

Carbon-Based CsPbI₃ Perovskite Solar Cells

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Abstract

The perovskite solar cells (PSCs) based on carbon electrode (C-PSCs) are expected to address the instability issues faced by conventional PSCs. Recently, inorganic perovskites have been widely used as the light absorber in C-PSCs, which tended to further enhance device stability. Among various inorganic perovskites, CsPbI₃ perovskite has been showing the greatest promise due to its suitable band gap (~1.7 eV) and high chemical stability. Benefiting from the progresses on phase stability, crystal quality and surface defect passivation, CsPbI₃ C-PSCs have achieved the efficiency of over 15% and exhibited considerable enhancement in device stability. In this perspective, the main advances on CsPbI₃ C-PSCs will be highlighted and the future research directions will be proposed.

Key words: Perovskite solar cells; Inorganic perovskites; CsPbI₃; Carbon electrode.

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Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted great attention because high power conversion efficiencies (PCE, 25.7%) could be easily achieved by low-cost solution-based processes^[1]. The great achievement in PCE is attributed to the advantages of the perovskite absorber: high absorption coefficient, high mobility, long balanced carrier diffusion length and low exciton binding energy^[2]. However, the poor stability has seriously limited their practical application.

For conventional PSCs (e.g., FTO/TiO₂/perovskite/organic hole transport material (HTM)/metal electrode, Fig. 1a), the high-performance organic HTM is commonly doped with ions (e.g., Li⁺), which is humidity-sensitive and is easy to degrade, while the metal electrode tends to be ionized during operation, which would migrate through HTM to react with perovskite layer for inducing device degradation^[3–4]. To address these issues, the PSCs based on carbon electrodes (C-PSCs, Fig. 1b) were developed, in which carbon electrode simultaneously replaced organic HTM and metal electrode. Since carbon materials are stable, hydrophobic and inert to ion migration, device stability was well enhanced^[5].

Though C-PSCs exhibited considerably higher stability than conventional PSCs, the organic ions (e.g., CH₃NH₃⁺) in the organic-inorganic hybrid perovskites (e.g., CH₃NH₃PbI₃) would be lost under harsh condition (e.g., high temperature and high humidity), which still limits the device stability. To solve this problem, inorganic perovskites (e.g., CsPbBr₃, CsPbI_{3-x}Br_x and CsPbI₃) have been employed in C-PSCs^[6]. The inorganic ions (e.g., Cs⁺) in the inorganic perovskite well enhanced the material and device stability, especially thermal stability.

In 2016, inorganic CsPbBr₃ was for the first time used as the

light absorber in C-PSCs. The PCEs of 5%^[7] and 6.7%^[8] were achieved, which were comparable to the PCEs achieved by the CsPbBr₃ PSCs with the conventional architecture. Most importantly, the CsPbBr₃ C-PSCs exhibited considerably enhanced thermal stability compared with organic-inorganic hybrid C-PSCs. Soon after, great progresses have been made on CsPbBr₃ C-PSCs with the PCE raising up to over 11.08%^[9]. Although CsPbBr₃ C-PSCs show superior stability and decent PCE was reported, the large E_g (~2.30 eV) of CsPbBr₃ means that it could only absorb the visible light below 540 nm and the theoretical PCE is only about 16%^[10].

For achieving higher PCE, it is necessary to find new inorganic perovskite materials with narrower E_g (Fig. 1c). Fortunately, gradually substituting Br with I in CsPbBr₃ would reduce the E_g . CsPbIBr₂ and CsPbI₂Br are the two representative mixed-halide perovskites, whose E_g were calculated to be 2.05 and 1.90 eV, respectively^[10]. By employing CsPbI_{3-x}Br_x as light absorbers in C-PSCs, the light absorption range was extended and the short-circuit current density (J_{sc}) was improved. As a result, the champion PCE of 12.05%^[11] and 15.24%^[12] were achieved by CsPbIBr₂ and CsPbI₂Br C-PSCs, respectively.

Compared with mixed-halide CsPbI_{3-x}Br_x perovskites, the full-I CsPbI₃ perovskite owns the narrowest E_g (~1.7 eV)^[13]. However, due to the small size of Cs cations (1.69 Å), the tolerance factor (t) of CsPbI₃ perovskite is only 0.81, which is too low to support a stable perovskite structure at low temperature^[14]. Consequently, CsPbI₃ perovskite phases (α , β and γ) would spontaneously transit to yellow non-perovskite phase (δ , E_g =2.82 eV) at ambient temperature^[15–17]. Therefore, it is a great challenge to grow CsPbI₃ perovskite for PSCs and only

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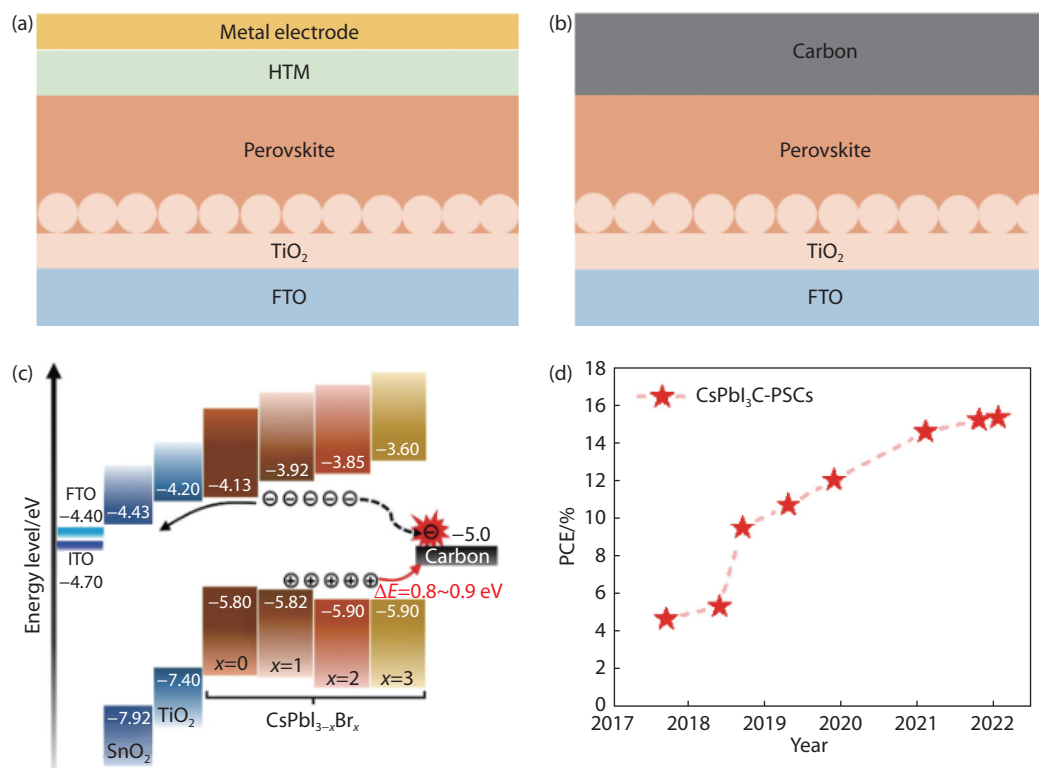


Fig. 1 The device structure of (a) conventional PSCs and (b) PSCs based on carbon electrodes (C-PSCs). (c) Energy band diagrams of CsPbI_{3-x}Br_x C-PSCs^[10]. Copyright 2021, Elsevier Ltd. (d) Evolution of the reported PCEs of CsPbI₃ C-PSCs^[13,15,18-23].

very low performance was obtained for the initial CsPbI₃ C-PSCs^[18].

To address the above issues, two effective strategies have been developed in our group. First, excess CsI was introduced into the PbI₂/CsI precursor solution, which would lead to the generation of Cs₄PbI₆ intermediate phase. After immersing the Cs₄PbI₆ in isopropyl alcohol (IPA), partial CsI would dissolve and the Cs₄PbI₆ could be converted to stable CsPbI₃ perovskite phase^[19]. On the other hand, HPbI₃ (or DMAPbI₃, DMA⁺ = (CH₃)₂NH₂⁺) was used to replace PbI₂ as the precursor to induce the formation of DMAPbI₃ and Cs₄PbI₆ intermediates. After removing DMAI, Cs₄PbI₆ was converted to stable CsPbI₃ perovskite. By applying such CsPbI₃ perovskite in C-PSCs, a promising PCE of 9.5%^[20] was obtained with high stability.

Though the phase stability of CsPbI₃ has been well improved, the crystal quality was still low, limiting the device performance. To improve crystal quality, elemental doping has been exploited^[21]. For B site doping, Sb³⁺ ions were incorporated into CsPbI₃ solution^[19]. After deposition, Sb partially replaced the Pb in CsPbI₃ lattice. As indicated, crystal quality was improved accompanied with the enhancement in phase stability. In addition to B site doping, A site doping was also implemented and alkali metal ions (Li⁺, Na⁺, K⁺ and Rb⁺) have been used to partially replace the Cs⁺ ions in CsPbI₃. Interestingly, all these ions well improved the crystal quality of CsPbI₃ perovskite and hence elevated the PCE of CsPbI₃ C-PSCs to about 11%^[22].

For better passivating the interface and surface defects of CsPbI₃ perovskite, a systematic and in-depth study on the growth processes of CsPbI₃ crystals was conducted and the

solution components were regulated to obtain stable CsPbI₃ perovskite and realize the passivation of excess PbI₂ on crystal defects^[15]. By further treating the CsPbI₃ films with medium polarity solvent (e.g., ethanol, IPA), the harmful DMAPbI₃ residual could be well converted to PbI₂ passivator, which not only eliminated the negative effects of DMAPbI₃ but also enhanced the defect passivating effects. As a result, CsPbI₃ C-PSCs achieved a PCE of 15.35%^[23], a record PCE for inorganic C-PSCs. In addition to PbI₂, CsX (X: F, Cl, Br) ethanol solutions were also used to treat the CsPbI₃ perovskite. The larger size mismatch between X⁻ and I⁻ ions would induce the more obvious cation segregation. The moderate size mismatch between I⁻ and Cl⁻ ions allows a partial substitution of I⁻ ions with Cl⁻ ions in CsPbI₃, and induces the generation of 2D Cs₂PbI₂Cl₂ nanosheets on the surface, which considerably reduced defect density and suppressed carrier recombination. As a result, the CsPbI₃ C-PSCs achieved an PCE of 15.23%^[13].

As stated above, much progress has been made on CsPbI₃ C-PSCs in recent years (Fig. 1d) and about 15% PCE has been achieved, but the PCE still largely lags behind those achieved by the conventional CsPbI₃ PSCs (over 20%)^[24-25]. To further improve the PCE of CsPbI₃ C-PSCs, higher quality CsPbI₃ film should be prepared with enhanced phase stability and reduced defect density. Besides, hole selectivity at the CsPbI₃/carbon should be improved to enhance hole transfer, and energy level alignment at the interface needs to be paid more attention.

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

Qixian Zhang: Investigation, Data Acquisition, Writing-Original Draft; Huicong Liu: Resources, Project Administration; Weiping Li: Conceptualization, Funding Acquisition; Haining Chen: Conceptualization, Methodology, Writing-Review & Editing.

REFERENCES

1. M. Kim, J. Jeong, H. Lu, K. Lee Tae, T. Eickemeyer Felix, Y. Liu, W. Choi In, J. Choi Seung, Y. Jo, H.-B. Kim, S.-I. Mo, Y.-K. Kim, H. Lee, G. An Na, S. Cho, R. Tress Wolfgang, M. Zakeeruddin Shaik, A. Hagfeldt, Y. Kim Jin, M. Grätzel and S. Kim Dong, *Science*, 2022, 375, 302
2. X. Luo, Z. Shen, Y. Shen, Z. Su, X. Gao, Y. Wang, Q. Han and L. Han, *Adv. Mater.*, 2022, 34, 2202100
3. J. Y. Seo, S. Akin, M. Zalibera, M. A. R. Preciado, H. S. Kim, S. M. Zakeeruddin, J. V. Milić and M. Grätzel, *Advanced Functional Materials*, 2021, 31, 2102124
4. C. Ding, R. Huang, C. Ahläng, J. Lin, L. Zhang, D. Zhang, Q. Luo, F. Li, R. Österbacka and C.-Q. Ma, *Journal of Materials Chemistry A*, 2021, 9, 7575
5. H. Chen and S. Yang, *Adv. Mater.*, 2017, 29, 1603994
6. H. Chen, S. Xiang, W. Li, H. Liu, L. Zhu and S. Yang, *Solar RRL*, 2018, 2, 1700188
7. X. Chang, W. Li, L. Zhu, H. Liu, H. Geng, S. Xiang, J. Liu and H. Chen, *ACS Applied Materials & Interfaces*, 2016, 8, 33649
8. J. Liang, C. Wang, Y. Wang, Z. Xu, Z. Lu, Y. Ma, H. Zhu, Y. Hu, C. Xiao, X. Yi, G. Zhu, H. Lv, L. Ma, T. Chen, Z. Tie, Z. Jin and J. Liu, *Journal of the American Chemical Society*, 2016, 138, 15829
9. Q. Zhou, J. Duan, J. Du, Q. Guo, Q. Zhang, X. Yang, Y. Duan and Q. Tang, *Adv. Sci.*, 2021, 8, 2101418
10. C. Dong, B. Xu, D. Liu, E. G. Moloney, F. Tan, G. Yue, R. Liu, D. Zhang, W. Zhang and M. I. Saidaminov, *Materials Today*, 2021, 50, 239
11. Q. Guo, J. Duan, J. Zhang, Q. Zhang, Y. Duan, X. Yang, B. He, Y. Zhao and Q. Tang, *Adv. Mater.*, 2022, 34, 2202301
12. W. Zhu, J. Ma, W. Chai, T. Han, D. Chen, X. Xie, G. Liu, P. Dong, H. Xi, D. Chen, J. Zhang, C. Zhang and Y. Hao, *Solar RRL*, 2022, 6, 2200020
13. H. Wang, H. Liu, Z. Dong, T. Song, W. Li, L. Zhu, Y. Bai and H. Chen, *Nano Energy*, 2021, 89, 106411
14. X. Fu, W. Li, X. Zeng, C. Yan, X. Peng, Y. Gao, Q. Wang, J. Cao, S. Yang and W. Yang, *J. Phys. Chem. Lett.*, 2022, 13, 2217
15. H. Wang, H. Liu, Z. Dong, W. Li, L. Zhu and H. Chen, *Nano Energy*, 2021, 84, 105881
16. W. Meng, Y. Hou, A. Karl, E. Gu, X. Tang, A. Osvet, K. Zhang, Y. Zhao, X. Du, J. Garcia Cerrillo, N. Li and C. J. Brabec, *ACS Energy Letters*, 2020, 5, 271
17. Z. Li, F. Zhou, Q. Wang, L. Ding and Z. Jin, *Nano Energy*, 2020, 71, 104634
18. J. Liang, C. Wang, P. Zhao, Z. Lu, Y. Ma, Z. Xu, Y. Wang, H. Zhu, Y. Hu, G. Zhu, L. Ma, T. Chen, Z. Tie, J. Liu and Z. Jin, *Nanoscale*, 2017, 9, 11841
19. S. Xiang, W. Li, Y. Wei, J. Liu, H. Liu, L. Zhu and H. Chen, *Nanoscale*, 2018, 10, 9996
20. S. Xiang, Z. Fu, W. Li, Y. Wei, J. Liu, H. Liu, L. Zhu, R. Zhang and H. Chen, *ACS Energy Letters*, 2018, 3, 1824
21. J. Liang, X. Han, J. H. Yang, B. Zhang, Q. Fang, J. Zhang, Q. Ai, M. M. Ogle, T. Terlier, A. A. Marti and J. Lou, *Adv. Mater.*, 2019, 31, 1903448
22. S. Xiang, W. Li, Y. Wei, J. Liu, H. Liu, L. Zhu, S. Yang and H. Chen, *iScience*, 2019, 15, 156
23. H. Wang, H. Liu, Z. Dong, X. Wei, Y. Song, W. Li, L. Zhu, Y. Bai and H. Chen, *Nano Energy*, 2022, 94, 106925
24. S. Tan, B. Yu, Y. Cui, F. Meng, C. Huang, Y. Li, Z. Chen, H. Wu, J. Shi, Y. Luo, D. Li and Q. Meng, *Angew. Chem. Int. Ed. Engl.*, 2022, 61, e202201300
25. X. Wang, Y. Wang, Y. Chen, X. Liu and Y. Zhao, *Adv. Mater.*, 2021, 33, 2103688



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