Cation-Diffusion-Based Passivation for High Bandgap Single Junction Perovskite Cell and Double Junction Perovskite-Perovskite Tandem with Record Fill Factors

Md Arafat Mahmud[1,2], Jianghui Zheng[1,2,3,4], Shi Tang[1,2], Chwenhaw Liao[1,2], Guoliang Wang[1,2], Jueming Bing[1,2], Tik Lun Leung[1,2], Anh Dinh Bui[5], Hongjun Chen[1,2], Jianpeng Yi[1,2], Stephen P. Bremner[3], Hieu T. Nguyen[5], and Anita W. Y. Ho-Baillie[1,2,3]**

Affiliations:

[1]School of Physics, The University of Sydney, Sydney, NSW 2006, Australia

[2]The University of Sydney Nano Institute (Sydney Nano), The University of Sydney, Sydney, NSW 2006, Australia

[3]Australian Centre for Advanced Photovoltaics (ACAP), School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney 2052, Australia

[4]Sustainable Energy Research Centre, School of Engineering, Macquarie University, Sydney, NSW 2109, Australia

[5]School of Engineering, The Australian National University, ACT 2601, Australia

*Correspondence to: anita.ho-baillie@sydney.edu.au (A. H.-B.), md.mahmud@sydney.edu.au (M. A. M.)

Metal halide perovskite solar cell is the fastest-growing photovoltaic technology in terms of efficiency improvement. The best laboratory 1.53 eV cell efficiency has reached 25.7% from 3.8% in just over 10 years.[1] As a wide range (1.2 eV to 2.3 eV) of bandgap is realisable for perovskites by tuning their composition in precursor preparation, perovskites are suitable for low-cost, solution-processable multi-junction tandem solar cells, having an efficiency potential over 40%.[2] High bandgap (1.7 eV to 2.0 eV) perovskite cells are integral to such tandems, but current demonstrations suffer from high voltage deficit[3] compared to their low mid-bandgap (1.5 eV to 1.6 eV) counterparts producing lower voltage outputs, lower fill factors (FF) in high bandgap devices (Figure 1) indicating room for improving bulk and interface quality,[4] reducing their susceptibilities to carrier recombination.

A number of recent studies have focussed on bulk[5-10] and/or surface passivation[11-17] of high bandgap perovskite films to reduce their trap-assisted recombination. A major limitation in the demonstrated passivation strategies is that the passivation effect is confined to either bulk or only at one perovskite/charge-transport-layer interface. Another limitation is the type of perovskite devices that have benefited from successful passivation strategies. For example, double-sided interface passivation has been shown to be successful for mid bandgap perovskite cells which are predominantly n-i-p devices[18-21] where the n-type layers are fabricated first and p-type layers are fabricated last. However, p-i-n devices can achieve higher efficiency potentials than n-i-p ones for tandem application,[22] as they have less optically absorptive transport layers on the sun-facing side.

Highlights of the Work

In this work, we develop a double-sided surface passivation that is compatible with p-i-n perovskite cells that also provides simultaneous bulk passivation for high bandgap perovskite cells for the first time. This concurrent bulk-passivation and surface-passivation scheme is based on the partial diffusion of bulky organic cations from the surface-layer into the bulk passivating defects while the surface-remaining cations passivate the perovskite surface. This is different to previous work[23] whereby diffused-halide (inorganic anions) was responsible for the passivation of the perovskite bulk amid the bulk only.

Evidence of the cation diffusion have been found using ionic distribution profiling, Fourier transform infrared spectroscopy, and crystallography and one of its effect on the perovskite device is bandgap widening.

More importantly, performance of high-bandgap (1.75eV) champion p-i-n perovskite solar cell devices improved by 1% absolute after implementing the concurrent bulk and surface passivation scheme on one side and another 1% absolute if implemented on both sides (Table 1). The champion cell achieved the highest FF of 86.5% and power conversion efficiency of 20.2%. These values are the highest for perovskite cells with bandgap > 1.7eV (Figure 1). This strategy has also been implemented in high bandgap cells for the demonstration of perovskite-perovskite tandems. Latest tandem cell results will be provided in the conference presentation.

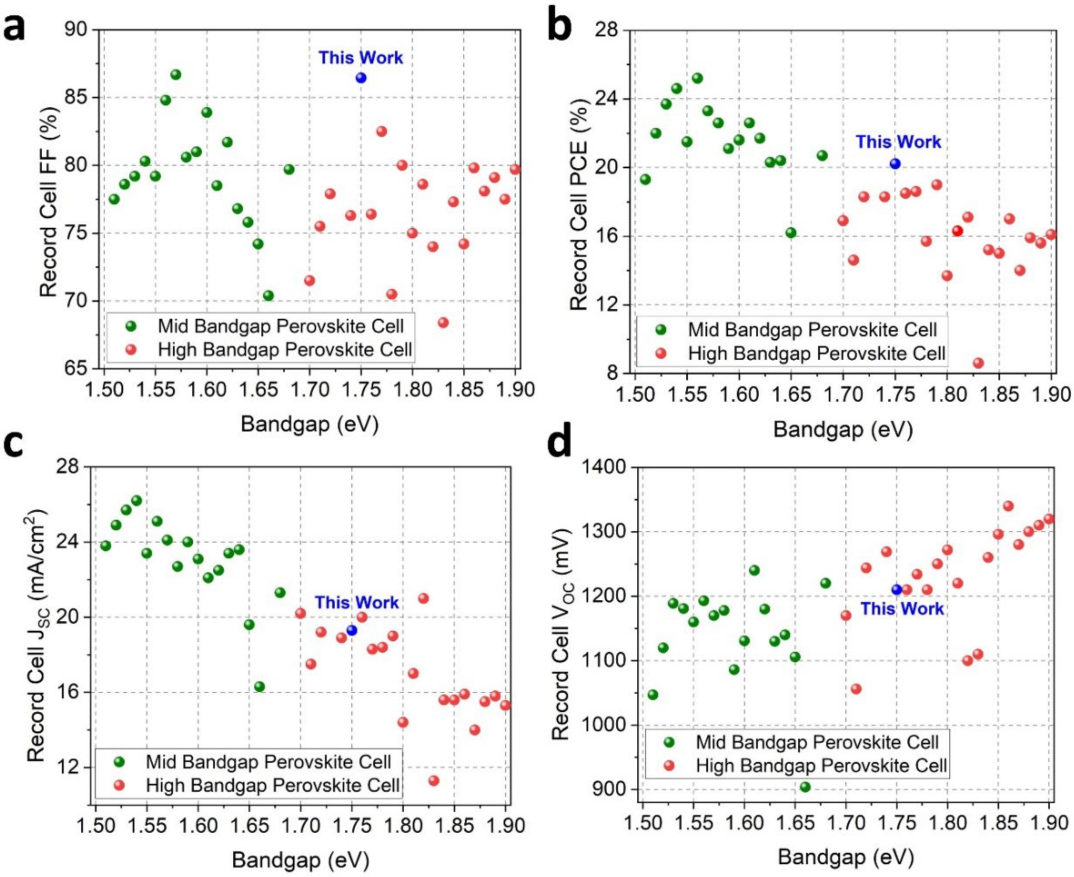

Figure 1. Fill factors (FF), b. power conversion efficiency (PCE), c. short circuit current density (J_{SC}), and d. open circuit voltage (V_{OC}) of mid- and high- band gap solar cells with record-efficiencies reported in peer-reviewed articles[24]

Table 1 Photovoltaic parameters - averaged from 15 cells and measured for the champion device in each category: control (un-passivated), single side (SS) passivated and double-side passivated perovskite solar cells

Device	Average /Champion	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Control	Average	1085±11	19.3±0.1	84.3±0.5	17.6±0.2
	Champion	1104	19.4	84.7	18.1
SS Passivation	Average	1179±7	19.2±0.2	84.5±0.6	19.1±0.1
	Champion	1187	19.2	85.0	19.3
DS Passivation	Average	1208±7	19.3±0.1	85.6±0.5	19.9±0.2
	Champion	1210	19.3	86.5	20.2

References

1. NREL Best Research Cell Efficiency Chart. https://www.nrel.gov/pv/cell-efficiency.html (accessed 1 October, 2021).

2. Ho-Baillie, A. W. Y.; Zheng, J.; Mahmud, M. A.; Ma, F.-J.; McKenzie, D.; Green, M., Recent progress and future prospects of perovskite tandem solar cells. *Applied Physics Review* **2021**.

3. Green, M. A.; Ho-Baillie, A. W. Y., Pushing to the Limit: Radiative Efficiencies of Recent Mainstream and Emerging Solar Cells. *ACS Energy Letters* **2019,** *4* (7), 1639-1644.

4. Mahesh, S.; Ball, J. M.; Oliver, R. D. J.; McMeekin, D. P.; Nayak, P. K.; Johnston, M. B.; Snaith, H. J., Revealing the origin of voltage loss in mixed-halide perovskite solar cells. *Energy & Environmental Science* **2020,** *13* (1), 258-267.

5. Zhou, Y.; Jia, Y.-H.; Fang, H.-H.; Loi, M. A.; Xie, F.-Y.; Gong, L.; Qin, M.-C.; Lu, X.-H.; Wong, C.-P.; Zhao, N., Composition-Tuned Wide Bandgap Perovskites: From Grain Engineering to Stability and Performance Improvement. **2018,** *28* (35), 1803130.

6. Jiang, F.; Yang, D.; Jiang, Y.; Liu, T.; Zhao, X.; Ming, Y.; Luo, B.; Qin, F.; Fan, J.; Han, H.; Zhang, L.; Zhou, Y., Chlorine-Incorporation-Induced Formation of the Layered Phase for Antimony-Based Lead-Free Perovskite Solar Cells. *Journal of the American Chemical Society* **2018,** *140* (3), 1019-1027.

7. Zhang, J.; Wang, Z.; Mishra, A.; Yu, M.; Shasti, M.; Tress, W.; Kubicki, D. J.; Avalos, C. E.; Lu, H.; Liu, Y.; Carlsen, B. I.; Agarwalla, A.; Wang, Z.; Xiang, W.; Emsley, L.; Zhang, Z.; Grätzel, M.; Guo, W.; Hagfeldt, A., Intermediate Phase Enhances Inorganic Perovskite and Metal Oxide Interface for Efficient Photovoltaics. *Joule* **2020,** *4* (1), 222-234.

8. Xiang, W.; Wang, Z.; Kubicki, D. J.; Tress, W.; Luo, J.; Prochowicz, D.; Akin, S.; Emsley, L.; Zhou, J.; Dietler, G.; Grätzel, M.; Hagfeldt, A., Europium-Doped CsPbI₂Br for Stable and Highly Efficient Inorganic Perovskite Solar Cells. *Joule* **2019,** *3* (1), 205-214.

9. Zhao, H.; Han, Y.; Xu, Z.; Duan, C.; Yang, S.; Yuan, S.; Yang, Z.; Liu, Z.; Liu, S., A Novel Anion Doping for Stable CsPbI2Br Perovskite Solar Cells with an Efficiency of 15.56% and an Open Circuit Voltage of 1.30 V. **2019,** *9* (40), 1902279.

10. Yang, S.; Zhao, H.; Han, Y.; Duan, C.; Liu, Z.; Liu, S., Europium and Acetate Co-doping Strategy for Developing Stable and Efficient CsPbI2Br Perovskite Solar Cells. **2019,** *15* (46), 1904387.

11. Wang, L.; Yan, Z.; Qiu, J.; Wu, J.; Zhen, C.; Tai, K.; Jiang, X.; Yang, S., Interface regulation enables hysteresis free wide-bandgap perovskite solar cells with low VOC deficit and high stability. *Nano Energy* **2021,** *90*, 106537.

12. Duong, T.; Pham, H.; Yin, Y.; Peng, J.; Mahmud, M. A.; Wu, Y.; Shen, H.; Zheng, J.; Tran-Phu, T.; Lu, T.; Li, L.; Kumar, A.; Andersson, G. G.; Ho-Baillie, A.; Liu, Y.; White, T.; Weber, K.; Catchpole, K., Efficient and stable wide bandgap perovskite solar cells through surface passivation with long alkyl chain organic cations. *Journal of Materials Chemistry A* **2021,** *9* (34), 18454-18465.

13. Gharibzadeh, S.; Fassl, P.; Hossain, I. M.; Rohrbeck, P.; Frericks, M.; Schmidt, M.; Duong, T.; Khan, M. R.; Abzieher, T.; Nejand, B. A.; Schackmar, F.; Almora, O.; Feeney, T.; Singh, R.; Fuchs, D.; Lemmer, U.; Hofmann, J. P.; Weber, S. A. L.; Paetzold, U. W., Two birds with one stone: dual grain-boundary and interface passivation enables >22% efficient inverted methylammonium-free perovskite solar cells. *Energy & Environmental Science* **2021,** *14* (11), 5875-5893.

14. Duong, T.; Pham, H.; Kho, T. C.; Phang, P.; Fong, K. C.; Yan, D.; Yin, Y.; Peng, J.; Mahmud, M. A.; Gharibzadeh, S.; Nejand, B. A.; Hossain, I. M.; Khan, M. R.; Mozaffari, N.; Wu, Y.; Shen, H.; Zheng, J.; Mai, H.; Liang, W.; Samundsett, C.; Stocks, M.; McIntosh, K.; Andersson, G. G.; Lemmer, U.; Richards, B. S.; Paetzold, U. W.; Ho-Ballie, A.; Liu, Y.; Macdonald, D.; Blakers, A.; Wong-Leung, J.; White, T.; Weber, K.; Catchpole, K., High Efficiency Perovskite-Silicon Tandem Solar Cells: Effect of Surface Coating versus Bulk Incorporation of 2D Perovskite. **2020,** *10* (9), 1903553.

15. Gharibzadeh, S.; Abdollahi Nejand, B.; Jakoby, M.; Abzieher, T.; Hauschild, D.; Moghadamzadeh, S.; Schwenzer, J. A.; Brenner, P.; Schmager, R.; Haghighirad, A. A.; Weinhardt, L.; Lemmer, U.; Richards, B. S.; Howard, I. A.; Paetzold, U. W., Record Open-Circuit Voltage Wide-Bandgap Perovskite Solar Cells Utilizing 2D/3D Perovskite Heterostructure. **2019,** *9* (21), 1803699.

16. Ye, Q.; Zhao, Y.; Mu, S.; Ma, F.; Gao, F.; Chu, Z.; Yin, Z.; Gao, P.; Zhang, X.; You, J., Cesium Lead Inorganic Solar Cell with Efficiency beyond 18% via Reduced Charge Recombination. **2019,** *31* (49), 1905143.

17. Chen, C.; Song, Z.; Xiao, C.; Zhao, D.; Shrestha, N.; Li, C.; Yang, G.; Yao, F.; Zheng, X.; Ellingson, R. J.; Jiang, C.-S.; Al-Jassim, M.; Zhu, K.; Fang, G.; Yan, Y., Achieving a high open-circuit voltage in inverted wide-bandgap perovskite solar cells with a graded perovskite homojunction. *Nano Energy* **2019,** *61*, 141-147.

18. Peng, J.; Khan, J. I.; Liu, W.; Ugur, E.; Duong, T.; Wu, Y.; Shen, H.; Wang, K.; Dang, H.; Aydin, E.; Yang, X.; Wan, Y.; Weber, K. J.; Catchpole, K. R.; Laquai, F.; De Wolf, S.; White, T. P., A Universal Double-Side Passivation for High Open-Circuit Voltage in Perovskite Solar Cells: Role of Carbonyl Groups in Poly(methyl methacrylate). **2018,** *8* (30), 1801208.

19. Mahmud, M. A.; Duong, T.; Yin, Y.; Pham, H. T.; Walter, D.; Peng, J.; Wu, Y.; Li, L.; Shen, H.; Wu, N.; Mozaffari, N.; Andersson, G.; Catchpole, K. R.; Weber, K. J.; White, T. P., Double-Sided Surface Passivation of 3D Perovskite Film for High-Efficiency Mixed-Dimensional Perovskite Solar Cells. *Advanced Functional Materials* **2020,** *30* (7), 1907962.

20. Mahmud, M. A.; Duong, T.; Yin, Y.; Peng, J.; Wu, Y.; Lu, T.; Pham, H. T.; Shen, H.; Walter, D.; Nguyen, H. T.; Mozaffari, N.; Tabi, G. D.; Liu, Y.; Andersson, G.; Catchpole, K. R.; Weber, K. J.; White, T. P., In Situ Formation of Mixed-Dimensional Surface Passivation Layers in Perovskite Solar Cells with Dual-Isomer Alkylammonium Cations. *Small* **2020,** *16* (49), 2005022.

21. Zhao, Y.; Li, Q.; Zhou, W.; Hou, Y.; Zhao, Y.; Fu, R.; Yu, D.; Liu, X.; Zhao, Q., Double-Side-Passivated Perovskite Solar Cells with Ultra-low Potential Loss. **2019,** *3* (2), 1800296.

22. Al-Ashouri, A.; Köhnen, E.; Li, B.; Magomedov, A.; Hempel, H.; Caprioglio, P.; Márquez, J. A.; Vilches, A. B. M.; Kasparavicius, E.; Smith, J. A.; Phung, N.; Menzel, D.; Grischek, M.; Kegelmann, L.; Skroblin, D.; Gollwitzer, C.; Malinauskas, T.; Jošt, M.; Matič, G.; Rech, B.; Schlatmann, R.; Topič, M.; Korte, L.; Abate, A.; Stannowski, B.; Neher, D.; Stolterfoht, M.; Unold, T.; Getautis, V.; Albrecht, S., Monolithic perovskite/silicon tandem solar cell with >29% efficiency by enhanced hole extraction. **2020,** *370* (6522), 1300-1309.

23. Mahmud, M. A.; Pham, H. T.; Duong, T.; Yin, Y.; Peng, J.; Wu, Y.; Liang, W.; Li, L.; Kumar, A.; Shen, H.; Walter, D.; Nguyen, H. T.; Mozaffari, N.; Tabi, G. D.; Andersson, G.; Catchpole, K. R.; Weber, K. J.; White, T. P., Combined Bulk and Surface Passivation in Dimensionally Engineered 2D-3D Perovskite Films via Chlorine Diffusion. **2021,** *31* (46), 2104251.

24. Almora, O.; Baran, D.; Bazan, G. C.; Berger, C.; Cabrera, C. I.; Catchpole, K. R.; Erten-Ela, S.; Guo, F.; Hauch, J.; Ho-Baillie, A. W. Y.; Jacobsson, T. J.; Janssen, R. A. J.; Kirchartz, T.; Kopidakis, N.; Li, Y.; Loi, M. A.; Lunt, R. R.; Mathew, X.; McGehee, M. D.; Min, J.; Mitzi, D. B.; Nazeeruddin, M. K.; Nelson, J.; Nogueira, A. F.; Paetzold, U. W.; Park, N.-G.; Rand, B. P.; Rau, U.; Snaith, H. J.; Unger, E.; Vaillant-Roca, L.; Yip, H.-L.; Brabec, C. J., Device Performance of Emerging Photovoltaic Materials (Version 2). **2021,** *11* (48), 2102526.