*Supporting information*

# In-situ formation of 2D/3D heterostructure for efficient and stable $CsPbI_2Br$ solar cells

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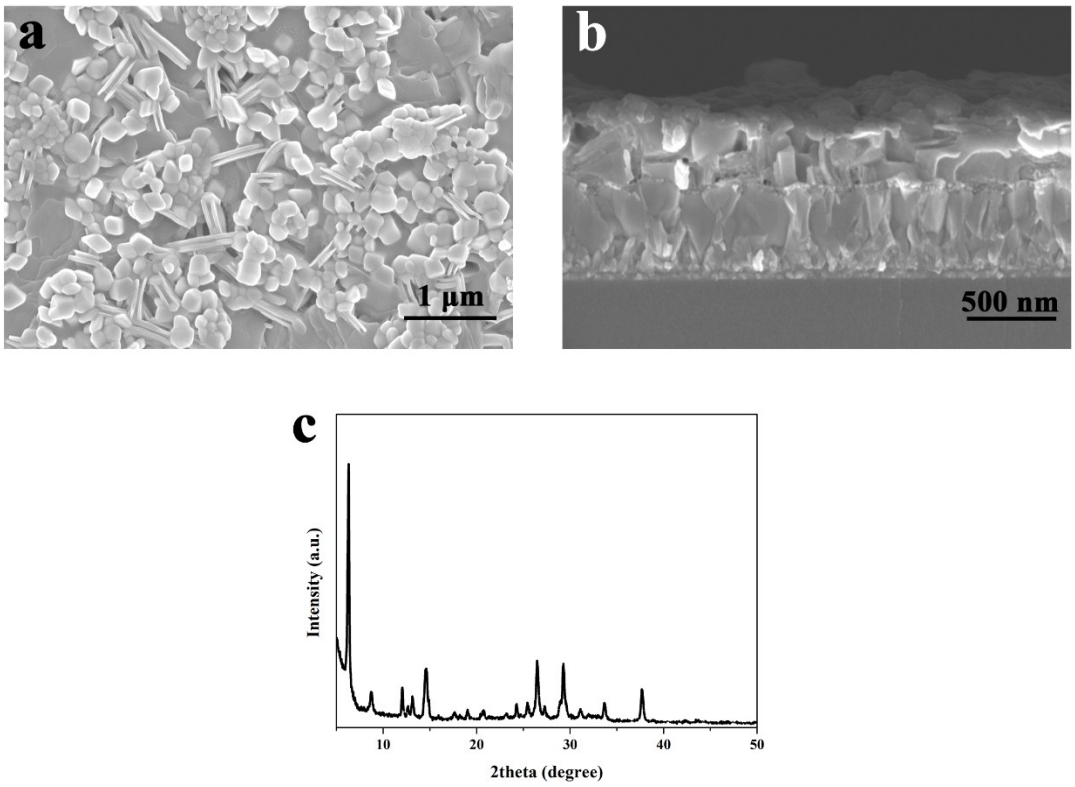


**Figure S1** Surface SEM image **(a),** cross-section SEM image **(b)** and XRD pattern **(c)** of perovskite sample fabricated by dropping 5 mg/mL BAI solution in CB/1 vol% DMSO on top of $CsPbI_2Br$ film before spinning at 4000 r for 30 s.

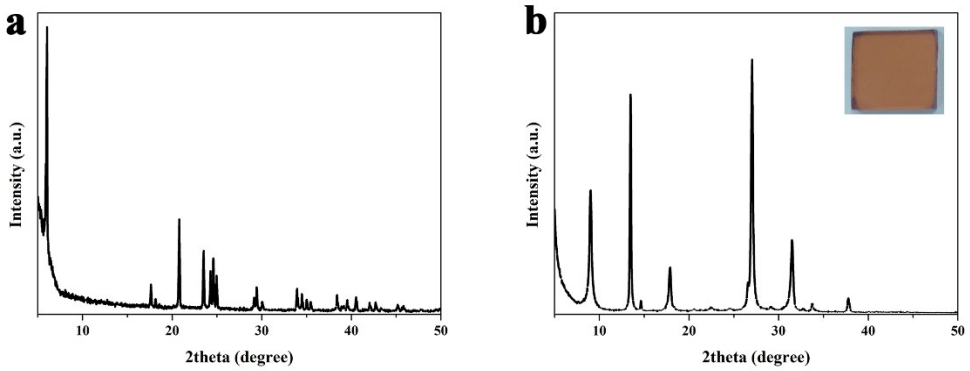


**Figure S2 (a)**XRD pattern of BAI powder. **(b)**XRD pattern of $BA_2CsPb_2I_6Br$ film. Inset shows the optical photograph. (The film was deposited by spin-coating a 0.4 M 4:1 volume ratio DMF/DMSO solution containing BAI/CsI/$PbI_2$/$PbBr_2$ with the ratio of 2:1:1.5:0.5)

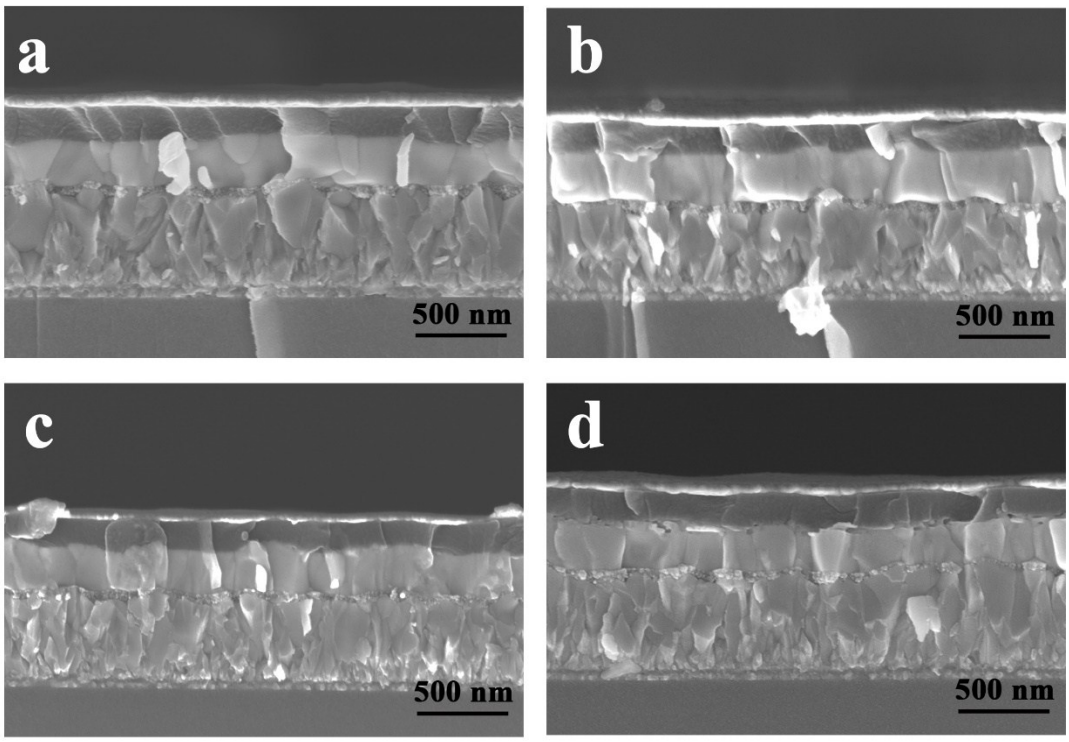


**Figure S3** Cross section SEM images of $CsPbI_2Br$ sample modified with different concentration of BAI: **(a)** pure $CsPbI_2Br$, **(b)** 1 mg, **(c)** 3 mg and **(d)** 5 mg.

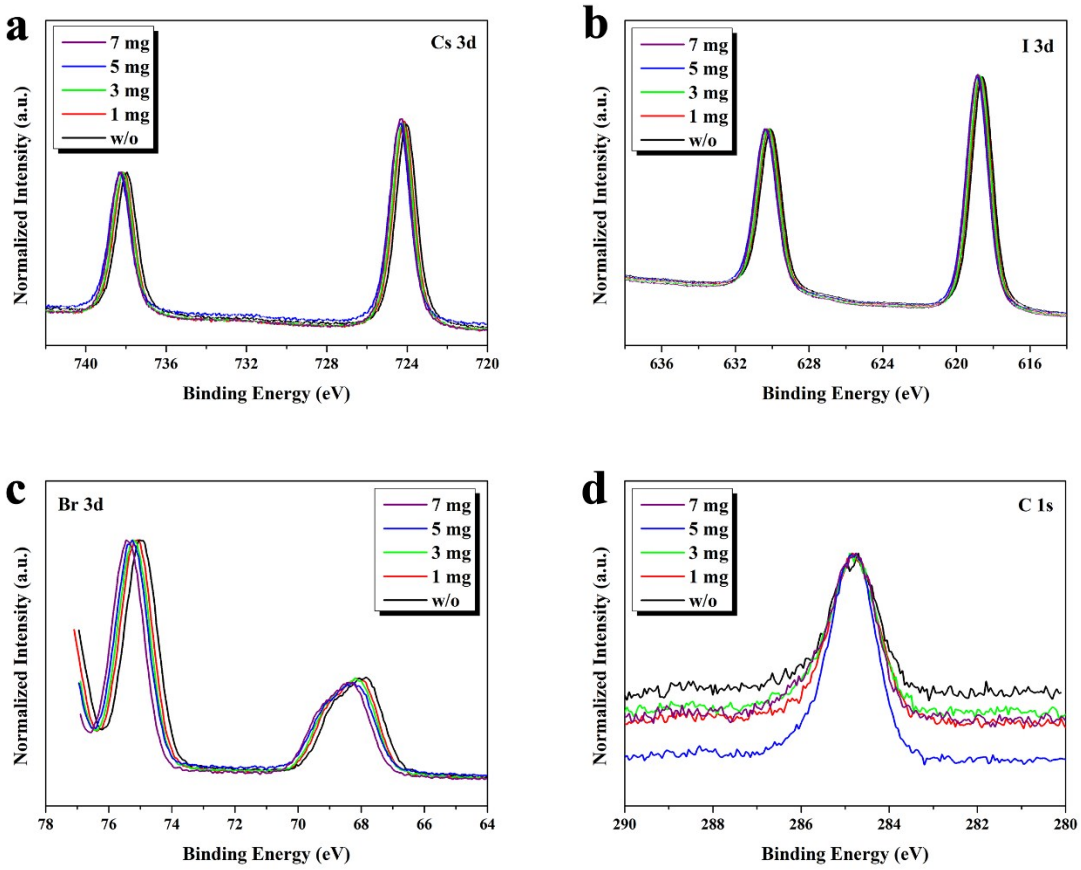


**Figure S4** Normalized XPS spectra of Cs 3d **(a)**, I 3d **(b)**, Br 3d **(c)** and C 1s **(d)** core levels.

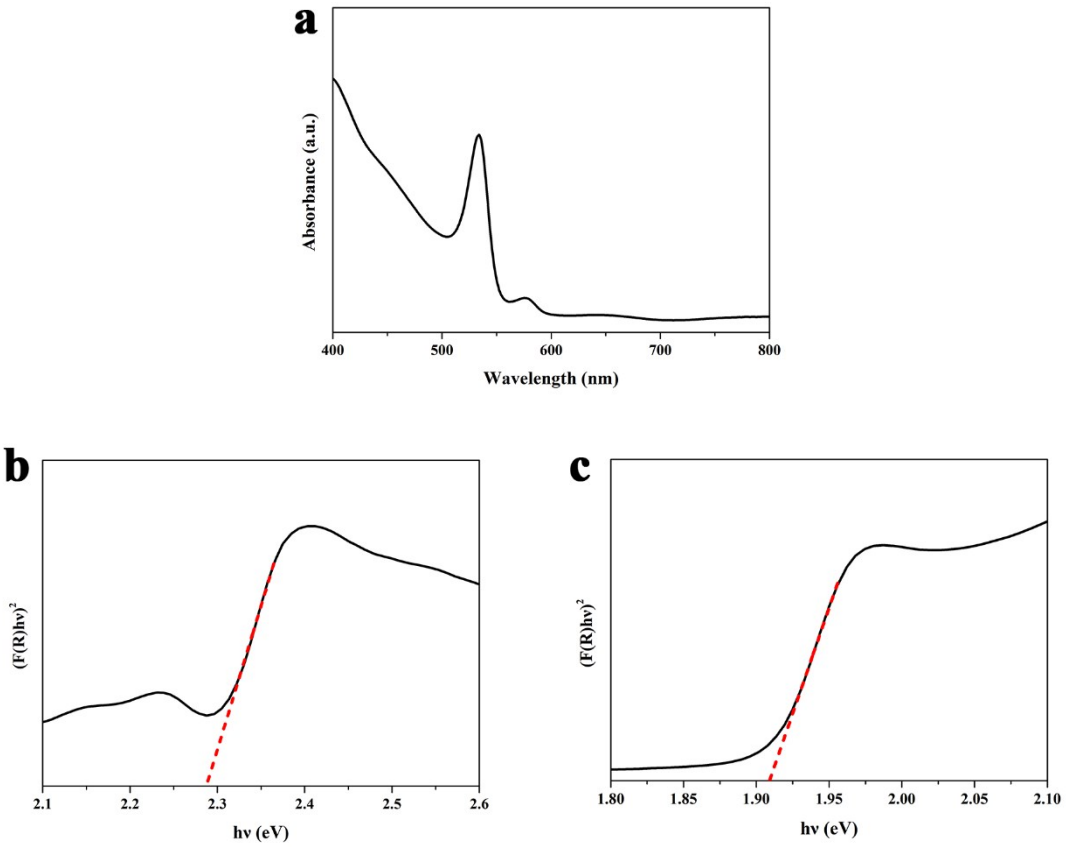


**Figure S5** UV-Vis absorption spectrum of $BA_2CsPb_2I_6Br$ film **(a)** and bandgap of $BA_2CsPb_2I_6Br$ **(b)** and $CsPbI_2Br$ **(c)** calculated from UV-Vis reflection spectrum.

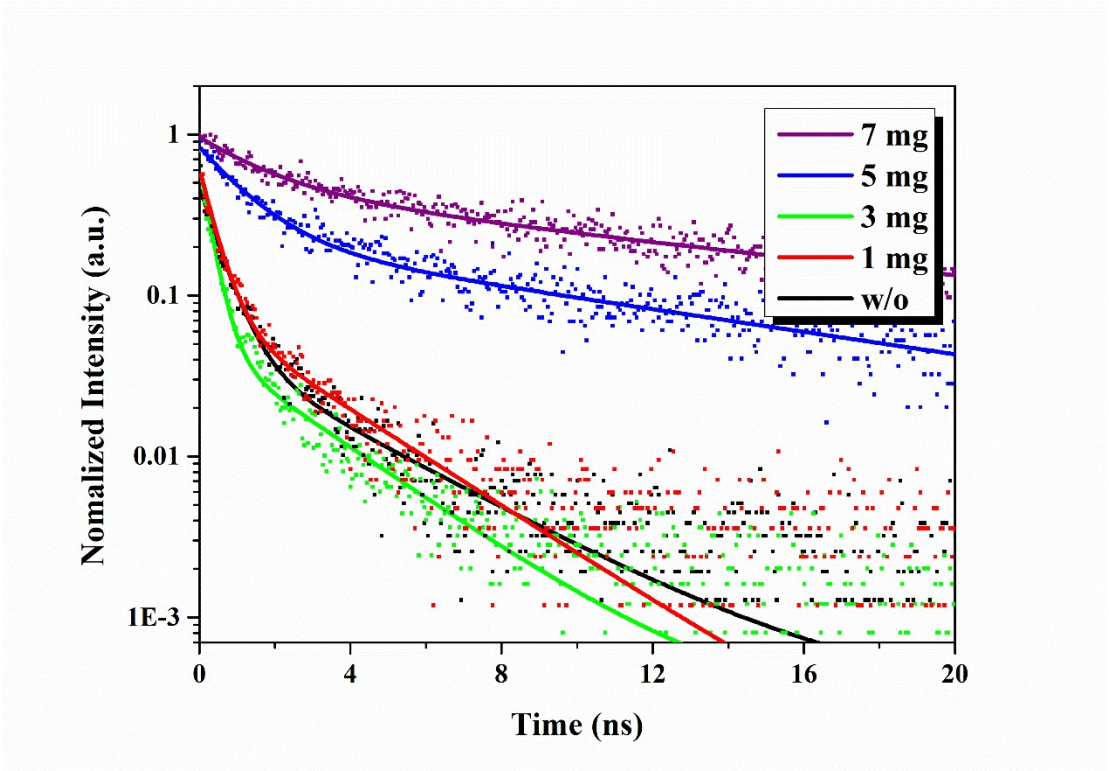


**Figure S6** TRPL decay curves of pure $CsPbI_2Br$ and 1, 3, 5, 7 mg BAI treated $CsPbI_2Br$ films based on FTO/perovskite/HTM structure.

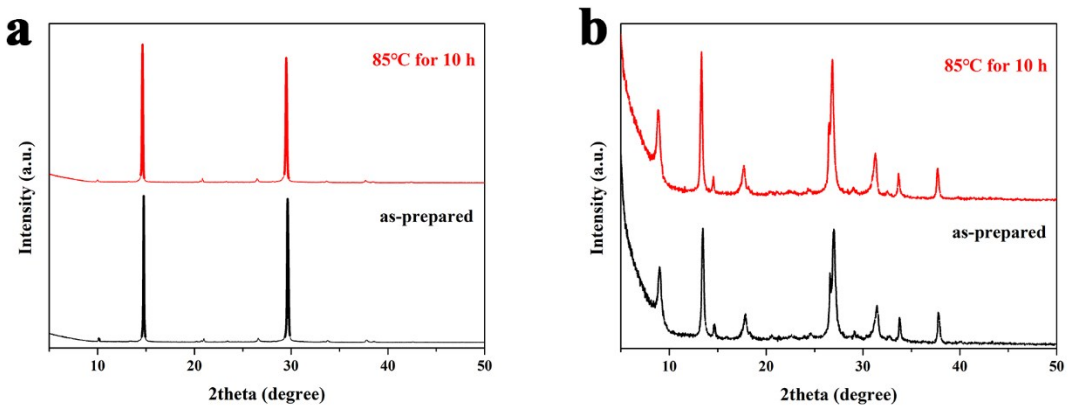


**Figure S7** XRD pattern of **(a)**3 mg BAI treated $CsPbI_2Br$ film and **(b)** $BA_2CsPb_2I_6Br$ film as-prepared and heated at 85 °C for 10 hours in a $N_2$-filled glovebox.

**Table S1** TRPL characterization of different perovskite films based on FTO/perovskite/HTM structure

| | **w/o** | **1 mg** | **3 mg** | **5 mg** | **7 mg** |
|---|---|---|---|---|---|
| $\tau_1$ (ns) | 0.54 | 0.42 | 0.30 | 1.28 | 1.76 |
| $\tau_2$ (ns) | 3.42 | 2.90 | 2.68 | 11.18 | 14.17 |
| **Average τ** (ns) | 1.72 | 1.66 | 1.31 | 9.66 | 12.62 |

**Table S2** Summary of device configurations and PCEs of $CsPbI_2Br$ perovskite solar cells previously reported

| Device configuration | PCE (%) | Reference |
|---|---|---|
| FTO/c-$TiO_2$-PCBM/$CsPbI_2Br$(2D modified)/spiro/Au | 14.5 | This work |
| FTO/c-$TiO_2$/$CsPbI_2Br$/P3HT/Au | 7.7 | [1] |
| FTO/c-$TiO_2$/mp-TiO2/$CsPb_{0.98}Sr_{0.02}I_2Br$/P3HT/Au | 11.2 | [2] |
| FTO/c-$TiO_2$/$CsPbI_2Br$/spiro/Ag | 9.8 | [3] |
| ITO/Ca/C60/$CsPbI_2Br$/TAPC/TAPC:$MoO_3$/Ag | 11.8 | [4] |
| FTO/c-$TiO_2$/$Cs_{0.925}K_{0.075}PbI_2Br$/spiro/Ag | 10.0 | [5] |
| ITO/c-$TiO_2$/$CsPbI_2Br$/spiro/Ag | 10.3 | [6] |
| ITO/c-$TiO_2$/$CsPbI_2Br$/P3HT/Au | 12.02 | [7] |
| FTO/c-$TiO_2$/$CsPbI_2Br$(3D-2D-0D)/PTAA/Au | 12.39 | [8] |
| FTO/$NiO_x$/$CsPbI_2Br$/ZnO-C60/Ag | 13.3 | [9] |
| FTO/NiMgLiO/$CsPbI_2Br$/PCBM/BCP/Ag | 9.14 | [10] |
| FTO/c-$TiO_2$/$CsPbI_2Br$/$CsPbI_3$ QDs/PTAA/Au | 14.4 | [11] |
| ITO/$NiO_x$/$CsPbI_2Br$/C60/BCP/Ag | 10.4 | [12] |
| FTO/c-$TiO_2$/mp-$TiO_2$/$CsPbI_2Br$/spiro/Au | 12 | [13] |
| ITO/$SnO_2$/ZnO/$CsPbI_2Br$/$MoO_3$/Ag | 14.6 | [14] |
| FTO/c-$TiO_2$/$CsPbI_2Br$/carbon | 10 | [15] |
| FTO/c-$TiO_2$/$CsPbI_2Br$/$FA^+$ QDs/PTAA/Au | 14.81 | [16] |
| FTO/c-$TiO_2$/$CsPbI_2Br$/spiro/Ag | 12.6 | [17] |
| FTO/$SnO_2$/$CsPbI_2Br$/spiro/Ag | 12.34 | [18] |
| ITO/c-$TiO_2$/$CsPbI_2Br$/spiro/Au | 16.07 | [19] |
| FTO/c-$TiO_2$/mp-$TiO_2$/$CsPb_{0.95}Eu_{0.05}I_2Br$/spiro/Au | 13.71 | [20] |
| ITO/$SnO_2$-PN4N/$CsPbI_2Br$/PDCBT/$MoO_3$/Ag | 16.2 | [21] |
| FTO/c-$TiO_2$/mp-$TiO_2$/BaI:$CsPbI_2Br$/P3HT/Au | 14.85 | [22] |

## References:


[1] Q. Ma, S. Huang, S. Chen, M. Zhang, C. F. J. Lau, M. N. Lockrey, H. K. Mulmudi, Y. Shan, J. Yao, J. Zheng, *The Journal of Physical Chemistry C* **2017**, *121*, 19642-19649.

[2] C. F. J. Lau, M. Zhang, X. Deng, J. Zheng, J. Bing, Q. Ma, J. Kim, L. Hu, M. A. Green, S. Huang, *ACS Energy Letters* **2017**, *2*, 2319-2325.

[3] R. J. Sutton, G. E. Eperon, L. Miranda, E. S. Parrott, B. A. Kamino, J. B. Patel, M. T. Hörantner, M. B. Johnston, A. A. Haghighirad, D. T. Moore, *Adv. Energy Mater.* **2016**, *6*, 1502458.

[4] C. Y. Chen, H. Y. Lin, K. M. Chiang, W. L. Tsai, Y. C. Huang, C. S. Tsao, H. W. Lin, *Adv. Mater.* **2017**, *29*, 1605290.

[5] J. K. Nam, S. U. Chai, W. Cha, Y. J. Choi, W. Kim, M. S. Jung, J. Kwon, D. Kim, J. H. Park, *Nano Lett.* **2017**, *17*, 2028-2033.

[6] J. S. Niezgoda, B. J. Foley, A. Z. Chen, J. J. Choi, *ACS Energy Letters* **2017**, *2*, 1043-1049.

[7] Q. Zeng, X. Zhang, X. Feng, S. Lu, Z. Chen, X. Yong, S. A. Redfern, H. Wei, H. Wang, H. Shen, *Adv. Mater.* **2018**, *30*, 1705393.

[8] J. Zhang, D. Bai, Z. Jin, H. Bian, K. Wang, J. Sun, Q. Wang, S. F. Liu, *Adv. Energy Mater.* **2018**, *8*, 1703246.

[9] C. Liu, W. Li, C. Zhang, Y. Ma, J. Fan, Y. Mai, *J. Am. Chem. Soc.* **2018**, *140*, 3825-3828.

[10] S. Zhang, S. Wu, W. Chen, H. Zhu, Z. Xiong, Z. Yang, C. Chen, R. Chen, L. Han, W. Chen, *Materials Today Energy* **2018**, *8*, 125-133.

[11] H. Bian, D. Bai, Z. Jin, K. Wang, L. Liang, H. Wang, J. Zhang, Q. Wang, S. F. Liu, *Joule* **2018**, *2*, 1500-1510.

[12] H. Rao, S. Ye, F. Gu, Z. Zhao, Z. Liu, Z. Bian, C. Huang, *Adv. Energy Mater.* **2018**, *8*, 1800758.

[13] Z. Zeng, J. Zhang, X. Gan, H. Sun, M. Shang, D. Hou, C. Lu, R. Chen, Y. Zhu, L. Han, *Adv. Energy Mater.* **2018**, *8*, 1801050.

[14] L. Yan, Q. Xue, M. Liu, Z. Zhu, J. Tian, Z. Li, Z. Chen, Z. Chen, H. Yan, H. L. Yip, *Adv. Mater.* **2018**, *30*, 1802509.

[15] C. Dong, X. Han, Y. Zhao, J. Li, L. Chang, W. Zhao, *Solar RRL* **2018**, *2*, 1800139.

[16] D. Bai, H. Bian, Z. Jin, H. Wang, L. Meng, Q. Wang, S. F. Liu, *Nano Energy* **2018**, *52*, 408-415.

[17] Y. Li, Y. Wang, T. Zhang, S. Yoriya, S. Chen, X. Guo, Y. Zhao, *Chem. Commun.* **2018**, *54*, 9809-9812.

[18] J. Yuan, L. Zhang, C. Bi, M. Wang, J. Tian, *Solar RRL* **2018**, *2*, 1800188.

[19] W. Chen, H. Chen, G. Xu, R. Xue, S. Wang, Y. Li, Y. Li, *Joule* **2019**, *3*, 191-204.

[20] W. Xiang, Z. Wang, D. J. Kubicki, W. Tress, J. Luo, D. Prochowicz, S. Akin, L. Emsley, J. Zhou, G. Dietler, *Joule* **2019**, *3*, 205-214.

[21] J. Tian, Q. Xue, X. Tang, Y. Chen, N. Li, Z. Hu, T. Shi, X. Wang, F. Huang, C. J. Brabec, *Adv. Mater.* **2019**, *31*, 1901152.

[22] S. S. Mali, J. V. Patil, C. K. Hong, *Nano Lett.* **2019**, DOI: 10.1021/acs.nanolett.9b02277.