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Forming a composite electron blocking layer to enhance the performance of carbon-based CsPbI₃ perovskite solar cells†

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Carbon-based CsPbI₃ perovskite solar cells (C-PSCs) have attracted much interest due to their high chemical stability. However, their efficiency still largely lags behind those achieved by conventional CsPbI₃ PSCs because of the electron back transfer from the perovskite to the carbon electrode. Herein, we address the above issue by forming a composite electron blocking layer at the CsPbI₃/carbon interface. The CsPbCl₃ quantum dots (QDs) layer is first deposited on the CsPbI₃ film by spin coating a QDs solution, while the Cs₂PbI₂Cl₂ nanosheets are then generated on the surface by the post treatment of a CsCl solution. The composite blocking layer not only well suppresses electron back transfer but also passivates crystal defects. As a result, the efficiency of CsPbI₃ C-PSCs is boosted from 12.51% to 16.10%.

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Introduction

Perovskite solar cells (PSCs) have attracted intense attention in the past few years due to their high power conversion efficiency (PCE) based on solution-based processes.^{1–6} However, their low stability has greatly inhibited the commercial application of PSCs.^{7–10} Generally, their low stability mainly originates from the use of organic-inorganic hybrid perovskites, made from organic hole transport materials (HTMs) and metal electrodes.^{11–13} After replacing the HTM and metal electrode with a carbon electrode, carbon-based PSCs (C-PSCs) are made, and the device stability could be well improved because carbon materials are stable, inert to ion migration and inherently H₂O-resistant.^{14–19}

Although C-PSCs have shown obvious enhancement in device stability, the organic components in organic-inorganic hybrid perovskites can be easily removed from the crystal structure, which still limits the device stability. In order to address the issue, researchers have introduced inorganic perovskites to replace the organic-inorganic hybrid perovskites as light absorbers in C-PSCs.^{20–25} Among various inorganic perovskites, CsPbI₃ has shown great prospects due to the suitable bandgap of 1.73 eV.^{26–32} So far, great progress has been made on CsPbI₃ C-PSCs and over 16% PCE has been achieved.³³

However, the above PCE still largely lags behind those achieved by the conventional CsPbI₃ PSCs (about 21%).³⁴ The low hole selectivity of the carbon electrode is the main cause because the photogenerated electrons tend to transfer to the carbon electrode for inducing serious recombination loss.^{11,35} To suppress the electron back transport, forming an electron blocking layer at the CsPbI₃/carbon interface has been employed.^{36–38} For example, phenylethylamine iodide (PEAI)³⁹ or CsCl⁴⁰ have been used to treat the CsPbI₃ layer to grow a 2D perovskite layer *in situ* acting as an electron blocking layer. However, the performance improvement is still limited for a single electron blocking layer and a new strategy is needed.

Herein, both CsPbCl₃ QDs and 2D Cs₂PbI₂Cl₂ were deposited on the CsPbI₃ perovskite layer to form a composite electron blocking layer. Firstly, CsPbCl₃ QDs were spin coated on the CsPbI₃ perovskite layer by using a CsPbCl₃ QDs cyclohexane solution. Then, a CsCl ethanol solution was also spin coated on the QDs-coated CsPbI₃ perovskite layer to form 2D Cs₂PbI₂Cl₂. Such architecture forms a favorable energy level alignment for electron blocking. In addition, crystal defects were also effectively passivated. As a result, the PCE of CsPbI₃ C-PSCs was promoted from 12.51% to 16.10%.

Results and discussion

The CsPbCl₃ QDs were synthesized using the thermal injection method described in the Experimental section.^{41,42} The TEM image in Fig. S1a (ESI†) shows that the CsPbCl₃ QDs have a regular square structure with a size of about 12 nm. The X-ray

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diffraction (XRD) pattern in Fig. S1b (ESI[†]) indicates that all diffraction peaks match well with the tetragonal structure of the CsPbCl₃ perovskite (JCPDS 18-0366).¹⁹ Therefore, CsPbCl₃ QDs have been successfully prepared.

For preparing the CsPbI₃ perovskite films, a precursor solution containing CsI, PbI₂ and DMAI was spin coated on the TiO₂ substrate, followed by annealing at 220 °C for 5 min. After the deposition of the CsPbI₃ perovskite films, three kinds of samples were obtained by the processes illustrated in Fig. 1. For the CsPbI₃-CsCl film, the as-deposited CsPbI₃ perovskite films were treated with a CsCl ethanol solution (1 mg ml⁻¹) by spin coating. For the CsPbI₃-QDs film, a CsPbCl₃ QDs cyclohexane solution was spin-coated on the as-deposited CsPbI₃ perovskite film. For the CsPbI₃-QDs/CsCl film, the as-deposited CsPbI₃ perovskite films were successively treated with a CsPbCl₃ QDs solution and CsCl solution.

Scanning electron microscopy (SEM) was employed to evaluate the film morphology (Fig. 2 and Fig. S2, ESI[†]). The control CsPbI₃ film exhibits uniform morphology (Fig. 2a). 2D nanosheets estimated to be around 200–350 nm in width appear on the surface of the CsPbI₃-CsCl film (Fig. 2b and f). They are uniformly distributed on the surface and are perpendicular to the surface of the perovskite film. The CsPbCl₃ QDs are uniformly distributed on the surface of the QDs film after spin-coating the CsPbCl₃ QDs solution (Fig. 2c and g). After depositing the CsPbCl₃ QDs, the CsPbI₃-QDs film show a denser and more uniform surface morphology. For the CsPbI₃-QDs/CsCl film, the CsPbCl₃ QDs are uniformly dispersed and 2D nanosheets are also generated on the surface, forming a 2D/0D electron blocking layer. Atomic force microscopy (AFM) was further used to reveal the morphology change. The roughness of the QDs film is reduced from 41.8 to 28.6 nm compared with control CsPbI₃ film, while the roughness of the CsPbI₃-QDs/CsCl film is reduced from 72.5 to 48.1 nm compared with the control CsCl film, indicating that the CsPbCl₃ QDs are more easily deposited at the grain boundary and reduce the surface

roughness, which is conducive to the contact between CsPbI₃ and the carbon electrode.

The X-ray diffraction (XRD) patterns in Fig. 3a reveal that the control CsPbI₃ film exhibits two intense peaks at 14.3° and 28.8°, which are assignable to the (110) and (220) peaks of the CsPbI₃ perovskite, respectively. After post treatment with CsCl solution, an additional peak is observed at 9.5°. As reported in our previous work, this peak corresponds to the (002) plane of 2D Cs₂PbI₂Cl₂, resulting from the reaction between CsCl and CsPbI₃.^{40,43} For the CsPbI₃-QDs film, the peak corresponding to CsPbCl₃ appear. As expected, both Cs₂PbI₂Cl₂ and CsPbCl₃ peaks are found for the CsPbI₃-QDs/CsCl films. For more detailed observations in Fig. S3 (ESI[†]), the characteristic peaks of CsPbI₃ perovskite shift to a larger angle after QDs or CsCl treatment, implying the partial replacement of I⁻ ions with Cl⁻ ions.^{44,45}

X-ray photoelectron spectroscopy (XPS) measurements were further carried out to evaluate the composition of different CsPbI₃ films. As shown in Fig. S4 (ESI[†]), compared with the control CsPbI₃ film, the characteristic peaks of Cl 2p appeared in the CsPbI₃-CsCl, -QDs and -QDs/CsCl films,^{45,46} indicating that Cl has been incorporated after post treatment. Due to the difference in the chemical environment of the Cl element, compared with the CsPbI₃-CsCl film, the Cl 2p peak shifts to a lower binding energy for the CsPbI₃-QDs film. As expected, the Cl 2p in the CsPbI₃-QDs/CsCl films can be deconvoluted into two sets of Cl 2p peaks, corresponding to the presence of CsPbCl₃ QDs and Cs₂PbI₂Cl₂ nanosheets. Similarly, the Pb 4f peaks can also be deconvoluted into two sets of Pb 4f peaks. (Fig. 2d).

Ultraviolet-visible (UV-Vis) absorption spectra were subsequently measured for different films. As shown in Fig. 4a, the pristine CsPbI₃ film shows the absorption onset at around 741 nm. Due to the partial replacement of I with Cl, the absorption onset of the CsPbI₃-CsCl film blue shifts to about 737 nm. Similarly, a blue shift is also observed for the absorption onset of the CsPbI₃-QDs film (about 735 nm). More

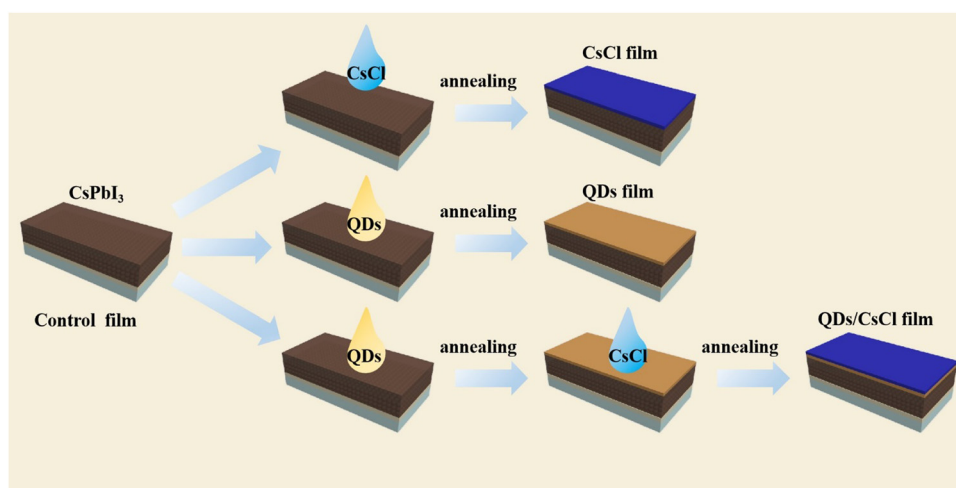


Fig. 1 Schematic illustrating the deposition processes of the CsPbI₃-CsCl, CsPbI₃-QDs and CsPbI₃-QDs/CsCl films.

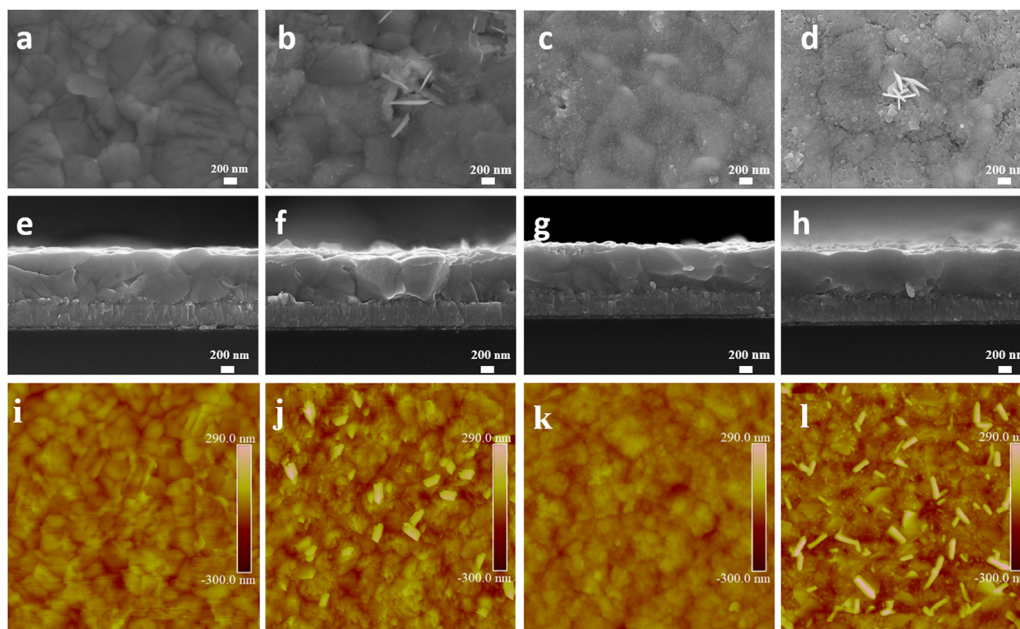


Fig. 2 SEM images of the (e and a) control, (b and f) CsPbI₃-CsCl, (c and g) CsPbI₃-QDs, and (d and h) CsPbI₃-QDs/CsCl films; AFM images of different perovskite films: (i) CsPbI₃, (j) CsPbI₃-CsCl, (k) CsPbI₃-QDs, and (l) CsPbI₃-QDs/CsCl films.

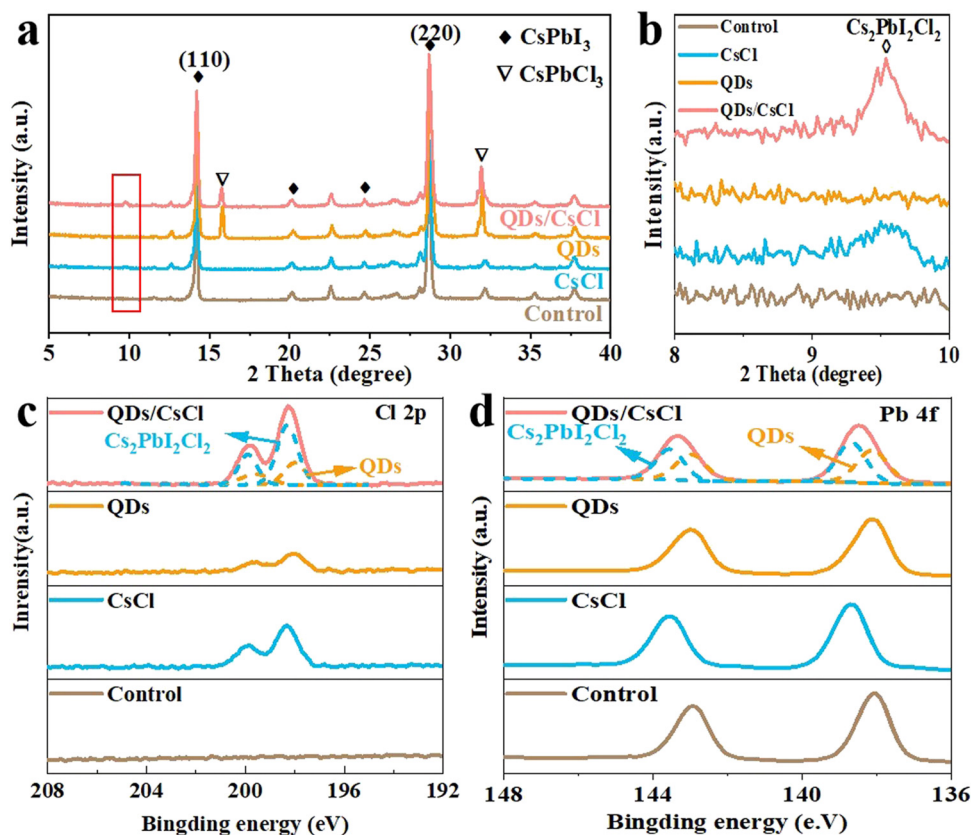


Fig. 3 (a) XRD patterns and (b) magnified XRD patterns (in the 2θ ranges of $8-10^\circ$) of different CsPbI₃ films. XPS spectra of (c) Cl 2p and (d) Pb 4f for different CsPbI₃ films.

obviously, the absorption onset of the CsPbI₃-QDs/CsCl film (ESI[†]), *E_g* for the pristine CsPbI₃, CsPbI₃-CsCl, CsPbI₃-QDs and CsPbI₃-QDs/CsCl films are calculated to be 1.671, 1.683, 1.686

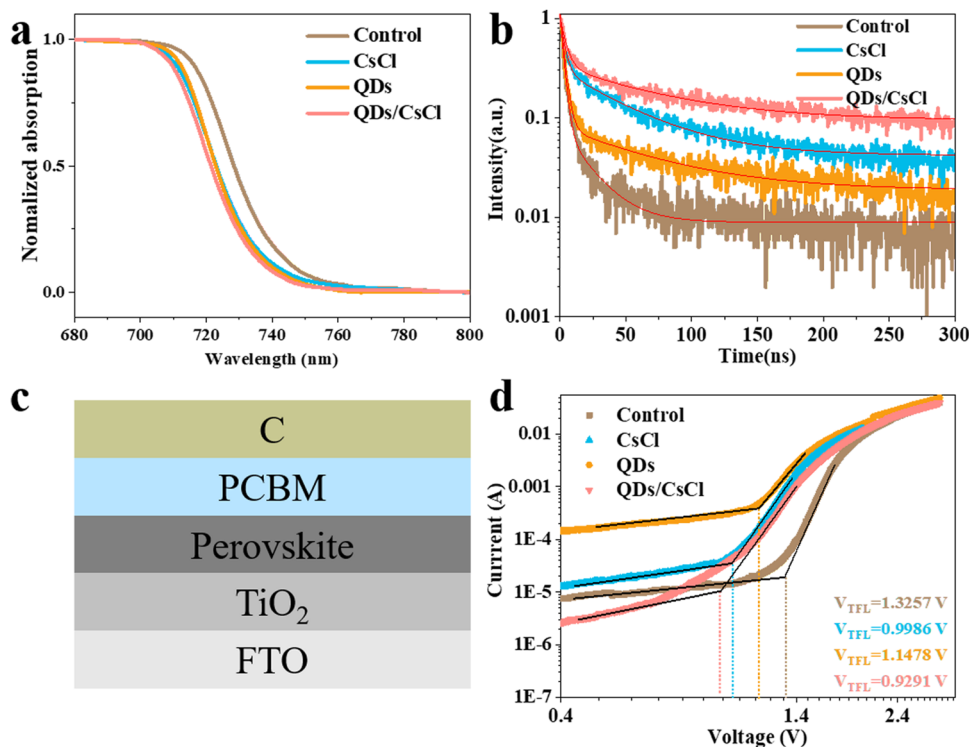


Fig. 4 (a) UV-Vis, (b) TRPL spectra, (c) architecture of the electro-only device for SCLC, and (d) SCLC results for different CsPbI₃ films.

and 1.688 eV, respectively. The confocal PL mappings in Fig. S6 (ESI[†]) further confirm the above phenomenon.

Time-resolved photoluminescence decay (TRPL) spectra were also taken for different films (Fig. 4b). By fitting the TRPL spectra with a double exponential decay model, the average lifetime (τ_{ave}) of the different films could be calculated. As shown in Table S1 (ESI[†]), the τ_{ave} of the control CsPbI₃ film is 8.87 ns, while the τ_{ave} of the CsPbI₃-CsCl, -QDs and -QDs/CsCl films are obviously increased to 40.60 ns, 38.94 ns and 60.24 ns, respectively. Therefore, post treatment has well prolonged the carrier lifetime due to the reduced defect density, especially for the CsPbI₃-QDs/CsCl film.⁴⁷

Space charge limited current (SCLC) measurements were performed by constructing an electron-only device of FTO/TiO₂/CsPbI₃/PCBM/C (Fig. 4c). According to the dark J - V curve (Fig. 4d), the trap density (n_t) can be calculated by the trap-filled limit voltage (V_{TFL}).

$$n_t = 2\varepsilon_0\varepsilon V_{\text{TFL}}/ed^2 \quad (1)$$

where ε_0 is the vacuum dielectric constant, ε is the relative dielectric constant of perovskite, d is the film thickness, e is the basic charge, and n_t is the density of trapped states.⁴⁸ The trap density values were calculated to be 1.807×10^{15} , 1.361×10^{15} , 1.564×10^{15} and $1.266 \times 10^{15} \text{ cm}^{-3}$ for the pristine CsPbI₃, CsPbI₃-CsCl, CsPbI₃-QDs and CsPbI₃-QDs/CsCl films, respectively. Therefore, the SCLC results further confirm that the post treatment processes have well reduced the trap density, especially for the CsPbI₃-QDs/CsCl film.

CsPbI₃ C-PSCs were fabricated by directly painting commercial carbon paste on the perovskite films, followed by annealing 120 °C (Fig. 5a). All processes were carried out in dry air. Fig. 5b show the architecture of the CsPbI₃ C-PSCs: FTO/c-TiO₂/m-TiO₂/CsPbI₃/carbon and the cross-sectional SEM image in Fig. 5c indicates the close contact at the CsPbI₃/carbon interface. The current density-voltage (J - V) curves in Fig. 5d and Table S2 (ESI[†]) indicate that the control device achieves a PCE of 12.51% with a V_{oc} of 1.081 V, J_{sc} of 16.46 mA cm⁻² and FF of 0.703. After treatment with CsCl, the CsPbI₃-CsCl PSCs device displays a PCE of 13.65% with a V_{oc} of 1.099, J_{sc} of 17.67 mA cm⁻² and FF of 0.703. The CsPbI₃-QDs device displays a PCE of 14.18% with a V_{oc} of 1.105, J_{sc} of 18.14 mA cm⁻² and FF of 0.708. Interestingly, the PCE of the CsPbI₃-QDs/CsCl device is significantly improved to 16.10% with a V_{oc} of 1.137 V, J_{sc} of 18.74 mA cm⁻² and FF of 0.755, respectively. As noted, the large improvement in the PCE for the CsPbI₃-QDs/CsCl device is mainly attributed to the increase in V_{oc} and FF, which should originate from the improvement in energy level alignment and the reduction in the surface roughness. The J - V curves obtained from forward and reverse scans (Fig. S7, ESI[†]) and the steady-state power output for the CsPbI₃-QDs/CsCl device demonstrate the small hysteresis and stable power output (Fig. S7, ESI[†]). The device stability was tested at 85 °C in N₂ conditions (Fig. S8, ESI[†]). The QDs/CsCl device maintains over 95% of its initial PCE after 140 h, while the PCE of the pristine device declines to about 84%.

Mott-Schottky (M-S) plots (Fig. 5e) were taken for different devices to obtain the built-in potential (V_{bi}). The V_{bi} for the

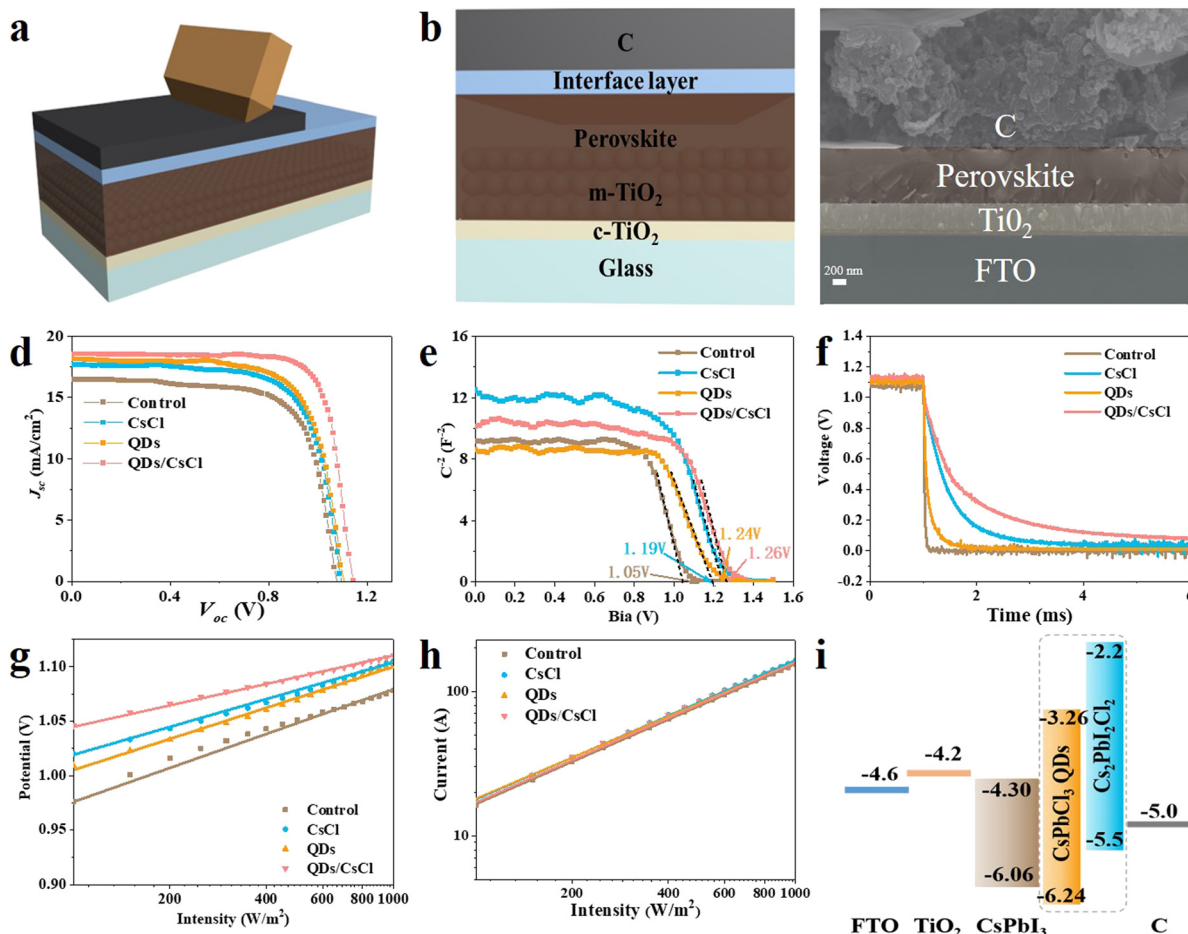


Fig. 5 Schematic diagram of (a) the fabrication process of carbon electrode and (b) device structure; (c) cross-section SEM image of CsPbI₃ C-PSCs; (d) J - V curves, (e) Mott-Schottky plots obtained at 10 kHz, (f) TPV, (g) dependence of V_{oc} on I , and (h) dependence of J_{sc} on I for different devices; (i) Energy level diagrams of the CsPbI₃-QDs/CsCl C-PSCs.

pristine CsPbI₃ device is calculated to be about 1.06 V. After post treatment, all devices show increased V_{bi} and the highest V_{bi} of 1.26 V is achieved for the CsPbI₃-QDs/CsCl device. The higher V_{bi} provides a larger driving force for carrier separation and collection, which is favorable for achieving higher V_{oc} and FF. The transient photo-voltage decay (TPV) results in Fig. 5f indicate that the CsPbI₃-QDs/CsCl device shows the slowest decay, further proving the most effective charge separation and the least charge recombination. The dark J - V curves of the pristine and QDs/CsCl devices are shown in Fig. S9 (ESI[†]). The QDs/CsCl device exhibits a much lower dark current density compared with the pristine device under a positive bias voltage, indicating that in the QDs/CsCl device the composite electron blocking layer well suppressed the back transfer of electrons from the perovskite to the carbon electrode.

The light intensity dependence of J_{sc} and V_{oc} are shown in Fig. 5g and h, respectively. The recombination mechanism can be understood according to eqn (2) and (3).

$$J_{sc} \propto I^{\alpha} \quad (\alpha \leq 1) \quad (2)$$

$$V_{oc} = \varepsilon(K_B T/e) \ln(I) + \text{constant} \quad (3)$$

where I is the light intensity, α is the exponential factor, ε is the ideality factor, K_B is the Boltzmann constant, T is the absolute temperature and the e is elementary charge. The α values are fitted and calculated to be 0.97, 0.96, 0.96 and 0.96 for the CsPbI₃, CsPbI₃-CsCl, CsPbI₃-QDs and CsPbI₃-QDs/CsCl devices, respectively. The α values closer to 1, indicate more effective charge separation and lower nonradiative recombination. The ε for the control CsPbI₃, CsPbI₃-CsCl, -QDs and -QDs/CsCl devices are calculated to be 1.79, 1.40, 1.53 and 1.28, respectively, which demonstrates that trap-assisted recombination has been well suppressed in the CsPbI₃-QDs/CsCl device.

Conclusion

We have formed a composite electron blocking layer (CsPbCl₃ QDs/Cs₂PbI₄Cl₂) on the CsPbI₃ film structure by successively treating the film with CsPbCl₃ QDs and CsCl solutions. Such architecture forms a favorable energy level alignment for electron blocking. Furthermore, the crystal defects of the CsPbI₃ film were also effectively passivated. As a result, the PCE of CsPbI₃ C-PSCs was promoted from 12.51% to 16.10%.

Conflicts of interest

There are no conflicts to declare.

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