Perovskite solar cell with improved performance passivated by all inorganic perovskite quantum dots

Jia Xing Cao*, Hui Feng Shen, Lei Cheng, Wen Tao Zhao, Dong Huan Zhu, Yan Sun, Bo Ni
No.3888, Yuanjiang Road, Minhang District, Shanghai
Shanghai Precision Metrology and Test Research Institute, 201109
caojx1017@foxmail.com

Abstract. Improving the efficiency and stability of perovskite solar cells is the main direction of realizing their commercial application. Interface passivation is one of the most effective methods. Through interface passivation, on the one hand, the energy level of the device can be adjusted and the photoelectric conversion efficiency (PCE) of the device can be improved; on the other hand, materials that are not sensitive to the environment can be selected to improve the stability of the device. All inorganic perovskite quantum dots (QDs) have excellent environmental stability and are similar to the crystal structure of the absorbing layer of perovskite solar cells, so they have the potential for interface passivation. In this paper, two kinds of all inorganic perovskite QDs with different morphology, size and crystal structure were synthesized by hot injection method, which were used as the passivation layer of perovskite solar cells, and improved the device performance. The PCE of the device treated with CsPbBr3 QDs can reach as high as 20.45%, and has excellent environmental stability.

1. Introduction
Recently, the best perovskite solar cell has a certification efficiency as high as 25.5%, which can be compared with that of traditional silicon solar cells.[1-3] Perovskite materials have the advantage that they can be prepared by solution methods, so they have great potential in saving costs and simplifying processes.[4, 5] However, the commercial application of perovskite solar cells has been limited by their poor stability.[6, 7] As ionic compounds, perovskite materials are easily corroded by moisture and oxygen. Therefore, how to improve the stability of perovskite solar cells has become the focus of the research in this field. The perovskite QDs with rich organic ligands and stable performance are used as the passivation layer to coat the absorbing layer in perovskite solar cell, which can block the environment impact and improve the device performance.[8-11]

In this paper, a series of perovskite QDs with different crystal structures and morphologies were synthesized by hot injection method. A layer of perovskite structure protective layer was constructed on the original perovskite absorbing layer by spin-coating the QDs. The QDs are not sensitive to the environment and have a passivation effect on the surface defects of the original absorbing layer, so the stability and efficiency of the device have been greatly improved. The PCE of the device passivated with QDs has increased from 18.19% to 20.45%, and can still maintain 95% of the initial efficiency after stored for 10 days.
2. Materials and Methods

2.1. A subsection Materials
Cesium carbonate \((\text{Cs}_2\text{CO}_3, 99\%)\), lead bromide \((\text{PbBr}_2, 99.9\%)\), octadecene \((\text{ODE}, \text{C}_{18}\text{H}_{36}, 90\%)\), oleic acid \((\text{OA}, \text{C}_{18}\text{H}_{34}\text{O}_2, 85\%)\), and oleylamine \((\text{OAm}, \text{C}_{18}\text{H}_{34}\text{O}, 80\%-90\%)\) were purchased from Aladdin. The fluorine-doped tin oxide \((\text{FTO})\) glass substrates were purchased from Liaoning Huite Optoelectronics Technology Co., Ltd. \(\text{SnO}_2\) solution \((15\% \text{SnO}_2 \text{ dispersed in water})\) was purchased from Alfa Aesar. \(\text{N, N-2 methyl formamide (DMF, 99.8\%)}, \text{ dimethyl sulfoxide (DMSO, 99.8\%)}, \text{ and chlorobenzene (CB, 99.9\%) were purchased from Sigma-Aldrich. Isopropanol (IPA, 99.8\%) was purchased from Innochem. Spiro-OMeTAD, lithium salt and 4-tert-butylpyridine (tBP, 96\%) were purchased from Lumtec. Iodoformamidine (FAI, 99.5\%), bromomethylamine (MABr, 99.5\%), and chloromethylamine (MACl, 99.5\%) were purchased from Xi'an Polymer Light Technology. All materials were used without any further purification.

2.2. Preparation of cesium oleate precursor
0.240 g \(\text{Cs}_2\text{CO}_3\), 10 mL \(\text{ODE}\) and 1 mL \(\text{OA}\) were added into a 25 mL three-necked flask and heated to 100 °C with rapid stirring. Nitrogen gas was used to remove the oxygen and water from the reagents in the flask. When \(\text{Cs}_2\text{CO}_3\) is completely dissolved, a clear cesium oleate precursor solution was obtained.

2.3. Synthesis of \(\text{CsPbBr}_3\) perovskite QDs
0.146 g \(\text{PbBr}_2\), 10 mL \(\text{ODE}\), 0.1 mL \(\text{OA}\) and 1 mL \(\text{OAm}\) were added into a 25 mL three-necked flask and heated to 100 °C under nitrogen. When \(\text{PbBr}_2\) was completely dissolved, the temperature was increased to 160 °C and kept for 10 min. Then, quickly injected 1.5 mL cesium oleate precursor into \(\text{PbBr}_2\) solution, and reacted for about 2 min. At this time, the reaction flask was removed and immediately placed into an ice-water bath for cooling. The solution gradually turned into a yellow-green crude liquid, and the reaction was completed. Finally, the reaction solution was centrifuged at 8000 RPM for 7 min to obtain the precipitated product and supernatant. The supernatant containing residual reaction raw materials was removed, and the precipitated product was dissolved in \(\text{n-hexane}\) to obtain clear and transparent \(\text{CsPbBr}_3\) QDs colloidal solution.

2.4. Synthesis of \(\text{Cs}_4\text{PbBr}_6\) perovskite QDs
0.146 g \(\text{PbBr}_2\), 10 mL of \(\text{ODE}\), 0.4 mL of \(\text{OA}\) and 0.6 mL of \(\text{OAm}\) were added into a 25 mL three-necked flask. Clear and transparent \(\text{Cs}_4\text{PbBr}_6\) QDs colloidal hexane solution were obtained by following the experiment steps, which are the same as \(\text{CsPbBr}_3\) QDs. The schematic diagram of the synthesis of perovskite QDs is shown in Figure 1.

2.5. Preparation of perovskite solar cells
FTO glass substrates was cleaned ultrasonically with detergent, deionized water, acetone and IPA in sequence, and treated under UV-ozone for 10 min. Then, the diluted \(\text{SnO}_2\) solution \((2.67\% \text{ in water})\) was spin-coated onto FTO substrates at 4000 rpm for 30 s and annealed on a hot plate at 150 °C for 20 min. Next, 1.3M \(\text{PbI}_2\) solution \((\text{dissolved in a mixed solvent of DMF and DMSO with a volume ratio of 9.5:0.5})\) was spin-coated on the \(\text{SnO}_2\) layer at 1500 rpm for 30 s, and annealed at 70 °C for 1 min. After that, when \(\text{PbI}_2\) was cooled to room temperature, the solution formed by dissolving 60 mg FAI, 6 mg MABr, and 6 mg MACl in 1 mL IPA was spin-coated at 1500 rpm for 30 s and annealed under ambient air environment \((30-40\% \text{ humidity})\) for 15 min. The hole transport layer was obtained by spin-coating Spiro-OMeTAD solution \((72.3\text{mg Spiro-OMeTAD, 35} \mu\text{L lithium salt solution, and } 30 \mu\text{L tBP in 1 mL CB})\) at 3000rpm for 30s. Finally, 100 nm Ag electrode was deposited through thermal evaporation. While measuring, the accurate active area was about 0.1 cm\(^2\) defined by a non-reflective mask.
2.6. Characterization
Bruker-D8 equipment with Cu Kα radiation as X-ray source was used to characterize the X-ray diffraction (XRD) pattern of the sample at a scan speed of 6°min⁻¹. JEOL JEM-2100 transmission electron microscope (TEM) was used to characterize the morphology and the size of the sample under an accelerating voltage of 200 kV, and the sample was drip-casted onto 300-mesh carbon-coated copper grids. TESCAN MIRA3 and Aztec X-MaxN80 equipment were used to characterize the composition of the sample, and the sample was prepared by drip-casting on a conductive silicon wafer. Current density (Jsc) and voltage (Voc) curve of the solar cell was measured by an Abet Technology Sun 2000 solar simulator and a Keithley 2400 source meter. The solar simulator output is 100mW cm⁻² under AM1.5G illumination (calibrated using a standard Si solar cells).

![Figure 1. Synthesis of different kinds of all inorganic perovskite quantum dots](image)

3. Results & Discussion
Different kinds of perovskite QDs, including cubic CsPbBr₃ and quasi-hexagonal Cs₄PbBr₆, were successfully synthesized by adjusting the ratio of ligands during the hot injection reaction. Figure 2a shows the XRD pattern of perovskite QDs synthesized when the ratio of OAm to OA ligand is 10:1, corresponds to the CsPbBr₃ standard card (PDF #54-0751). The main peak positions are at 2θ = 21.551° and 30.840°, corresponding to the (010) and (002) crystal planes of CsPbBr₃ crystals. No other impurity phase or second phase was observed. The crystal structure of CsPbBr₃ QDs belongs to a three-dimensional perovskite crystal structure. Figure 2b is a TEM image of CsPbBr₃ QDs. The synthesized cubic shape QDs are uniform in size with an average diameter of 8.04 nm. In hot injection method, the long-chain ligand hinders the further reaction between the reactive monomer and the crystal nucleus, thereby limiting the size of the synthesized product.

![Figure 2. (a) XRD pattern and (b) TEM image of as-prepared CsPbBr₃ QDs](image)
Figure 3a shows the XRD pattern of perovskite QDs synthesized when the ratio of OAm and OA is 3:2, corresponding to the Cs$_4$PbBr$_6$ standard card (PDF #54-0750). The main peak positions are at $2\theta = 22.583^\circ$, $25.546^\circ$, $27.751^\circ$, $28.813^\circ$ and $30.473^\circ$, correspond to the (101), (211), (610), (230) and (330) crystal planes of Cs$_4$PbBr$_6$ crystal, respectively. The crystal structure of Cs$_4$PbBr$_6$ QDs is a zero-dimensional perovskite crystal structure, which means the originally connected [PbBr$_6$]$^4-$ octahedral sequence is separated by Cs$^+$, forming an electronic structure different from three-dimensional perovskite. According to literature reports, the band gap of CsPbBr$_3$ QDs is about 2.3 eV, while the band gap of Cs$_4$PbBr$_6$ QDs is wider, about 3.9 eV.[12] Figure 3b is a TEM image of the synthesized Cs$_4$PbBr$_6$ QDs, which exhibit a quasi-hexagonal shape and uniform size. According to statistics, the average size of Cs$_4$PbBr$_6$ QDs is about 18.70 nm.

All inorganic perovskite QDs have excellent environmental stability, so they have great potential in passivating surface defects of the absorbing layer, blocking moisture and oxygen from the ambient air, and improving device stability in perovskite solar cells. CsPbBr$_3$ and Cs$_4$PbBr$_6$ perovskite QDs synthesized by hot injection method are quite different in morphology, crystal structure and electronic properties, and can be used to discover effective surface passivation materials. As shown in Figure 4a, it can be obtained that the PCE of the perovskite solar cell is significantly improved after QDs treatment. Among them, the PCE of CsPbBr$_3$ QDs treated perovskite solar cells has been increased from 18.19% to 20.45%, as shown in Table 1. Both CsPbBr$_3$ and Cs$_4$PbBr$_6$ QDs have a band gap larger than that of the perovskite absorbing layer, so the Voc of the QDs treated devices has been significantly improved. The Voc of the device passivated by CsPbBr$_3$ QDs reaches 1.08 eV, while the Voc of Cs$_4$PbBr$_6$ QDs treated device reaches 1.04 eV. Since the band gap of the perovskite absorbing layer is similar to that of CsPbBr$_3$ QDs, the CsPbBr$_3$ QDs passivation layer can adjust the energy level of the perovskite absorbing layer to better match the hole transport layer and effectively improve the device’s efficiency. At the same time, CsPbBr$_3$ QDs with an average size of only 8.04 nm can fill the surface defects of the perovskite absorbing layer. The abundant surface ligands enable the QDs and the perovskite absorbing layer to be better combined, thereby improving the device interface contact and the device filling factor (FF) increased from 77.18% to 80.11%. The band gap of Cs$_4$PbBr$_6$ QDs is wider than normal semiconductor, and cannot properly match the band gap of the perovskite absorbing layer and the hole transport layer. Therefore, the increasement of Voc of the device is lower than that of CsPbBr$_3$ QDs, and FF is slightly smaller.

Since the surface of CsPbBr$_3$ and Cs$_4$PbBr$_6$ QDs is coated with abundant organic ligands, which can block the ambient environment, the stability of the perovskite solar cell treated with QDs can be improved. Fig. 4b shows the curve of the PCE of the perovskite solar cell treated with QDs and its control group under different storage time. The efficiency of the untreated device dropped significantly, and the PCE was only 63% of the initial value after being stored for 10 days, which may be caused by partial decomposition of the perovskite absorbing layer due to the water and oxygen in the environment.
The devices treated with QDs have good stability. The PCE of the devices treated with CsPbBr$_3$ QDs can still maintain 95% of the initial value after being stored for 10 days, and the devices treated with Cs$_4$PbBr$_6$ QDs can also maintain 90% of the initial value. The improvement of device stability is attributed to the excellent environmental stability of all inorganic perovskite QDs.

![Figure 4](image)

Figure 4. (a) J-V curve and (b) stability of perovskite solar cells under different interfacial treatments

| Devices       | PCE (%) | Voc (V) | Jsc (mA cm$^{-2}$) | FF (%) |
|---------------|---------|---------|--------------------|--------|
| Control       | 18.19   | 1.02    | 23.10              | 77.18  |
| CsPbBr$_3$ QDs | 20.45   | 1.08    | 23.64              | 80.11  |
| Cs$_4$PbBr$_6$ QDs | 18.35   | 1.04    | 23.18              | 76.13  |

4. Conclusions
A series of all inorganic perovskite QDs were used to improve the interface contact between the absorbing layer and the hole transport layer of the perovskite solar cell, and improve the efficiency and stability of the device due to their excellent environmental stability. Both CsPbBr$_3$ and Cs$_4$PbBr$_6$ QDs passivation layers can increase the VOC and environment stability of the device. Among them, the PCE of the device treated with CsPbBr$_3$ QDs has increased from 18.19% to 20.45%, and can still maintain 95% of the initial value after being stored for 10 days. CsPbBr$_3$ QDs play an important role in adjusting device energy level, passivating interface defects, and blocking the external environment. Therefore, using all inorganic perovskite QDs as interface passivation layer provides a simple and efficient method to obtain high performance perovskite solar cells.

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