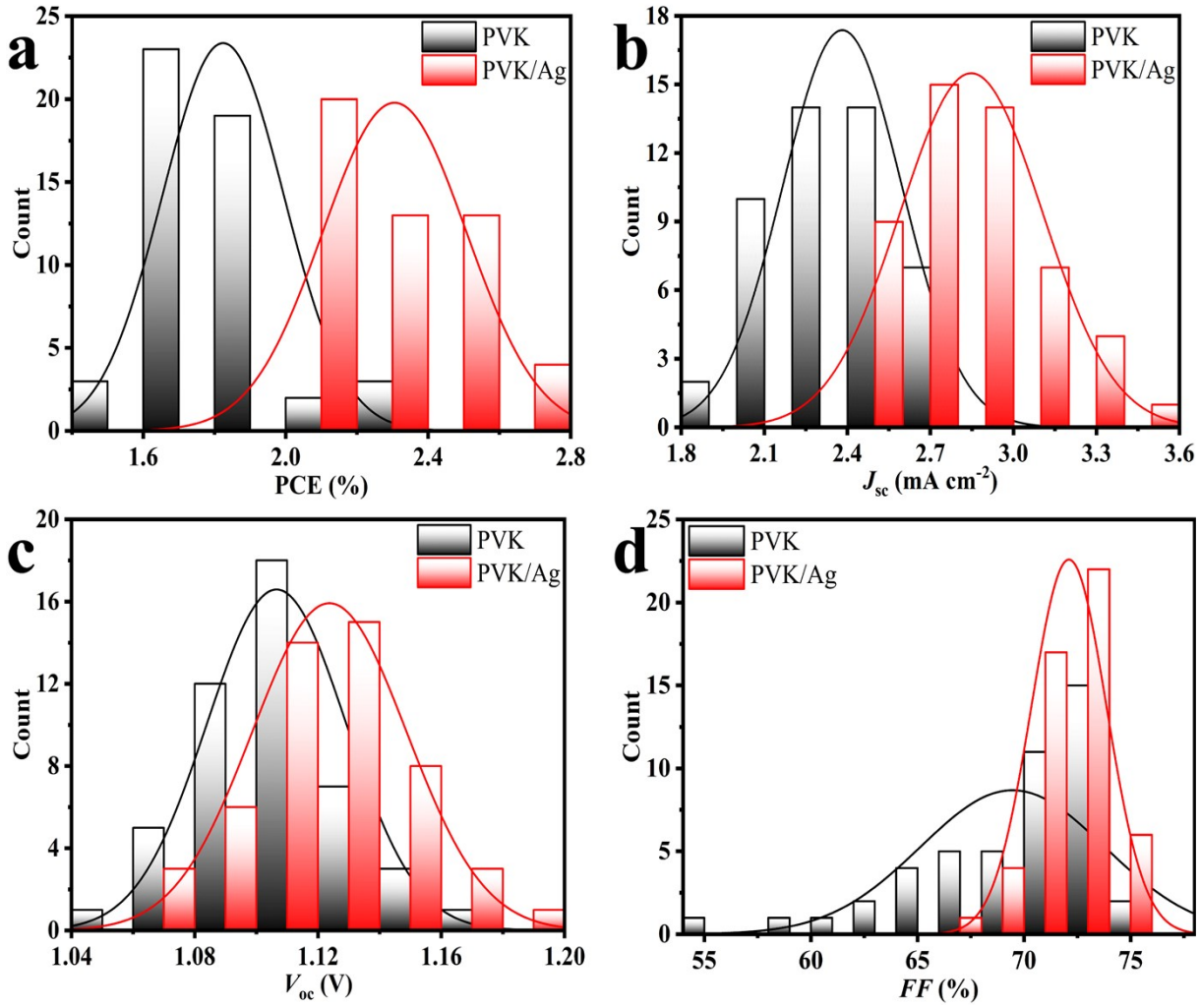

Fig. S9 Performance distributions of 50 PSCs without and with Ag NPs.

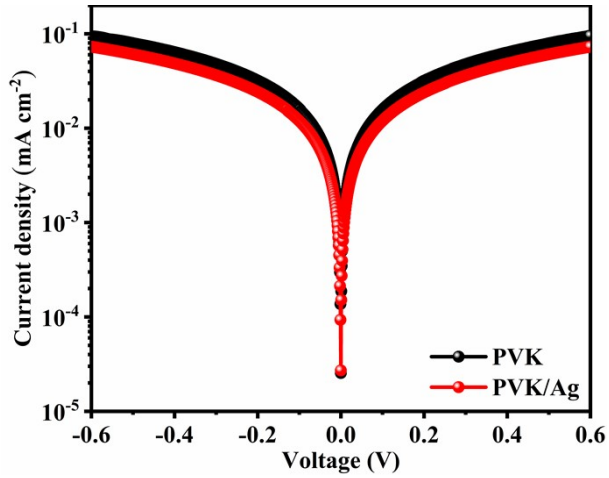

Fig. S10 Dark *J*-*V* plots of PSCs without and with Ag NPs.

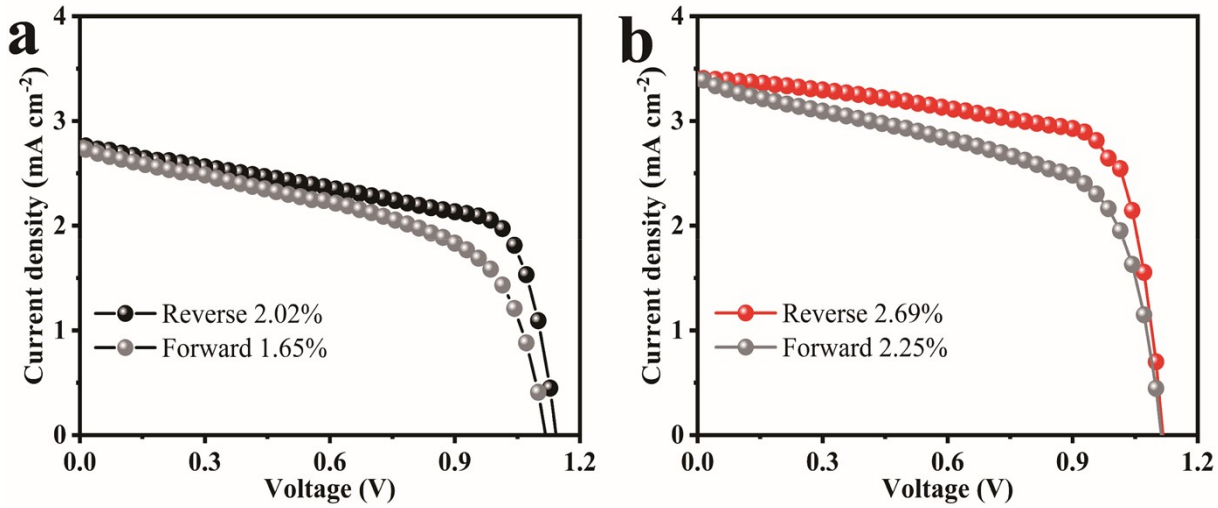

Fig. S11 Hysteresis characteristics of PSCs without (a) and with (b) Ag NPs.

Table S1 TRPL decay parameters of perovskite films without and with Ag NPs.

Perovskite	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{ave} (ns)
PVK	0.72	95.33	0.32	468.86	351.62
PVK/Ag	0.66	76.49	0.39	478.29	392.71

TRPL spectra are fitted with a bi-exponential decay model: $I_t = I_0 + A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2)$, where I_0 is a constant for baseline offset, τ_1 is the fast component related to trap-assisted non-relative recombination and τ_2 is the slow component corresponding to radiative recombination. A_1 and A_2 represent relative amplitudes of fast and slow processes, respectively. The average carrier lifetimes (τ_{ave}) can be calculated by the following equation: $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Table S2 Summary of average photovoltaic parameters of different devices.

Perovskite	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	PCE (%)
PVK	2.57 ± 0.12	1.08 ± 0.015	68.41 ± 1.54	1.85 ± 0.19
PVK/Ag	3.33 ± 0.08	1.11 ± 0.013	69.51 ± 1.23	2.57 ± 0.12

Table S3 Summary of photovoltaic parameters for previously reported $Cs_2AgBiBr_6$ PSCs.

Device structure	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	PCE (%)	Ref.
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$/Ag/C	3.41	1.12	0.71	2.69	This work
ITO/SnO_2/$Cs_2AgBiBr_6$/P3HT/Au	1.78	1.04	0.78	1.44	[1]
FTO/c-TiO_2/$Cs_2AgBiBr_6$/P3HT/Au	1.79	1.12	0.68	1.37	[2]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$/Spiro-OMeTAD/Au	3.93	0.98	0.63	2.43	[3]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$/N719/Spiro-OMeTAD/Ag	5.13	1.06	0.52	2.84	[4]
ITO/Cu-NiO/$Cs_2AgBiBr_6$/C60/BCP/Ag	3.19	1.01	0.69	2.23	[5]
FTO/Ti_3C_2Tx@TiO_2/$Cs_2AgBiBr_6$/Spiro-OMeTAD/MoO_3/Ag	4.14	0.96	0.70	2.81	[6]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$/Spiro-OMeTAD/Au	3.2	1.09	0.68	2.3	[7]
FTO/TiO_2/$Cs_2AgBiBr_6$/Spiro-OMeTAD/MoO_3/Ag	3.82	1.01	0.65	2.51	[8]
FTO/c-TiO_2/m-TiO_2/C-Chl/$Cs_2AgBiBr_6$/Spiro-OMeTAD/Au	4.09	1.04	0.73	3.11	[9]
FTO/c-TiO_2/ m-TiO_2/$Cs_{1.99}Li_{0.01}AgBiBr_6$/C	3.15	1.17	0.69	2.57	[10]
FTO/c-TiO_2/$Cs_2AgBiBr_6$/P3HT/Cu	2.58	1.07	0.69	1.91	[11]
ITO/SnO_2/$Cs_2AgBiBr_6$/Spiro-OMeTAD/MoO_3/ITO	2.20	0.97	0.74	1.56	[12]

FTO/c-TiO_2/m-TiO_2/D149/$Cs_2AgBiBr_6$/Spiro-OMeTAD/Ag	8.24	0.73	0.70	4.23	[13]
FTO/ c-TiO_2/ m-TiO_2/$Cs_2AgBiBr_6$-1.0MABr / PTB7/ Au	3.5	0.95	0.76	2.53	[14]
ITO/SnO_2/$Cs_2AgBiBr_6$/Zn-Chl/Ag	3.83	0.99	0.74	2.79	[15]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$/PMMA/C	2.82	1.18	0.68	2.25	[16]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$-GuaSCN/Spiro-OMeTAD/Ag	5.24	1.04	0.58	3.19	[17]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$/ Spiro-OMeTAD /Au	1.77	1.05	0.72	1.33	[18]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$-$(PEA)_4AgBiBr_8$/Spiro-OMeTAD /Au	3.50	1.07	0.66	2.47	[19]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$-BMPyr/C	2.61	1.20	0.71	2.22	[20]
FTO/c-TiO_2/$Cs_2AgBiBr_6$/PBDB-T/MoO_x/Ag	3.37	1.28	0.77	3.31	[21]
FTO/m-TiO_2/$Cs_2AgBiBr_6$/SnS QDs/C	3.74	1.02	0.51	1.95	[22]
ITO/SnO_2/Hydrogenated-$Cs_2AgBiBr_6$/Spiro-OMeTAD/Au	11.40	0.92	0.61	6.37	[23]
FTO/m-TiO_2/$Cs_2(Ag_{0.9}Zn_{0.1})BiBr_6$/C	4.23	1.00	0.51	2.16	[24]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$-thiourea/Spiro-OMeTAD/Au	5.14	1.03	0.58	3.07	[25]
FTO/c-TiO_2/m-TiO_2/$Cs_2AgBiBr_6$/PyDAnCBZ/Au	3.73	1.06	0.74	2.92	[26]

ITO/SnO_2/$Cs_2AgBiBr_6$-CBH/Spiro-OMeTAD/Au	2.03	1.05	0.59	1.57	[27]

References

1. C. Wu, Q. Zhang, Y. Liu, W. Luo, X. Guo, Z. Huang, H. Ting, W. Sun, X. Zhong, S. Wei, S. Wang, Z. Chen and L. Xiao, *Adv. Sci.*, 2018, **5**, 1700759.

2. M. Wang, P. Zeng, S. Bai, J. Gu, F. Li, Z. Yang and M. Liu, *Solar RRL*, 2018, **2**, 1800217.

3. E. Greul, Michiel L. Petrus, A. Binek, P. Docampo and T. Bein, *J. Mater. Chem. A*, 2017, **5**, 19972-19981.

4. X. Yang, Y. Chen, P. Liu, H. Xiang, W. Wang, R. Ran, W. Zhou and Z. Shao, *Adv. Funct. Mater.*, 2020, **30**, 2001557.

5. W. Gao, C. Ran, J. Xi, B. Jiao, W. Zhang, M. Wu, X. Hou and Z. Wu, *Chemphyschem*, 2018, **19**, 1696-1700.

6. Z. Li, P. Wang, C. Ma, F. Igbari, Y. Kang, K.-L. Wang, W. Song, C. Dong, Y. Li, J. Yao, D. Meng, Z.-K. Wang and Y. Yang, *J. Am. Chem. Soc.*, 2021, **143**, 2593-2600.

7. N. Daem, J. Dewalque, F. Lang, A. Maho, G. Spronck, C. Henrist, P. Colson, S. D. Stranks and R. Cloots, *Solar RRL*, 2021, **5**, 2100422.

8. F. Igbari, R. Wang, Z.-K. Wang, X.-J. Ma, Q. Wang, K.-L. Wang, Y. Zhang, L.-S. Liao and Y. Yang, *Nano Lett.*, 2019, **19**, 2066-2073.

9. B. Wang, N. Li, L. Yang, C. Dall'Agnese, A. K. Jena, S.-i. Sasaki, T. Miyasaka, H. Tamiaki and X.-F. Wang, *J. Am. Chem. Soc.*, 2021, **143**, 2207-2211.

10. J. Li, J. Duan, J. Du, X. Yang, Y. Wang, P. Yang, Y. Duan and Q. Tang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 47408-47415.

11. M. Ghasemi, L. Zhang, J.-H. Yun, M. Hao, D. He, P. Chen, Y. Bai, T. Lin, M. Xiao, A. Du, M. Lyu and L. Wang, *Adv. Funct. Mater.*, 2020, **30**, 2002342.

12. G. Liu, C. Wu, Z. Zhang, Z. Chen, L. Xiao and B. Qu, *Solar RRL*, 2020, **4**, 2000056.

13. B. Wang, N. Li, L. Yang, C. Dall'Agnese, A. K. Jena, T. Miyasaka and X.-F. Wang, *J. Am. Chem. Soc.*, 2021, **143**, 14877-14883.

14. H. Wu, Y. Wang, A. Liu, J. Wang, B. J. Kim, Y. Liu, Y. Fang, X. Zhang, G. Boschloo and E. M. J. Johansson, *Adv. Funct. Mater.*, 2022, **32**, 2109402.

15. B. Wang, L. Yang, C. Dall'Agnese, A. K. Jena, S.-i. Sasaki, T. Miyasaka, H. Tamiaki and X.-F. Wang, *Solar RRL*, 2020, **4**, 2000166.

16. J. Li, F. Yan, P. Yang, Y. Duan, J. Duan and Q. Tang, *Solar RRL*, 2022, **6**, 2100791.

17. X. Yang, A. Xie, H. Xiang, W. Wang, R. Ran, W. Zhou and Z. Shao, *Appl. Phys. Rev.*, 2021, **8**, 041402.

18. D. Zhao, C. Liang, B. Wang, T. Liu, Q. Wei, K. Wang, H. Gu, S. Wang, S. Mei and G. Xing, *Energy Environ. Mater.*, 2022, **5**, 1317-1322.

19. M. T. Sirtl, R. Hooijer, M. Armer, F. G. Ebadi, M. Mohammadi, C. Maheu, A. Weis, B. T. van Gorkom, S. Häringer, R. A. J. Janssen, T. Mayer, V. Dyakonov, W. Tress and T. Bein, *Adv. Energy Mater.*, 2022, **12**, 2103215.

20. J. Li, X. Meng, Z. Wu, Y. Duan, R. Guo, W. Xiao, Y. Zhang, Y. Li, Y. Shen, W. Zhang and G. Shao, *Adv. Funct. Mater.*, 2022, **32**, 2112991.

21. B. Li, X. Wu, S. Zhang, Z. Li, D. Gao, X. Chen, S. Xiao, C.-C. Chueh, A. K. Y. Jen and Z. Zhu, *Chem. Eng. J.*, 2022, **446**, 137144.

22. Y. Ou, J. Lu, X. Zhong, X. Li, S. Wu, P. Chen and L. Zhou, *Mater. Lett.*, 2022, **312**, 131672.

23. Z. Zhang, Q. Sun, Y. Lu, F. Lu, X. Mu, S.-H. Wei and M. Sui, *Nat. Commun.*, 2022, **13**, 3397.

24. Y. Ou, Z. Lu, J. Lu, X. Zhong, P. Chen, L. Zhou and T. Chen, *Opt. Mater.*, 2022, **129**, 112452.

25. X. Yang, H. Xiang, J. Huang, C. Zhou, R. Ran, W. Wang, W. Zhou and Z. Shao, *J. Colloid Interface Sci.*, 2022, **628**, 476-485.

26. P. Huang, M. Sheokand, D. Payno Zarceño, S. Kazim, L. Lezama, M. K. Nazeeruddin, R. Misra and S. Ahmad, *ACS Appl. Energy Mater.*, 2023, **6**, 7955-7964.

27. Y. Fan, F. Qiao, D. Du, J. Bao, J. Liang, H. Liu and W. Shen, *ACS Appl. Mater. Interfaces*, 2023, **15**, 36233-36241.