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Short Communication

Interface engineering gifts $CsPbI_{2.25}Br_{0.75}$ solar cells high performance ☆

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Organic-inorganic halide perovskite (ABX_3) solar cells (PSCs) have made great progress in recent years [1]. The power conversion efficiency (PCE) has increased up to 25.2% (NREL Best Research-Cell Efficiency Chart, https://www.nrel.gov/pv/cell-efficiency.html, Accessed August 2019). However, they suffer from poor thermal stability due to the volatile A-site organic cations. All-inorganic $CsPbI_{3-x}Br_x$ perovskite materials can tolerate temperature exceeding 400 °C, while organic–inorganic halide PSCs rapidly deteriorated at greater than 200 °C [2]. The excellent thermal stability of inorganic perovskites makes them promising materials for PSCs [3]. Their relatively low PCE is due to two reasons. One is the wide bandgap, which leads to insufficient light absorption and low J_{sc}. Developing tandem solar cells is an effective approach to absorb sunlight as much as possible [4]. Another is the large energy loss (E_{loss}), leaving much room for increasing V_{oc}. Interface engineering can reduce the E_{loss} and increase the PCE. Wang et al. [5] reported a 17.06% PCE by using PTABr-treated $CsPbI_3$ as the absorber. The post-treatment with PTABr can realize gradient Br-doping and surface passivation, leading to enhanced V_{oc} and *FF*. They also modified $CsPbI_3$ surface with choline iodine (CHI), which increased the charge-carrier lifetime and improved the energy level alignment between $CsPbI_3$ and charge-transport layers. CHI-$CsPbI_3$ solar cells gave a PCE of 18.4% [6]. Besides, choosing electron-transport layers (ETLs) and hole-transport layers (HTLs) with suitable energy levels is also effective for improving V_{oc} [7]. In our previous work, we applied DPPA-modified ZnO as ETL for $CsPbI_{2.25}Br_{0.75}$ solar cells, obtaining a 15.98% PCE with an enhanced V_{oc} [8]. Yan et al. [9] used SnO_2/ZnO bilayer as ETL to get high V_{oc}. They also used PN4N-modified SnO_2 as ETL and PDCBT as HTL in $CsPbI_2Br$ solar cells, obtaining a 16.2% PCE with a 1.30 V V_{oc} [10]. In this work, we made inorganic PSCs with a structure of ITO/SnO_2/ZnO/$CsPbI_{2.25}Br_{0.75}$/HTL/MoO_3/Ag (Fig. 1a). PTAA doped with polymer donor PBD2T [11] was used as HTL (D-PTAA). The deep highest occupied molecular orbital (HOMO) level of PBD2T matches HOMO of $CsPbI_{2.25}Br_{0.75}$ well. Meanwhile, PBD2T can passivate the trap states on perovskite surface and suppress interfacial charge recombination. The solar cells with D-PTAA delivered a 17.37% PCE, which is the highest efficiency for Br-doped inorganic PSCs.

Fig. 1b presents the chemical structure of PBD2T. D-PTAA films were made by adjusting PTAA/PBD2T ratio (*w*/*w*). The UV–vis absorption spectra of $CsPbI_{2.25}Br_{0.75}$ and $CsPbI_{2.25}Br_{0.75}$/D-PTAA films are shown in Fig. S1 (online). Fig. 1c shows the energy level diagram. The conduction band of SnO_2 and ZnO are −4.05 eV [12] and −3.69 eV [8], respectively. The cascade energy level alignment between $CsPbI_{2.25}Br_{0.75}$, ZnO and SnO_2 can facilitate electron extraction and reduce the E_{loss} [9]. The HOMO levels for PBD2T and PTAA are −5.40 eV [11] and −5.14 eV [13], respectively. The deeper HOMO of PBD2T provides a better energy level matching with $CsPbI_{2.25}Br_{0.75}$. When adding PBD2T into PTAA, a cascade

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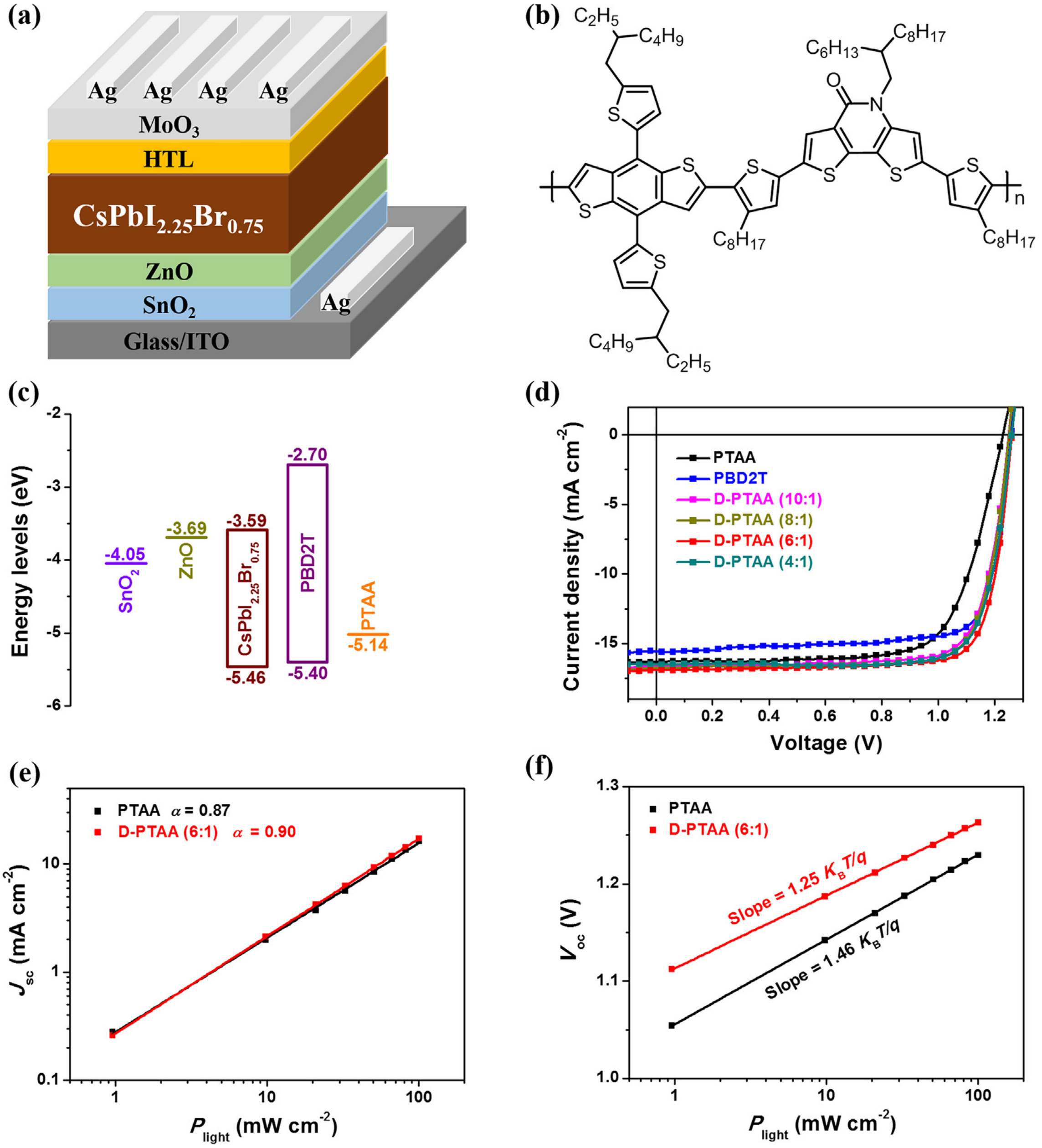

Fig. 1. Interface engineering for $CsPbI_{2.25}Br_{0.75}$ solar cells. (a) Device structure; (b) the chemical structure of PBD2T; (c) the energy level diagram; (d) *J-V* curves for $CsPbI_{2.25}Br_{0.75}$ solar cells with different HTLs; (e) J_{sc}-P_{light} plots; (f) V_{oc}-P_{light} plots.

energy level alignment between $CsPbI_{2.25}Br_{0.75}$, PBD2T and PTAA was built, thus improving the hole extraction and reducing the E_{loss}. In addition, sulfur (S) atoms in PBD2T could form S-Cs and S-Pb bonds and effectively passivate the trap states on perovskite surface, thus reducing the interfacial charge recombination [10,14,15].

Solar cells with a structure of ITO/SnO_2/ZnO/$CsPbI_{2.25}Br_{0.75}$/HTL/MoO_3/Ag were made and PBD2T content was optimized. *J-V* curves for the solar cells with different HTLs are shown in Fig. 1d, and the corresponding performance data are listed in Table S1 (online). The optimal PTAA:PBD2T ratio is 6:1 (wt). Compared with the control device, the solar cells with D-PTAA HTLs offered enhanced PCEs. The increase of V_{oc} results from the energy level matching between $CsPbI_{2.25}Br_{0.75}$ and PBD2T. J_{sc} increases first and then decreases as PBD2T content increases. The energy level matching between $CsPbI_{2.25}Br_{0.75}$ and D-PTAA HTLs could improve the hole extraction. When PTAA:PBD2T ratio decreases below 6:1 (PBD2T content increases), J_{sc} decreases because of the lower hole mobility of PBD2T (1.3×10^{-4} cm^2 V^{-1} s^{-1}) [9] than PTAA (4×10^{-3} cm^2 V^{-1} s^{-1}) [11]. Solar cells with PBD2T HTL gave the lowest J_{sc}. The improvement of *FF* was due to efficient hole extraction and reduced interfacial charge recombination. The thickness (Table S2 online) and annealing temperature (Fig. S2, Table S3, online) for HTLs were optimized. Solar cells with PTAA HTL gave a V_{oc} of 1.23 V, a J_{sc} of 16.34 mA cm^{-2}, an *FF* of 71.63% and a PCE of 14.39%. The best cell with D-PTAA (6:1) HTL gave enhanced V_{oc} (1.26 V), J_{sc} (17.16 mA cm^{-2}), and *FF* (80.14%), and a higher PCE of 17.37% with a lower E_{loss} of 0.61 eV. The integrated photocurrents from EQE spectra for the cells with PTAA and D-PTAA (6:1) HTLs are 15.64 and 16.28 mA cm^{-2}, respectively (Fig. S3a online). J_{sc} stability for the best cell was studied (Fig. S3b online). The hysteresis for *J-V* curves was checked, and the D-PTAA cells presented less hysteresis than the control device (Fig. S4, Table S4, online).

The dependence of J_{sc} and V_{oc} on the incident light intensity (P_{light}) was studied (Fig. 1e and f). J_{sc} exhibits a power law dependence on P_{light}:$J_{sc} \propto P_{light}{}^{\alpha}$ ($\alpha \le 1$). The α values for PTAA and D-PTAA (6:1) solar cells are 0.87 and 0.90, respectively. The larger α suggests that the energy level matching between $CsPbI_{2.25}Br_{0.75}$ and D-PTAA is better and the holes can be extracted efficiently. The slope for V_{oc} vs. LogP_{light} plots for D-PTAA (6:1) cell (1.25 K_BT/q) is smaller than that for PTAA cell (1.46 K_BT/q). Generally, a slope larger than 1 indicates the presence of trap-assisted charge recombination. The smaller slope suggested that the trap-assisted charge recombination is effectively suppressed by PBD2T [7,8].

In summary, a polymer donor PBD2T was added into PTAA to make HTL for $CsPbI_{2.25}Br_{0.75}$ solar cells. The cascade energy level alignment between $CsPbI_{2.25}Br_{0.75}$, PBD2T and PTAA can improve the hole extraction and reduce the E_{loss}. Meanwhile, the formation of S-Cs and S-Pb bonds can passivate perovskite surface effectively, suppressing the interfacial charge recombination. $CsPbI_{2.25}Br_{0.75}$ solar cells with D-PTAA HTL deliver a 17.37% PCE, which is the highest efficiency for Br-doped inorganic PSCs. This work provides an effective approach for developing high-performance inorganic PSCs.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Zhimin Fang and Xianyi Meng performed the experiments. Dan Li synthesized PBD2T. Chuantian Zuo, Zuo Xiao, Chenyi Yi, Mingkui Wang, Zhiwen Jin and Shangfeng Yang participated in the discussion on experimental results. Liming Ding directed this project.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2019.09.023.

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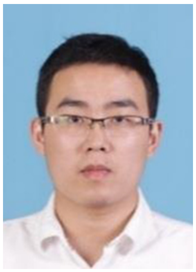

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