Effects of CsSn$_x$Pb$_{1-x}$I$_3$ quantum dots as interfacial layer on photovoltaic performance of carbon-based perovskite solar cells

Chi Zhang, Zhiyuan He, Xuanhui Luo, Rangwei Meng, Mengwei Chen, Haifei Lu and Yingping Yang*

*correspondence: ypyang@whut.edu.cn

Department of Physics, School of Science, Wuhan University of Technology, Wuhan 430070, P. R. China

Abstract

In this work, inorganic tin-doped perovskite quantum dots (PQDs) are incorporated into carbon-based perovskite solar cells (PSCs) to improve their photovoltaic performance. On the one hand, by controlling the content of Sn$^{2+}$ doping, the energy level of the tin-doped PQDs can be adjusted, to realize optimized band alignment and enhanced separation of photogenerated electron-hole pairs. On the other hand, the incorporation of tin-doped PQDs provided with a relatively high acceptor concentration due to the self-p-type doping effect, is able to reduce the width of the depletion region near the back surface of the perovskite, thereby enhancing the hole extraction. Especially, after the addition of CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs, improvement of the power conversion efficiency (PCE) from 12.80% to 14.22% can be obtained, in comparison to the pristine device. Moreover, the experimental results are analyzed through the simulation of the one-dimensional perovskite/tin-doped PQDs heterojunction.

Keywords: Tin-doped perovskite quantum dots, photovoltaic performance, carbon-based perovskite solar cells
Introduction

In past few years, perovskite materials have been widely applied in solar cells due to their excellent electrical and optical properties, such as suitable bandgap width, large light absorption coefficient and good defect tolerance [1-6]. Interface engineering, as a strategy to modify the interface characteristics of thin film devices, has become one of the approaches to improve the performance of perovskite solar cells (PSCs) [7,8]. Recently, lead-based halide perovskite quantum dots (PQDs) in the form of APbX$_3$ (A = CH$_3$NH$_3^+$ (MA$^+$), Cs$^+$; X = Cl$^-$, Br$^-$, I$^-$) are often used as interfacial layers or additives for optimized band alignment thanks to their adjustable band structures [9-15]. The combination of perovskite absorbers and PQDs is regarded as an effective method for enhanced charge extraction and improved PSC properties. It is worth noting that most of the relevant researches are based on PSCs with hole-transporting layers (HTLs). But in recent years, carbon-based HTL-free PSCs with simple preparation processes and low costs have been given much attention [16-18]. Similarly, PQDs can also be used in this PSC structure. However, some other requirements besides band alignment should be taken into consideration. First, the lattice structures of lead-based PQDs are not very stable due to Pb$^{2+}$ with a large ionic radius reducing the tolerance factor. Therefore, lead-reduced PQDs are promising candidates. Second, because of the lack of HTLs, the hole transport performance is bound to be weakened. Consequently, the added PQDs are required to supply extra free holes, so that photogenerated holes can be smoothly transferred from the perovskite layer to the carbon electrode.

The ion exchange method using metal cations with smaller ionic radii (such as Cu$^{2+}$, Zn$^{2+}$, Sn$^{2+}$, Cd$^{2+}$) to partially replace Pb$^{2+}$ has been proven to improve the lattice stability of PQDs.
Among these metal cations, Sn$^{2+}$ is easily oxidized to Sn$^{4+}$, which can introduce self-p-type doping effects to enhance hole transfer [22-24]. Especially, Liu et al. synthesized CsSn$_{0.6}$Pb$_{0.4}$I$_3$ QDs featuring a hole mobility of 40.12 cm$^2$ V$^{-1}$ s$^{-1}$ and good stability in the ambient air [25]. Xu and co-workers incorporated CsSnBr$_{3-x}$I$_x$ QDs between the CsPbBr$_3$ perovskite and the carbon electrode to promote charge extraction [26]. Very recently, Duan et al. found that MAPbI$_3$/CsSnI$_3$ heterojunction as the light-harvester in the carbon-based HTL-free PSC could facilitate the hole transfer [27]. Inspired by these above, we propose that tin-doped PQDs with appropriate energy levels and self-p-type doping effects are able to function like HTLs to modify the injection and transport characteristics of holes.

In this work, tin-doped PQDs in the form of CsSn$_x$Pb$_{1-x}$I$_3$ were incorporated between the MAPbI$_3$ perovskite and the carbon electrode to achieve optimized band alignment and improved hole transfer. An increment in power conversion efficiency (PCE) of 11.09%, from 12.80% to 14.22%, could be obtained after the addition of CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs.

**Methods**

**Materials**

Tin iodide (SnI$_2$; 99.99%) was bought from Youxuan technology (China). Cesium carbonate (Cs$_2$CO$_3$; 99%), 1-octadecene (ODE; >90%), oleic acid (OA; 99%), oleylamine (OAM; 80%-90%), methyl acetate (MeOAc; 98%) and trioctylphosphine (TOP; 90%) were purchased from Macklin (China). Lead iodide (PbI$_2$; 99.99%) and methylammonium iodide (MAI; 99.5%) were obtained from Xi’an p-OLED (China). Titanium diisopropoxide bis (acetylacetonate; 75%), dimethylsulfoxide (DMSO; 99.9%) and N,N-dimethylformamide (DMF; 99.8%) were
purchased from Sigma-Aldrich (US). The TiO$_2$ paste (30NR-D) and the low-temperature carbon electrode paste were obtained from Shanghai MaterWin New Materials (China).

4 **Synthesis and purification of tin-doped PQDs**

We adopted a simple mixed-heating procedure to synthesize tin-doped PQDs. Briefly, Cs$_2$CO$_3$, SnI$_2$ and PbI$_2$ with a specific molar ratio (CsSn$_{0.1}$Pb$_{0.9}$I$_3$ QDs: 0.037 mmol Cs$_2$CO$_3$, 0.2 mmol PbI$_2$, 0.15 mmol SnI$_2$; CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs: 0.037 mmol Cs$_2$CO$_3$, 0.2 mmol PbI$_2$, 0.2 mmol SnI$_2$; CsSn$_{0.3}$Pb$_{0.7}$I$_3$ QDs: 0.037 mmol Cs$_2$CO$_3$, 0.2 mmol PbI$_2$, 0.25 mmol SnI$_2$) were mixed with 10 mL of ODE, 0.5 mL of OA, 0.5 mL of OAM and 0.5 mL of TOP in a 50-mL three-neck flask. OA, OAM and TOP were utilized to limit the particle size and to passivate the surface defects of tin-doped PQDs. Then, the mixture was stirred and heated at 100 °C for 30 minutes under nitrogen atmosphere to obtain a red solution, including nano-sized and micron-sized tin-doped perovskites. To extract and purify tin-doped PQDs, 10 mL of MeOAc was added into the red solution, followed by centrifuging at 7000 rpm for 5 minutes. The supernatant was discarded, and the brown black precipitate was dispersed in 5 mL of hexane. Finally, the brown black solution was centrifuged at 3000 rpm for 5 minutes, and the red supernatant contained only the tin-doped PQDs.

19 **Device fabrication**

Fluorine-doped SnO$_2$ (FTO) glasses were washed with water, acetone, isopropanol and ethanol in sequence for 30 minutes each in an ultrasonic cleaner. After that, the FTO glasses were treated by ultraviolet (UV) for 20 minutes to remove residual organic solvents. The compact TiO$_2$ (c-
TiO$_2$) layer was fabricated on the FTO layer by spin-coating a solution of acetylacetonate (0.1 mL) diluted in ethanol (1.9 mL) with the speed of 4000 rpm for 30 s. Then the glasses were annealed at 150 °C for 5 minutes and at 500 °C for 30 minutes. Subsequently, the mesoporous TiO$_2$ (m-TiO$_2$) layer was obtained by spin-coating a solution of TiO$_2$ paste diluted in ethanol onto the c-TiO$_2$ layer at 3500 rpm for 20 s, and annealed at 500 °C for 30 minutes. The annealing process at 500 °C is to obtain TiO$_2$ layers with improved electron transport performance. Next, to prepare the MAPbI$_3$ precursor solution, PbI$_2$ (0.5 mmol) and MAI (0.5 mmol) were mixed with DMF (300 mg) and DMSO (39 mg). Afterwards, the MAPbI$_3$ layer was fabricated by spin-coating the MAPbI$_3$ precursor solution (35 μL) onto the m-TiO$_2$ layer, with the speed of 1000 rpm for 10 s and 4000 rpm for 20 s, followed by heating at 100 °C for 10 minutes. After that, tin-doped PQDs dispersed in toluene (10 mg mL$^{-1}$) were spin-coated onto the perovskite layer at 4000 rpm for 30 s and annealed at 90 °C for 5 minutes to remove the residual toluene. Finally, the carbon electrode paste was screen-printed on the device and annealed at 100 °C for 10 minutes.

**Characterization**

Transmission electron microscope (TEM) images, selected area electron diffraction (SAED) views and energy dispersive X-ray spectroscopy (EDS) analyses of tin-doped PQDs were obtained by a field emission high-resolution transmission electron microscope (JEM-2100F, JEOL, Japan) at an accelerating voltage of 200 kV. The valence band (VB) edges of different materials were acquired from an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific, US). Absorption and steady-state photoluminescence (PL) characteristics
were collected via an UV-visible spectrophotometer (UV-3600, Shimadzu, Japan) and a fluorescence spectrometer (RF-6000, Shimadzu, Japan), respectively. The cross-section image of the PSC and the surface morphologies of perovskite films were obtained by a scanning electron microscope (Zeiss Ultra Plus, Zeiss, Germany). Curves of photocurrent density versus on voltage (J-V) were measured by a sourcemeter (2400, Keithley, US) with a sunlight simulator (Oriel Sol3A, Newport, US), under AM 1.5G simulated illumination (100 mW cm\(^{-2}\)). Monochromatic incident photon-to-electron conversion efficiency (IPCE) spectra and electrochemical impedance spectroscopies (EIS) were obtained from an electrochemical workstation (Zahner, Kronach, Germany). Finally, X-ray diffraction (XRD) patterns of perovskite films were acquired from an X-ray diffractometer (Empyrean, PANalytical, Netherlands).

**Results and Discussion**

Three kinds of tin-doped PQDs were studied in this work, including CsSn\(_{0.1}\)Pb\(_{0.9}\)I\(_3\) QDs, CsSn\(_{0.2}\)Pb\(_{0.8}\)I\(_3\) QDs and CsSn\(_{0.3}\)Pb\(_{0.7}\)I\(_3\) QDs. The actual atomic ratio of Sn in these PQDs were estimated to be 13.03%, 22.12% and 32.57%, respectively (shown in Fig. S1 and Table S1-S3). As shown in Fig. 1, blue-shifts of the steady-state PL peak (673 nm, 669 nm and 656 nm in turn) and the edge of Tauc plot (1.79 eV, 1.80 eV and 1.81 eV in turn) were observed with the increase of Sn doping. The bandgap is known to increase with the decrease of the unit cell volume [19]. Therefore, more Sn\(^{2+}\) substitution would further intensify the lattice contraction, which led to the increased bandgap width, consistent with the reported research [28].
Fig. 1  a Normalized PL spectra and b-d Tauc plots of different tin-doped PQDs

The TEM images of these tin-doped PQDs are exhibited in Fig. 2a-c. These tin-doped PQDs were all square, consistent with the theoretical lattice structure of cubic phase. Besides, all these PQDs showed an average size of about 15 nm with good homogeneity. The size of the three kinds of quantum dots was not much different. That was because the size of PQDs was mainly determined by the reaction temperature, and the synthesis temperature of these three kinds of PQDs was kept at 100°C. Besides, corresponding SAED measurements are shown in Fig. 2d-f. By comparing the interplanar spacing values of different diffraction rings with corresponding standard values (CsPbI$_3$ in cubic phase, ICSD, 181288), some crystal planes including (100), (110), (200) and (220) could be identified, which also indicated that these tin-doped PQDs were mostly composed of cubic nanocrystals (NCs) [20]. Moreover, enlarged
TEM images shown in Fig. 2g-i are utilized to further study the crystal plane characteristics. The interplanar distances of (200) plane of these tin-doped PQDs were determined to be 0.308 nm, 0.303 nm and 0.296 nm in turn, which could demonstrate that increasing substitution of Pb$^{2+}$ by Sn$^{2+}$ further led to the lattice shrinkage, in accordance with their optical characteristics mentioned above.

**Fig. 2** a-c TEM images, d-f SAED patterns and g-i enlarged TEM images of CsSn$_{0.1}$Pb$_{0.9}$I$_3$ QDs, CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs and CsSn$_{0.3}$Pb$_{0.7}$I$_3$ QDs.

To further study the lattice structures of these tin-doped PQDs, we performed XRD measurements, shown in Fig. 3. According to the standard XRD data of CsPbI$_3$ in orthorhombic
and cubic phase [20, 29], the diffraction peaks of these tin-doped PQDs associated with orthorhombic and cubic phase were marked with “*” and “#”, respectively. As the amount of Sn doping in PQDs increased, the diffraction angle corresponding to (200) plane slightly increased, showing that the interplanar distance of (200) plane was reduced, in line with the analysis above. Meanwhile, the intensities of orthorhombic phase diffraction peaks also showed increasing trends, which indicated that the phase transition process in the PQDs increased. That was because the increase in the amount of Sn doping would intensify the oxidation reaction of the PQDs in the air, resulting in more Sn vacancies, which may make Pb refill these vacancies to form an unstable perovskite structure.

![XRD patterns of different tin-doped PQDs](image)

**Fig. 3** XRD patterns of different tin-doped PQDs

Optimized band alignment is crucial for enhancing the extraction of photogenerated carriers and suppressing charge recombination [30-33]. Fig. 4 shows the band structures of various materials including FTO, TiO₂, MAPbI₃, CsSn₀.₁Pb₀.₉I₃ QDs, CsSn₀.₂Pb₀.₈I₃ QDs, CsSn₀.₃Pb₀.₇I₃ QDs and carbon. Corresponding UPS and Tauc plots are shown in Fig. S2. It is clear that the valence band (VB) edge of CsSn₀.₁Pb₀.₉I₃ QDs (−5.53 eV) and CsSn₀.₂Pb₀.₈I₃ QDs
(−5.50 eV) was higher than that of MAPbI$_3$ (−5.54 eV), satisfying the band alignment requirement. It was able to eliminate the large Schottky barrier formed by the MAPbI$_3$/carbon junction, thus enhancing the hole extraction ability (discussed later) [31]. Furthermore, the higher conduction band (CB) edges of these tin-doped PQDs were expected to hinder the flow of electrons from MAPbI$_3$ to the carbon electrode. However, the VB edge of CsSn$_{0.3}$Pb$_{0.7}$I$_3$ QDs was lower than that of MAPbI$_3$, which would block the hole injection, leading to more charge recombination at the interface between MAPbI$_3$ and the PQDs.

**Fig. 4** Band structures of different materials in PSCs

Moreover, the VB edge originates from the interactions between Pb and I orbitals, which is also determined by the Sn doping amount. On the one hand, the substitution of Pb$^{2+}$ by Sn$^{2+}$ will shrink the lattice structure, leading to shorter Pb-I bonds and stronger interactions between Pb and I orbitals, so that the VB tends to shift to a higher energy [19]. On the other hand, more lattice distortions (transformation from cubic NCs to orthorhombic NCs) will be introduced into the PQDs with the excessive Sn$^{2+}$ substitution, resulting in expanded volume of [PbI$_6$]
octahedra and weaker Pb-I interactions, thus moving the VB to a lower energy position [21].

As a result, a reasonable Sn doping content is the key to obtaining an appropriate band structure.

Unlike ordinary lead-based PQDs, tin-doped PQDs will partially undergo oxidation in air due to the presence of Sn\(^{2+}\), described by

\[
2\text{CsSn}_x\text{Pb}_{1-x}\text{I}_3 + x\text{O}_2 \rightarrow x\text{Cs}_2\text{SnI}_6 + (2 - 2x)\text{CsPbI}_3 + x\text{SnO}_2
\]  

(1)

CsSn\(_x\)Pb\(_{1-x}\)I\(_3\) can be assumed to be the combination of CsSnI\(_3\) and CsPbI\(_3\) with a certain molar ratio. Among the compounds, only CsSnI\(_3\) participates in the oxidation reaction. And then, this process can be simplified to

\[
2\text{CsSnI}_3 + \text{O}_2 \rightarrow \text{Cs}_2\text{SnI}_6 + \text{SnO}_2
\]  

(2)

In reaction (2), the transformation from CsSnI\(_3\) to Cs\(_2\)SnI\(_6\) is regarded as breaking the connections between [SnI\(_6\)] octahedra. The reason is that CsSnI\(_3\) is formed by corner sharing [SnI\(_6\)] octahedra while Cs\(_2\)SnI\(_6\) is made up of isolated [SnI\(_6\)] octahedra [22]. Therefore, this half of Sn atoms do not leave the perovskite lattice. However, the other half of Sn atoms are oxidized to SnO\(_2\), leaving a lot of Sn vacancies in the lattice, which will accept electrons (or supply holes) and act as p-type dopants. It can be described by the equation (3) below

\[
\text{Sn}^{2+} + \text{O}_2 \rightarrow \text{SnO}_2 + 2\text{h}^+
\]  

(3)

That is the reason for the self-p-type doping effects of tin-doped PQDs. Accordingly, under the premise that the lattice structure of tin-doped PQDs can be stabilized, the more Sn\(^{2+}\) doping, the higher acceptor concentration of the PQDs.

The cross-sectional image of the PSC is shown in Fig. 5a. The widths of FTO layer and TiO\(_2\)/MAPbI\(_3\) composite layer were about 400 nm and 800 nm, respectively. Because of the low concentration of the PQD solution (10 mg mL\(^{-1}\)), it was hard to observe a PQD layer that
could be distinguished from the underlying MAPbI$_3$ film. Besides, as shown in Fig. 5b-f, there were many small-sized white PbI$_2$ particles on the original perovskite film, which was caused by the partial decomposition of the perovskite in the air. After adding tin-doped PQDs, the number of white particles decreased, and the perovskite films exhibited slightly better grain uniformity and compactness than the control sample. However, the morphology difference between the various perovskite films was still not obvious. In order to further distinguish their surface characteristics, we performed grazing incidence XRD (GIXRD) patterns of perovskite films with different tin-doped PQDs, exhibited in Fig. 6. The diffraction peak at about 12.7° is associated with PbI$_2$ [34]. After the modification of tin-doped PQDs, the intensity of PbI$_2$-peak was weakened while the intensity of the diffraction peak corresponding to (110) plane of the perovskite increased, indicating that the decomposition process of the perovskite film was suppressed.

**Fig. 5** a Cross-sectional image of the PSC. b-f Perovskite films without and with tin-doped PQDs.
Fig. 6 GIXRD patterns of different perovskite films

The curves of photocurrent density versus voltage ($J_V$) of different PSCs are displayed in Fig. 7a, and photovoltaic parameters including short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and PCE are shown in Table 1. The values of $J_{sc}$, $V_{oc}$, FF, and PCE of the PSC without modification by tin-doped PQDs were 22.69 mA cm$^{-2}$, 0.99 V, 56.78% and 12.80%, respectively. For the CsSn$_{0.1}$Pb$_{0.9}$I$_3$ QDs-added PSC, various parameters were improved. However, the improvement was not optimal, which might ascribe to the relatively low Sn doping of the PQDs. In contrast, with the incorporation of CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs, a $J_{sc}$ of 23.30 mA cm$^{-2}$, a $V_{oc}$ of 1.05 V, a FF of 57.90% and a PCE of 14.22% could be obtained. The significant increase in each parameter indicated the reduction of non-radiative recombination and the effective extraction of photogenerated holes. Besides, as shown in Fig. S3, PCE values for 90% of CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs-added PSCs surpassed 13%, showing good repeatability. But for the PSC modified by CsSn$_{0.3}$Pb$_{0.7}$I$_3$ QDs, the values of $J_{sc}$ and FF seriously dropped to 16.82 mA cm$^{-2}$ and 47.40%, respectively. The lower VB edge of the PQDs would hinder the hole transfer from the MAPbI$_3$ film to the carbon electrode. Furthermore, when the Sn content of
PQDs was too high, more Sn vacancies would be introduced, which would not only provide more free holes, but also result in more phase transformation products with large bandgap widths [29, 35-37], and thus seriously impeding the transport process of photogenerated carriers.

As described in Fig. 7b, the IPCE spectra in a wavelength range from 350 nm to 800 nm increased in the order of CsSn<sub>0.3</sub>Pb<sub>0.7</sub>I<sub>3</sub> QDs-added device < control device < CsSn<sub>0.1</sub>Pb<sub>0.9</sub>I<sub>3</sub> QDs-added device < CsSn<sub>0.2</sub>Pb<sub>0.8</sub>I<sub>3</sub> QDs-added device, in agreement with the corresponding trend of $J_{sc}$ acquired from the $J-V$ curves. It is clear that the difference of these IPCE curves was mainly reflected in the wavelength range from 550 nm to 800 nm. Tin-doped PQDs added onto the perovskite film would significantly affect the built-in electric field near the back surface of the perovskite (analyzed in detail later). At the same time, these long-wavelength lights were mainly absorbed by the perovskite near the back surface due to their low energy. After these photons were converted into carriers, their transport properties would be more easily changed by the above-mentioned built-in electric field than those photogenerated carriers of short-wavelength lights.

In addition, EIS measurements, in a frequency range from 4 MHz to 0.2 MHz at a bias of 0.8 V under simulated AM 1.5G radiation, were performed to analyze the charge transport resistance ($R_{CT}$) and the barrier capacitance ($C_T$) near the carbon electrode, described in Fig. 7c. Corresponding EIS parameters are also shown in Table 1. With the addition of CsSn<sub>0.2</sub>Pb<sub>0.8</sub>I<sub>3</sub> QDs, the $R_{CT}$ value was reduced, which meant the promoted hole extraction and the decreased energy loss on the back surface of MAPbI<sub>3</sub>. Furthermore, compared with the pristine and the CsSn<sub>0.1</sub>Pb<sub>0.9</sub>I<sub>3</sub> QDs-added PSCs, the value of $C_T$ increased, so that a shorter depletion width near the back surface of MAPbI<sub>3</sub> ($W_D$) could be deduced based on the following formulas,
suggesting facilitated hole transfer.

\[ C_T = \frac{C_1 C_2}{C_1 + C_2} \]  

(4)

\[ C_1 = \frac{\varepsilon_{\text{MAPbI}_3} A}{W_D} \]  

(5)

\[ C_2 = \frac{\varepsilon_{\text{QD}} A}{d_{\text{QD}}} \]  

(6)

where \( A \) is the active area and \( d_{\text{QD}} \) is the width of the PQD layer. It is worth noting that the contact between MAPbI\(_3\) and the PQDs would form a hole depletion region in MAPbI\(_3\). Then, the contact between the PQDs and the carbon electrode would generate a Schottky barrier, which led to a hole depletion region in the PQD layer. Both the depletion regions in MAPbI\(_3\) and the PQDs contributed to the barrier capacitance value. For the PSC in the presence of CsSn\(_{0.3}\)Pb\(_{0.7}\)I\(_3\) QDs, the lower VB edge of the PQDs allowed more holes to migrate from the PQD layer to the MAPbI\(_3\) film. These holes gradually moved away from the MAPbI\(_3\)/PQDs interface under the isotype heterojunction electric field, thereby increasing the \( W_D \). This might be the reason why the \( C_T \) value of CsSn\(_{0.3}\)Pb\(_{0.7}\)I\(_3\) QDs-added device was low.

To get insight on the carrier transfer process, the steady-state PL spectra for the pure MAPbI\(_3\) film and MAPbI\(_3\) films covered by different tin-doped PQDs were measured. As shown in Fig. 7d, the PL peak intensity at about 775 nm was obviously decreased after the incorporation of CsSn\(_{0.1}\)Pb\(_{0.9}\)I\(_3\) QDs or CsSn\(_{0.2}\)Pb\(_{0.8}\)I\(_3\) QDs. There were two explanations for the weakening of PL intensity: first, the PQDs cause additional non-radiative pathways to capture photogenerated carriers; second, the higher VB edges of PQDs allow more photogenerated holes to migrate to the PQD layer, thus the number of carriers participating in direct recombination is reduced. However, after adding CsSn\(_{0.3}\)Pb\(_{0.7}\)I\(_3\) QDs with more orthorhombic
by-products and lower VB edge, the PL intensity increased, which showed that more carriers were limited in the perovskite film without being trapped by defects. Therefore, the PL quench of the perovskite film with CsSn$_{0.1}$Pb$_{0.9}$I$_3$ QDs or CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs was caused by the optimized band alignment promoting the hole extraction, instead of interfacial trap-assisted recombination.

Fig. 7 a) J-V curves, b) IPCE spectra and c) EIS measurements of different PSCs. d) PL spectra of perovskite films with and without tin-doped PQDs.
Table 1 Photovoltaic parameters of different PSCs

| Device                  | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | PCE (%) | $R_{CT}$ (Ω) | $C_{T}$ (nF) |
|-------------------------|-------------|-------------------------|--------|---------|-------------|-------------|
| Control                 | 0.99        | 22.69                   | 56.78  | 12.80   | 56.5        | 35.5        |
| With CsSn$_{0.1}$Pb$_{0.9}$I$_3$ QDs | 1.01        | 22.85                   | 57.81  | 13.38   | 47.0        | 32.9        |
| With CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs | 1.05        | 23.30                   | 57.90  | 14.22   | 43.0        | 44.7        |
| With CsSn$_{0.3}$Pb$_{0.7}$I$_3$ QDs | 1.01        | 16.82                   | 47.40  | 8.07    | 81.4        | 16.3        |

In order to further understand the effects of tin-doped PQDs on the hole transport in MAPbI$_3$ films, a one-dimensional MAPbI$_3$/tin-doped PQDs heterojunction model was constructed, shown in Fig. 8a. To simplify the analysis, this structure was regarded as a mutant isotype heterojunction, and MAPbI$_3$ and tin-doped PQDs were determined to be p-type semiconductors. Theoretically, MAPbI$_3$ is a kind of intrinsic semiconductor with low doping amount, but in the carbon-based perovskite PSCs with no HTLs, the perovskite layer needs to undergo p-type doping treatment. A small amount of DMSO were added in the precursor of perovskite to form a complex with PbI$_2$, so that there was a small amount of Pb vacancy in the perovskite, which made the perovskite become a p-type semiconductor. Moreover, Laban and Etgar utilized Mott-Schottky analysis to find that the acceptor concentration of MAPbI$_3$ was \(2.14 \times 10^{17} \text{ cm}^{-3}\), belonging to the doping level of p-type semiconductor [38]. The contact of two semiconductors with different Fermi levels would form an electric field from the one with a high Fermi level to the another with a low Fermi level. Consequently, the p-p isotype heterojunction energy-band diagram under the equilibrium condition could be obtained, shown in Fig. 8b. According to the Poisson’s equation, the field continuity condition and the depletion...
approximation [39], barrier distributions of the isotype heterojunction were expressed by the following equations

\[
\exp\left(\frac{qV_{D,\text{QD}}}{k_BT} - 1\right) = \frac{\varepsilon_{\text{MAPbi}}N_{A,\text{MAPbi}}}{\varepsilon_{\text{QD}}N_{A,\text{QD}}} \frac{qV_{D,\text{MAPbi}}}{k_BT}
\]

(7)

\[
qV_{D,\text{MAPbi}} + qV_{D,\text{QD}} = E_{\text{Fermi, QD}} - E_{\text{Fermi, MAPbi}}
\]

(8)

\[
E_{\text{Fermi}}^p = \frac{1}{2} E_{\text{CB}} + E_{\text{VB}} - \frac{1}{2} k_BT \ln \left(\frac{N_C}{N_V} \right) - k_BT \ln \left(\frac{N_a}{n_i} \right)
\]

(9)

\[
W_D = \sqrt{\frac{2\varepsilon_{\text{MAPbi}}V_{D,\text{MAPbi}}}{qN_{A,\text{MAPbi}}}}
\]

(10)

where \(q\) is the elementary charge, \(\varepsilon_{\text{QD}}\) and \(N_{A,\text{QD}}\) are the dielectric coefficient and the acceptor concentration for tin-doped PQDs, respectively. \(V_{D,\text{MAPbi}}\) and \(V_{D,\text{QD}}\) are the potential difference in MAPbi and tin-doped PQDs in turn. \(E_{\text{Fermi, MAPbi}}\) and \(E_{\text{Fermi, QD}}\) stand for the Fermi levels of MAPbi and tin-doped PQDs, respectively. \(k_b\) is the Boltzmann constant and \(T\) is the room temperature. \(N_C\) and \(N_V\) are the effective density of states of electrons in conduction band and the effective density of states of holes in valence band, respectively. \(N_a\) is the acceptor concentration, \(n_i\) is the intrinsic carrier concentration and \(W_D\) is the depletion width in MAPbi.

The simulation results are exhibited in Fig. 8c. As the acceptor concentration of tin-doped PQDs increased, both \(V_{D,\text{MAPbi}}\) and \(W_D\) showed downward trends, indicating that the hole transfer process in the MAPbi film was gradually facilitated. Besides, less electrons would be drifted to the interface between MAPbi and the PQD layer to recombine with holes. On the contrary, the direct contact between MAPbi and the carbon electrode would generate a large Schottky barrier in MAPbi, resulting in higher values of \(V_{D,\text{MAPbi}}\) and \(W_D\), shown in Fig. 8d. In one word, MAPbi films modified by tin-doped PQDs with higher acceptor concentrations would be provided with much enhanced hole transport performance. This simulation result explained...
why the photovoltaic performance of the CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs-added PSC was better than the pristine and the CsSn$_{0.1}$Pb$_{0.9}$I$_3$ QDs-added device.

Fig. 8 a The one-dimensional MAPbI$_3$/PQDs heterojunction model. b Corresponding energy-band diagram under the equilibrium condition. c and d Simulation results for MAPbI$_3$/PQDs and MAPbI$_3$/carbon heterojunctions.

Conclusions

In summary, tin-doped PQDs were added between MAPbI$_3$ and the carbon electrode for enhanced PSC performance, due to their flexible energy levels and self-p-type doping effects. Especially, with the incorporation of CsSn$_{0.2}$Pb$_{0.8}$I$_3$ QDs, the PCE value could be improved from 12.80% to 14.22%, in comparison to the pristine device. It was attributed to the band alignment and the appropriate Sn$^{2+}$ doping content of the PQDs facilitating the hole extraction. This work is prospected to provide a direction for the interface optimization of carbon-based
PSCs based on PQDs.

**Abbreviations**

PSCs: perovskite solar cells; PQDs: perovskite quantum dots; HTLs: hole-transporting layers; PCE: power conversion efficiency; ODE: 1-octadecene; OA: oleic acid; OAM: oleylamine; MeOAc: methyl acetate; TOP: trioctylphosphine; MAI: methylammonium; DMSO: dimethylsulfoxide; DMF: N,N-dimethylformamide; FTO: fluorine-doped SnO$_2$; c-TiO$_2$: compact TiO$_2$; m-TiO$_2$: mesoporous TiO$_2$; TEM: transmission electron microscope; SAED: selected area electron diffraction; EDS: energy dispersive X-ray spectroscopy; VB: valence band; PL: photoluminescence; IPCE: incident photon-to-electron conversion; EIS: electrochemical impedance spectroscopy; XRD: X-ray diffraction.

**Authors’ contributions**

CZ performed the experiments and drafted the manuscript with the help of ZYH, XHL, RWM. MWC, HFL and YPY helped to revised the manuscript. All authors read and approved the final manuscript.

**Funding**

This work was supported by the National Natural Science Foundation of China (NSFC) (11704293, 11974266) and the Fundamental Research Funds for the Central Universities under Grant WUT (2020IB022).
Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

Acknowledgements

Not applicable

References

1. Rong YG, Hu Y, Mei AY, Tan HR, Saidaminov MI, Seok SI, McGehee MD, Sargent EH, Han HW. Challenges for commercializing perovskite solar cells. Science. 2018;361:eaat8235.

2. Liao JF, Wu WQ, Jiang Y, Zhong JX, Wang LZ, Kuang DB. Understanding of carrier dynamics, heterojunction merits and device physics: towards designing efficient carrier transport layer-free perovskite solar cells. Chem Soc Rev. 2020;49:354-381.

3. Huang JS, Yuan YB, Shao YC, Yan YF. Understanding the physical properties of hybrid perovskites for photovoltaic applications. Nat Rev Mater. 2017;2:17042.

4. Hwang T, Yun AJ, Kim J, Cho D, Kim S, Hong S, Park B. Electronic traps and their correlations to perovskite solar cell performance via compositional and thermal annealing controls. ACS Appl Mater Interfaces. 2019;11:6907-6917.

5. Zhou R, Yang Z, Xu JZ, Cao GZ. Synergistic combination of semiconductor quantum dots...
and organic-inorganic halide perovskites for hybrid solar cells. Coord Chem Rev. 2018;374:279-313.

6. Eperon GE, Habisreutinger SN, Leijtens T, Bruijnaers BJ, Van Franeker JJ, DeQuilettes DW, Pathak S, Sutton RJ, Grancini G, Ginger DS, Janssen RAJ, Petrozza A, Snaith HJ. The importance of moisture in hybrid lead halide perovskite thin film fabrication. ACS Nano. 2015;9:9380-9393.

7. Meng FN, Liu AM, Gao LG, Cao JM, Yan YL, Wang N, Fan MQ, Wei GY, Ma TL. Current progress in interfacial engineering of carbon-based perovskite solar cells. J Mater Chem A. 2019;7:8690-8699.

8. Chen K, Wu P, Yang WQ, Su R, Luo DY, Yang XY, Tu YG, Zhu R, Gong QH. Low-dimensional perovskite interlayer for highly efficient lead-free formamidinium tin iodide perovskite solar cells. Nano Energy. 2018;49:411-418.

9. Akin S, Altintas Y, Mutlugun E, Sonmezoglu S. Cesium-lead based inorganic perovskite quantum-dots as interfacial layer for highly stable perovskite solar cells with exceeding 21% efficiency. Nano Energy. 2019;60:557-566.

10. Zheng XP, Troughton J, Gasparini N, Lin YB, Wei MY, Hou Y, Liu JK, Song KP, Chen ZL, Yang C, Turedi B, Alsalloum AY, Pan J, Chen J, Zhumekenov AA, Anthopoulos TD, Han Y, Baran D, Mohammed OF, Sargent EH, Bakr OM. Quantum dots supply bulk- and surface-passivation agents for efficient and stable perovskite solar cells. Joule. 2019;3:1963-1976.

11. Chen LC, Tien CH, Tseng ZL, Ruan JH. Enhanced efficiency of MAPbI$_3$ perovskite solar cells with FAPbX$_3$ perovskite quantum dots. Nanomaterials. 2019;9:121.
12. Gao YB, Wu YJ, Lu HB, Chen C, Liu Y, Bai X, Yang LL, Yu WW, Dai QL, Zhang Y. CsPbBr$_3$ perovskite nanoparticles as additive for environmentally stable perovskite solar cells with 20.46% efficiency. Nano Energy. 2019;59:517-526.

13. Cha MY, Da PM, Wang J, Wang WY, Chen ZH, Xiu FX, Zheng GF, Wang ZS. Enhancing perovskite solar cell performance by interface engineering using CH$_3$NH$_3$PbBr$_{0.9}$I$_{2.1}$ quantum dots. J Am Chem Soc. 2016;138:8581-8587.

14. Sidhik S, Esparza D, Martínez-Benítez A, Lopez-Luke T, Carriles R, Mora-Sero I, de la Rosa E. Enhanced photovoltaic performance of mesoscopic perovskite solar cells by controlling the interaction between CH$_3$NH$_3$PbI$_3$ films and CsPbX$_3$ perovskite nanoparticles. J Phys Chem C. 2017;121:4239-4245.

15. Li B, Zhang YN, Zhang YL, Yin LW. Graded heterojunction engineering for hole-conductor-free perovskite solar cells with high hole extraction efficiency and conductivity. Adv Mater. 2017;29:1701221.

16. Chan CY, Wang YY, Wu GW, Diau EWG. Solvent-extraction crystal growth for highly efficient carbon-based mesoscopic perovskite solar cells free of hole conductors. J Mater Chem A. 2016;4:3872-3878.

17. Sheng YS, Mei AY, Liu SA, Duan M, Jiang P, Tian CB, Xiong YL, Rong YG, Han HW, Hu Y. Mixed (5-AVA)$_x$MA$_{1-x}$PbI$_{3-x}$(BF$_4$)$_x$ perovskites enhance the photovoltaic performance of hole-conductor-free printable mesoscopic solar cells. J Mater Chem A. 2018;6:2360-2364.

18. Xiong YL, Liu Y, Lan K, Mei AY, Sheng YS, Zhao DY, Han HW. Fully printable hole-conductor-free mesoscopic perovskite solar cells based on mesoporous anatase single
1. crystals. New J Chem. 2018;42:2669-2674.

2. Van der Stam W, Geuchies JJ, Altantzis T, Van den Bos KHW, Meeldijk JD, Van Aert S, Bals S, Vanmaekelbergh D, De Mello Donega C. Highly emissive divalent-ion-doped colloidal CsPb$_{1-x}$M$_x$Br$_3$ perovskite nanocrystals through cation exchange. J Am Chem Soc. 2017;139:4087-4097.

3. Zhang JB, Zhang LW, Cai P, Xue XG, Wang MK, Zhang J, Tu GL. Enhancing stability of red perovskite nanocrystals through copper substitution for efficient light-emitting diodes. Nano Energy. 2019;62:434-441.

4. Vitoreti ABF, Agouram S, de la Fuente MS, Muñoz-Sanjose V, Schiavon MA, Mora-Sero I. Study of the partial substitution of Pb by Sn in Cs-Pb-Sn-Br nanocrystals owing to obtaining stable nanoparticles with excellent optical properties. J Phys Chem C. 2018;122:14222-14231.

5. Gupta S, Cahen D, Hodes G. How SnF$_2$ impacts the material properties of lead-free tin perovskites. J Phys Chem C. 2018;122:13926-13936.

6. Mosconi E, Umari P, De Angelis F. Electronic and optical properties of mixed Sn-Pb organohalide perovskites: a first principles investigation. J Mater Chem A. 2015;3:9208-9215.

7. Chung I, Song JH, Im J, Androulakis J, Malliakas CD, Li H, Freeman AJ, Kenney JT, Kanatzidis MG. CsSnI$_3$: Semiconductor or metal? High electrical conductivity and strong near-infrared photoluminescence from a single material. High hole mobility and phase-transitions. J Am Chem Soc. 2012;134:8579-8587.

8. Liu F, Ding C, Zhang YH, Ripolles TS, Kamisaka T, Toyoda T, Hayase S, Minemoto T,
Yoshino K, Dai SY, Yanagida M, Noguchi H, Shen Q. Colloidal synthesis of air-stable alloyed CsSn$_{1-x}$Pb$_x$I$_3$ perovskite nanocrystals for use in solar cells. J Am Chem Soc. 2017; 139:16708-16719.

26. Xu HZ, Duan JL, Zhao YY, Jiao ZB, He BL, Tang QW. 9.13%-efficiency and stable inorganic CsPbBr$_3$ solar cells. Lead-free CsSnBr$_{3-x}$I$_x$ quantum dots promote charge extraction. J Power Sources. 2018;399:76-82.

27. Duan QQ, Ji JY, Hong X, Fu YC, Wang CY, Zhou K, Liu XQ, Yang H, Wang ZY. Design of hole-transport-material free CH$_3$NH$_3$PbI$_3$/CsSnI$_3$ all-perovskite heterojunction efficient solar cells by device simulation. Solar Energy. 2020;201:555-560.

28. Zhang XL, Cao WY, Wang WG, Xu B, Liu S, Dai HT, Chen SM, Wang K, Sun XW. Efficient light-emitting diodes based on green perovskite nanocrystals with mixed-metal cations. Nano Energy. 2016;30:511-516.

29. Swarnkar A, Marshall AR, Sanehira EM, Chernomordik BD, Moore DT, Christians JA, Chakrabarti T, Luther JM. Quantum dot-induced phase stabilization of a-CsPbI$_3$ perovskite for high-efficiency photovoltaics. Science. 2016;354:92-95.

30. Minemoto T, Murata M. Impact of work function of back contact of perovskite solar cells without hole transport material analyzed by device simulation. Curr Appl Phys. 2014;14:1428-1433.

31. Tian CB, Mei AY, Zhang SJ, Tian HR, Liu S, Qin F, Xiong YL, Rong YG, Hu Y, Zhou YH, Xie SY, Han HW. Oxygen management in carbon electrode for high-performance printable perovskite solar cells. Nano Energy. 2018;53:160-167.

32. Jeon NJ, Na H, Jung EH, Yang TL, Lee YG, Kim G, Shin HW, Seok SI, Lee J, Seo J. A
fluorene-terminated hole-transporting material for highly efficient and stable perovskite solar cells. Nat Energy. 2018;3:682-689.

33. Li C, Wang FZ, Xu J, Yao JX, Zhang B, Zhang CF, Xiao M, Dai SY, Li YF, Tan ZA. Efficient perovskite/fullerene planar heterojunction solar cells with enhanced charge extraction and suppressed charge recombination. Nanoscale. 2015;7:9771-9778.

34. Song JX, Bian J, Zheng EQ, Wang XF, Tian WJ, Miyasaka T. Efficient and environmentally stable perovskite solar cells based on ZnO electron collection layer. Chem Lett. 2015;44:610-612.

35. Sanehira EM, Marshall AR, Christians JA, Harvey SP, Ciesielski PN, Wheeler LM, Schulz P, Lin LY, Beard MC, Luther JM. Enhanced mobility CsPbI$_3$ quantum dot arrays for record-efficiency, high-voltage photovoltaic cells. Sci Adv. 2017;3:eaa04204.

36. Akkerman QA, Park S, Radicchi E, Nunzi F, Mosconi E, De Angelis F, Brescia R, Rastogi P, Prato M, Manna L. Nearly monodisperse insulator Cs$_4$PbX$_6$ (X = Cl, Br, I) nanocrystals, their mixed halide compositions, and their transformation into CsPbX$_3$ nanocrystals. Nano Lett. 2017;17:1924-1930.

37. De Weerd C, Lin JH, Gomez L, Fujiwara Y, Suenaga K, Gregorkiewicz T. Hybridization of single nanocrystals of Cs$_4$PbBr$_6$ and CsPbBr$_3$. J Phys Chem C. 2017;121:19490-19496.

38. Laban WA, Etgar L, Depleted hole conductor-free lead halide iodide heterojunction solar cells. Energy Environ Sci. 2013;6:3249-3253.

39. Kumar RC. On the solution of poisson equation for an isotype heterojunction under zero-current condition. Solid State Electron. 1968;11:543-551.