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Short Communication

$CsPbI_{2.25}Br_{0.75}$ solar cells with 15.9% efficiency

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Organic-inorganic perovskite (ABX_3) solar cells (PSCs) have attracted wide interest in recent years [1]. The power conversion efficiency (PCE) has increased up to 23.7% (NREL Best Research-Cell Efficiency Chart, https://www.nrel.gov/pv/cell-efficiency.html, Accessed January 2019). However, organic-inorganic PSCs suffer from poor thermal stability due to the volatile organic A-site cations. Recently, all-inorganic perovskite materials $CsPbX_3$ (X = I, Br) have received great attention due to their remarkable thermal stability [2]. The inorganic perovskites without volatile components now become promising materials for PSCs. Besides, $CsPbI_{3-x}Br_x$ perovskite materials show tunable bandgaps from 1.73 to 2.3 eV when x changes from 0 to 3. This makes it possible to fabricate tandem solar cells by combining with silicon solar cells or narrow bandgap organic solar cells.

The PCE of solar cells is determined by three parameters, J_{sc}, V_{oc}, and *FF*. Inorganic PSCs have high V_{oc} and relatively low J_{sc} because of its wide bandgap, and the PCE is lower than 18% till now. The J_{sc} can be improved via improving the crystallinity and increasing the grain size of perovskite film, and using charge transport layers with high charge mobility. The V_{oc} correlates with the energy loss in the device. The energy level matching between perovskite layer and electron/hole transport layers (ETLs/HTLs) affects V_{oc} significantly [3]. The *FF* relates to the quality of perovskite film, and the contact between perovskite and charge transport layers. PSCs have a typical sandwich structure, and the substrates (ETLs or HTLs) affect the growth of perovskite films significantly. Based on the above analysis, it is important to choose suitable ETLs or HTLs for PSCs. Among the ETLs, ZnO has excellent electron transport property and suitable conduction band energy level, being a promising ETL material for inorganic PSCs [4]. However, on ZnO surface, there exists hydroxyl groups and oxygen deficiency, which could accelerate perovskite decomposition and limit the PCE. In organic-inorganic PSCs, magnesium and aluminum were doped into ZnO to improve device stability, but the PCE is relatively low [5,6]. Cao et al. [7] achieved a PCE of 21.1% by using MgO and protonated ethanolamine passivated ZnO as ETL. They also constructed a ZnO-ZnS layer as ETL, and a PCE of 20.7% was obtained [8]. However, these approaches need high annealing temperature to prepare ETL. Hence, it is very important to find a simple and effective method to modify ZnO surface to improve both device efficiency and stability. In this work, we used 3,3-diphenylpropylamine (DPPA)-modified ZnO as ETL (Fig. 1a). DPPA can effectively passivate the defects on ZnO surface through Zn–N bond formation. Solar cells with this modified ZnO gave enhanced V_{oc}, J_{sc}, and *FF*. A PCE of 15.98% was achieved, which is the highest efficiency for inorganic PSCs with ZnO ETL.

The modified ZnO film was prepared by spin coating a DPPA/isopropanol solution onto ZnO film (Fig. 1b). To clarify the influence of DPPA modification to ZnO surface, we performed X-ray photoelectron spectroscopic (XPS) analysis. After DPPA modification, N 1s signal appears (Fig. S1a online). Zn 2p peaks for modified ZnO shift to higher binding energy slightly (Fig. S1b online). However, N 1s peak for ZnO/DPPA shifts to lower binding energy compared with that of DPPA (Fig. S2a online), suggesting the increase of negative charge on N atom within $-NH_2$ group. These results indicate the formation of Zn–N bonds. O 1s XPS spectra show two peaks at ~530.2 and 531.5 eV, which could be assigned to O^{2-} ions in Zn–O bonds and oxygen deficiency, respectively

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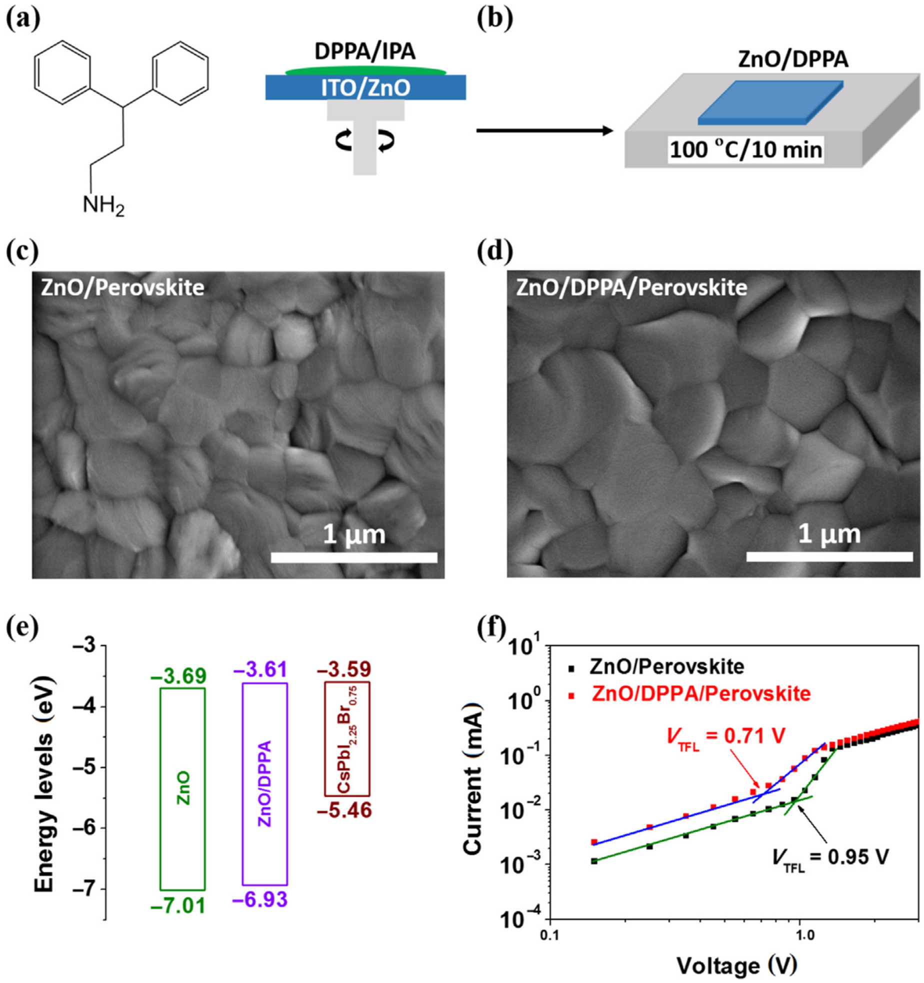

Fig. 1. Interface engineering in inorganic perovskite solar cells. (a) The structure of DPPA. (b) The preparation of ZnO/DPPA films. (c) SEM image for $CsPbI_{2.25}Br_{0.75}$ film on ZnO. (d) SEM image for $CsPbI_{2.25}Br_{0.75}$ film on ZnO/DPPA. (e) Energy level diagram. (f) Dark *I-V* curves for electron-only devices with a structure of ITO/ZnO (ZnO/DPPA)/Perovskite/$PC_{61}BM$/Ag.

(Fig. S2b online). For DPPA-modified ZnO, the decline of 531.5 eV peak indicates that the defects on ZnO surface have been effectively passivated by DPPA [9]. Fig. S3 (online) presents the Tauc plots and ultraviolet photoelectron spectroscopy (UPS) spectra of ZnO and ZnO/DPPA films. Both films show a bandgap of 3.32 eV. However, a slight shift to higher energy was observed. The VB/CB levels of ZnO and modified ZnO are −7.01/−3.69 eV and −6.93/−3.61 eV, respectively.

The precursor solution was prepared by dissolving CsI, PbI_2, $PbBr_2$ with a molar ratio of 0.8:0.5:0.3 in the mixed solvent DMF/DMSO (4:1, *v*/*v*). The energy dispersive X-ray (EDX) was performed to analyze the composition of the perovskite film (Fig. S4, Table S1, online), and the material was named as $CsPbI_{2.25}Br_{0.75}$. Fig. S5 (online) presents the XRD patterns for $CsPbI_{2.25}Br_{0.75}$ films on different substrates. The patterns show two diffraction peaks at 14.5° and 29.4°, which can be assigned to (1 0 0) and (2 0 0) planes, respectively. In XRD pattern of $CsPbI_{2.25}Br_{0.75}$ film on ZnO, the diffraction peak at 9.8° stands for (0 0 2) plane of the nonphotoactive δ-phase. The diffraction intensity of perovskite on ZnO/DPPA is higher than that of perovskite on ZnO, suggesting the higher crystallinity.

The morphology for $CsPbI_{2.25}Br_{0.75}$ films was studied by Scanning Electron Microscope (SEM). Fig. 1c and d reveals the formation of $CsPbI_{2.25}Br_{0.75}$ crystal film with larger grains on modified ZnO. The increase in grain size led to less grain boundaries, thus reducing charge recombination. The UV–vis absorption spectra for $CsPbI_{2.25}Br_{0.75}$ films are shown in Fig. S6a (online). The Tauc plot for $CsPbI_{2.25}Br_{0.75}$ film on ZnO is shown in Fig. S6b (online), indicating a bandgap of 1.87 eV. The VB/CB levels for $CsPbI_{2.25}Br_{0.75}$ perovskite are −5.46/−3.59 eV (Fig. S6c online). The higher CB of modified ZnO matches well with the CB of $CsPbI_{2.25}Br_{0.75}$ (Fig. 1e), which can reduce the energy loss in electron transfer from perovskite to ZnO.

The photoluminescence (PL) spectra for $CsPbI_{2.25}Br_{0.75}$ films on glass, glass/DPPA, ZnO and ZnO/DPPA substrates are shown in Fig. S7 (online). Compared with $CsPbI_{2.25}Br_{0.75}$ film on glass, the film on glass/DPPA shows an enhanced PL intensity, suggesting better crystallinity on ZnO/DPPA substrate as XRD indicated. Similar to ZnO, ZnO/DPPA can effectively quench the fluorescence of $CsPbI_{2.25}Br_{0.75}$. We measured current–voltage (*I*–*V*) characteristics in dark for devices with a structure of ITO/ZnO (ZnO/DPPA)/$CsPbI_{2.25}Br_{0.75}$/$PC_{61}BM$/Ag and evaluated the trap density (Fig. 1f). The trap state density was determined by the trap-filled limit voltage (V_{TFL}):

$$V_{TFL} = \frac{e n_{trap} L^2}{2\varepsilon_0 \varepsilon},$$

where e is the electron charge, n_{trap} is the trap state density, L is the thickness of the perovskite layer, ε is the relative dielectric constant for $CsPbI_{2.25}Br_{0.75}$, and ε_0 is the vacuum permittivity. The V_{TFL} for perovskite film on DPPA-modified ZnO is lower than that of perovskite film on pristine ZnO, suggesting a reduced electron trap density. Low trap density favors to reduce charge recombination.

Solar cells with a structure of ITO/ETL/$CsPbI_{2.25}Br_{0.75}$/PTAA/MoO_3/Ag were made and the concentration of DPPA solution was optimized. The device performance data are listed in Table S2 (online). Compared with the control device, all solar cells with DPPA modification gave an enhanced PCE (Fig. S8 online). The increases of V_{oc} and J_{sc} result from the energy level matching between ZnO and perovskite. As the concentration further increases, J_{sc} decreases because of DPPA insulation. The increase of *FF* was due to reduced charge recombination, which results from the reduced defects on ZnO surface and lower trap density in perovskite film. The optimal concentration of DPPA solution was 2 mg mL^{-1}. *J–V* curves for the best cells with ZnO or modified ZnO as ETL are shown in Fig. S9a (online). The cells with ZnO ETL gave a V_{oc} of 1.19 V, a J_{sc} of 16.10 mA cm^{-2}, an *FF* of 71.81% and a PCE of 13.77%. The cells with ZnO/DPPA ETL offered enhanced V_{oc} (1.23 V), J_{sc} (17.04 mA cm^{-2}), and *FF* (76.49%), leading to a PCE of 15.98%. The integrated photocurrents from EQE spectra for the cells with ZnO and ZnO/DPPA ETL are 15.40 and 16.13 mA cm^{-2}, respectively (Fig. S9b online). The hysteresis for *J–V* curves were checked (Fig. S10a, Table S3, online), and $CsPbI_{2.25}Br_{0.75}$ solar cells show a significant decrease in hysteresis after DPPA modification. The suppressed hysteresis resulted from the reduced defects on ZnO surface and better quality of perovskite film. J_{sc} stability for the best cell was studied (Fig. S10b online). After being stored in a N_2 glovebox for 55 days, $CsPbI_{2.25}Br_{0.75}$ solar cells with modified ZnO ETL show a better stability (Fig. S11 online). With this modified ZnO ETL, $CsPbI_2Br$ solar cells gave a PCE of 14.86% with a V_{oc} of 1.27 V (Fig. S12, Table S4, online).

In summary, we have developed an effective approach to modify ZnO ETL. The defects on ZnO surface were passivated due to Zn–N bond formation. $CsPbI_{2.25}Br_{0.75}$ film on modified ZnO exhibits improved crystallinity, larger grain size and reduced trap density. The conduction band of modified ZnO matches that of perovskite well, and $CsPbI_{2.25}Br_{0.75}$ solar cells with modified ZnO ETL gave enhanced V_{oc}, J_{sc} and *FF*. A PCE of 15.98% was achieved, which is the highest for inorganic PSCs with ZnO ETL. With modified ZnO as ETL, $CsPbI_2Br$ solar cells gave a PCE of 14.86% with an impressive V_{oc} of 1.27 V. Optimally modifying the interfaces or surfaces, we can significantly enhance the performance of PSCs.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Zhimin Fang, Ling Liu and Zhiming Zhang performed the experiments. Shangfeng Yang, Fangyang Liu and Mingzhen Liu participated in the discussion on experimental results. Liming Ding directed this project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.04.013.

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