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In Situ Passivation for Efficient PbS Quantum Dot Solar Cells by Precursor Engineering

Yongjie Wang, Kunyuan Lu, Lu Han, Zeke Liu, Guozheng Shi, Honghua Fang, Si Chen, Tian Wu, Fan Yang, Mengfan Gu, Sijie Zhou, Xufeng Ling, Xun Tang, Jiawei Zheng, Maria Antonietta Loi, and Wanli Ma*

Current efforts on lead sulfide quantum dot (PbS QD) solar cells are mostly paid to the device architecture engineering and postsynthetic surface modification, while very rare work regarding the optimization of PbS synthesis is reported. Here, PbS QDs are successfully synthesized using PbO and $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ as the lead sources. QD solar cells based on PbAc-PbS have demonstrated a high power conversion efficiency (PCE) of 10.82% (and independently certificated values of 10.62%), which is significantly higher than the PCE of 9.39% for PbO-PbS QD based ones. For the first time, systematic investigations are carried out on the effect of lead precursor engineering on the device performance. It is revealed that acetate can act as an efficient capping ligands together with oleic acid, providing better surface coverage and replace some of the harmful hydroxyl (OH) ligands during the synthesis. Then the acetate on the surface can be exchanged by iodide and lead to desired passivation. This work demonstrates that the precursor engineering has great potential in performance improvement. It is also pointed out that the initial synthesis is an often neglected but critical stage and has abundant room for optimization to further improve the quality of the resultant QDs, leading to breakthrough efficiency.

Lead sulfide quantum dots (PbS QDs), mainly due to the large tunability of their optoelectronic properties by adjusting size,^[1] composition^[2,3] and surface chemistry,^[4] have attracted great interest in applications including infrared sensors,^[5–8] light emitting diodes,^[9,10] transistors,^[11–14] and solar cells^[1,15,16] in the past

decade. Additionally, multiple exciton generation effect,^[17–19] peculiar for lead chalcogenide QDs, opens another avenue to lessen the transmission loss of solar photons in photovoltaic devices. The highest certified power conversion efficiency (PCE) reported in the literature for solar cells based on PbS QDs has reached 11.3%.^[16] This fast-growing efficiency has been realized mainly from the optimization of: (i) device architecture,^[15] based on which both device efficiency and stability have been improved, and (ii) postsynthetic surface modification, which helps to reduce a variety of mid-gap trap states.^[16,20] However, we should be aware of that the photovoltaic performance of PbS quantum dots can be actually determined by three stages: initial material synthesis, postsynthetic surface modification, and device engineering. Currently most efforts have been paid on the latter two stages. The effects of the initial material synthesis process on the device performance have largely been

neglected, but, however, could significantly affect the properties of the PbS QDs. Recently, Zherebetskyy et al. have shown the existence of surface hydroxyl (OH) groups on the surface of PbS QDs,^[21] which play a key role in stabilizing the PbS (111) facets during the initial synthesis process. However, the OH groups, proven as a source of sub-bandgap states and cannot removed completely in the postsynthetic and device fabrication stages,^[22] could be a stumbling block for the improvement of PbS QD solar cells. Thus engineering the initial synthesis process could be a potential method for the reduction of OH groups, leading to reduced sub-bandgap states and improved performance. Nonetheless, to the best of our knowledge, there was only one previous report specifically studied and compared the effect of precursors. Zhang et al. introduced lead halide as an alternative lead source in the synthesis process for in situ halide-passivated PbS and PbSe quantum dots and achieved a 6.5% PCE for PbS QDs solar cells.^[23] Although the efficiency is much lower than the state-of-the-art, this work inspired us that engineering of lead source can be a possible avenue for improving the quality of the quantum dots. The widely used lead source for PbS QD is lead oxide (PbO) and recently lead acetate trihydrate ($\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$) is also adopted as the lead precursor.^[15,16,20,24] However, little attention has been paid to the effects of these two lead precursors

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and the importance of precursor engineering has far from been realized. Herein in this work, we fabricated photovoltaic devices based on PbS QDs synthesized from both PbO and $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ (denoted as PbO-PbS QDs and PbAc-PbS QDs, respectively). PbAc-PbS QD based devices show much better performance than those based on PbO-PbS QDs. The mechanisms for the different performance were systematically studied. Based on the results of X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and time resolved photovoltage decay, we confirmed that acetate ligands could conduct in situ passivation on the QDs by partially replacing the hydroxyl groups during synthesis. Then these acetate ligands could be further removed in the postligand-exchange process. Therefore, the introduction of acetate groups during the initial synthesis stage could effectively decrease the amount of OH group and reduce the QD surface trap states, resulting in a significantly improved device efficiency of 10.82% (and independently National Center of Supervision and Inspection on Solar Photovoltaic Products Quality (CPVT) certificated values of 10.62%). In general, our results not only revealed the tremendous effect of initial materials synthesis on the QD properties but also provided exciting new path to further improve the device photovoltaic performance by precursor engineering.

PbS quantum dot synthesis was performed under nitrogen atmosphere using standard air-free Schlenk line techniques.^[25] For a typical synthesis of PbS QDs, PbO or $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ was dissolved in oleic acid (OA) and 1-octadecene (ODE) at 100 °C under vacuum condition. The reaction was initiated by rapid injection of the sulfide precursor, proper amount of hexamethyldisilathiane mixing with ODE. After synthesis, the crude solution was transferred into a nitrogen-filled glovebox. QDs

were purified and dispersed in hexane. As shown in Figure S1a in the Supporting Information, the absorption and PL spectra of the PbS QDs, which were synthesized from PbO and $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ at same condition, respectively, show no appreciable differences in the position of the absorption and photoluminescence peak. Meanwhile, the transmission electron microscopy images (Figure S1b,c, Supporting Information) of PbO-PbS and PbAc-PbS QDs exhibit almost the same size and size distribution (3.03 ± 0.64 and 3.05 ± 0.78 nm, respectively). In addition, the X-ray diffraction patterns of the oleic acid capped PbO-PbS QDs and PbAc-PbS QDs (Figure S2, Supporting Information) are almost identical, indicating the same crystal structure. These results suggest that alteration of the lead precursor from PbO to $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ will not influence the size, optical bandgap, and crystal structure of the resultant PbS QDs. However, we found they have great influence on the photovoltaic performance of the corresponding QDs. Devices based on PbO-PbS and PbAc-PbS QDs with the inverted architecture (indium-doped tin oxide (ITO)/ZnO/PbS-tetrabutylammonium iodide (TBAI)/PbS-ethanedithiol (EDT)/Au) (Figure 1a) have been fabricated and compared. Briefly, in the QD solar cells, the TBAI-exchanged PbS QD film, serving as the n-type active layer,^[4,26] was deposited onto the ZnO-nanoparticle-coated ITO glass substrates, followed by two layers of p-type PbS QD film treated with EDT.^[4] Figure 1b shows the cross-sectional scanning electron microscopy (SEM) image of the corresponding PbS QD photovoltaic device. Current-voltage characteristics of the representative devices under simulated AM 1.5G illumination are shown in Figure 1c. For PbAc-PbS QD based devices, an optimal PCE of 10.82% has been obtained in our lab

Figure 1. Device architecture and performance. a) Schematic of the device structure. A TBAI-treated PbS QD film is deposited on top of a ZnO layer, followed by two layers of EDT-treated PbS QDs and gold as the top contact. b) Cross-sectional SEM images of PbO-PbS and PbAc-PbS QD devices. c) J - V curves of PbS QD devices. d) J - V Curve of CPVT certified device based on PbAc-PbS QDs.

Table 1. Photovoltaic parameters of the PbO-PbS and devices. Statistics is based on 3 different devices.

Lead source	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF ^{a)} [%]	PCE ^{b)} [%]
PbO	0.558 ± 0.014	24.49 ± 0.91	63.57 ± 1.44	8.69 ± 0.38
Champion device	0.57	25.45	64.74	9.39
PbAc ₂ ·3H ₂ O	0.599 ± 0.010	25.39 ± 0.56	67.65 ± 1.60	10.29 ± 0.26
Champion device	0.60	25.69	70.21	10.82
CPVT certified device	0.62	25.29	67.74	10.62

^{a)} Fill factor (FF); ^{b)} Power conversion efficiency (PCE).

(Figure 1d). We have also obtained a confirmed PCE of 10.62% in another institute CPVT (Figure S3a,b, Supporting Information), which has provided certified efficiency for previous reported solar cells.^[27,28] In comparison, the PCE of 10.82% is significantly higher than the optimal PCE of 9.39% obtained for the PbO-PbS QD based devices. To ensure the reproducibility of the results, 36 separate devices using different batches of QD materials were fabricated and tested. Histograms of the device-performance characteristics are shown in Figure S4 in the Supporting Information and the average device parameters are tabulated in **Table 1**. We can observe that the PbAc-PbS QD based devices perform much better than PbO-PbS QD based ones, mainly due to the enhanced open circuit voltage (V_{oc}) and fill factors (FF). For the former, the V_{oc} values are highly reproducible and have an average value up to 0.60 V, while for the latter, the average V_{oc} is significantly lower at around 0.56 V.

The average FF for the two QDs based devices are 67.65% and 63.57%, respectively. When combined with high short-circuit current density (J_{sc}) ($>25 \text{ mA cm}^{-2}$), an average PCE of 10.29% and 8.69% was achieved for PbAc-PbS and PbO-PbS based devices, respectively. The external quantum efficiency (EQE) spectra of the PbO-PbS QDs and PbAc-PbS QDs based solar cells were measured and displayed in Figure S5 in the Supporting Information. We observe that the PbAc-PbS based device has higher EQE than the PbO-PbS QD solar cell in the wavelength region of 700–1100 nm. We speculated that the red light can penetrate deeper into the TBAI layer and the collection of generated electrons is limited by the traps of PbO-PbS QDs.^[29] The J_{sc} is also calculated from the EQE results, which are in good agreement with the results from the J – V measurements.

Compared with PbO-PbS based devices, the performance enhancement of PbAc-PbS based devices mainly came from the improvement of V_{oc} and FF. Thus in order to gain insight into the origin of performance enhancement, we measured the dependence of J_{sc} and V_{oc} on the illumination intensities to probe the charge recombination in device, which was considered as an origin of the loss of V_{oc} and FF.^[30] The power-law dependence of J_{sc} upon the illumination intensity can generally be expressed as $J_{sc} \propto I^\alpha$, where I is the light intensity and α is the exponential factor.^[30] The α value of the PbO-PbS QD based devices is 0.99 and is almost 1.00 for PbAc-PbS QD based ones (**Figure 2a**). This result indicates that both devices have very few bimolecular recombination at short-circuit condition. The slope of V_{oc} versus the light intensity gives nkT/q , where n ,

Figure 2. Device characteristics and optical characterization. a) Light-intensity dependence of J_{sc} . Solid lines: Linear fits. b) Light-intensity dependence of V_{oc} . Solid lines: Logarithmic fits with an ideality factor $n = 1.55$ for PbO-PbS QD device and $n = 1.18$ for PbAc-PbS QD device. c) Transient photovoltage decay curves of PbO-PbS and PbAc-PbS QD devices. d) Steady state PL spectra of TBAI and EDT-treated PbS QD films. e) Time resolved PL emission of TBAI and EDT-treated PbS QD films. f) 2D transient PL decay of TBAI-treated PbO-PbS and PbAc-PbS QD films.

k , T , and q are the diode ideality factor, the Boltzmann constant, temperature in Kelvin, and the elementary charge, respectively. The diode ideality factor n is an indicator of the dominant recombination mechanism.^[30] The larger the n value, the greater the probability of trap-assisted recombination at open-circuit condition. The slope of the plot for the PbAc-PbS QDs devices was much lower ($1.18\text{ kT}/q$) than that of the PbO-PbS QDs devices ($1.55\text{ kT}/q$), which indicates greatly reduced trap-assisted recombination (Figure 2b).^[31] The decrease of diode ideality factor suggests the reduction of trap states in PbAc-PbS QDs and hence results in decreased recombination and improved V_{oc} as well as FF, compared to PbO-PbS QDs.^[30,31]

To confirm the reduction of trap states in PbAc-PbS QD film, we used transient photovoltage decay to investigate the carrier dynamics along the entire pathway in a complete cell.^[32] Transient photovoltage measurements, which correlate to the electron lifetime in the absorber, provide insight into carrier recombination rates in the cell. Two devices with the same device structure based on PbO-PbS and PbAc-PbS QDs were measured and compared, with the results shown in Figure 2c. In both cases, the photovoltage decay constants are on the scale of microseconds, 45.4 and 69.9 μs for PbO-PbS QDs and PbAc-PbS QDs based devices, respectively. Note that PbAc-PbS QDs based device shows a $\approx 55\%$ longer lifetime than that of PbO-PbS QDs based ones. This greatly enhanced lifetime also reveals the largely reduced trap states in PbAc-PbS QD based devices.^[33] Meanwhile, we are aware of that the photoluminescence properties of the PbS QDs are also indications of the amount of trap states.^[26] Therefore we measured the PL emission spectra of the two PbS QD films after solid-state ligand exchange with the same processing in solar cell fabrication. As shown in Figure 2d, compared with the same absorption peak of TBAI or EDT exchanged PbO-PbS and PbAc-PbS QDs (Figure S6, Supporting Information), the PL peak position of TBAI-treated PbAc-PbS QD films (1014 nm) reveals a smaller Stokes shift than that of the PbO-PbS QD films (1028 nm), which is likely an indication of reduced bandtailing in the PbAc-PbS QDs compared to PbO-PbS QDs.^[34] Additionally, the PL intensity of PbAc-PbS QD film is about two times higher than that of PbO-PbS QD film. Furthermore, PbAc-PbS-TBAI film shows a significantly longer PL decay lifetime (800 ps) than that of PbO-PbS-TBAI film (696 ps) in 2D transient photoluminescence spectra (Figure 2e,f), further suggesting the reduction of sub-bandgap trap states.^[35] This observation is in good agreement with both the reduced diode ideality factor and longer voltage decay time in PbAc-PbS QD based devices. Furthermore, the trap density of TBAI exchanged PbO-PbS and PbAc-PbS QD films are measured by the space charge limited current (SCLC) method (see the Experimental Section).^[36] The trap density is 1.2×10^{17} and $7.5 \times 10^{16}\text{ cm}^{-3}$ for PbO-PbS QD film and PbAc-PbS QD film, respectively, which confirms the reduction of trap states in PbAc-PbS QDs. Moreover, diffusion length can be calculated from mobility and carrier lifetime. For PbAc-PbS QD films, the diffusion length is calculated to be 95.1 nm, while the diffusion length of PbO-PbS QD films is 61.3 nm, which is consistent with previously reported results.^[37]

The device stability is often used to evaluate the surface passivation of used QDs. Therefore, the air stability and photostability of both PbO-PbS and PbAc-PbS QDs based solar

cells were measured. After stored in ambient atmosphere for 360 h, PbAc-PbS QDs based devices showed very stable photovoltaic performance, while PbO-PbS QDs based devices only maintained $\approx 85\%$ of the original efficiency (Figure S7, Supporting Information). Furthermore, after 60 h continuous illumination by light emitting diode lamp in nitrogen atmosphere, PbO-PbS QD devices showed a fast degradation of efficiency, mainly resulting from the reduction of fill factor (Figure S8, Supporting Information). However, solar cells based on PbAc-PbS QDs almost retained the original efficiency, which indicated reduced trap states in PbAc-PbS QDs based devices.

Once we confirmed that the improved device performance stems from the reduced trap states for the PbAc-PbS QDs, further investigations were carried out to understand the process of trap passivation during the initial synthesis. Since the synthesis conditions are the same for both QDs except the lead source, we speculate the origin of the reduced sub-bandgap states is due to the alteration of lead source. First of all, in order to illustrate if the hydrate water in $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ has effects on the device performance, we synthesized PbS QDs using anhydrous lead acetate and achieved QDs with almost identical size, bandgap, and crystal structure compared to PbAc-PbS QDs. We then fabricated photovoltaic devices employing these QDs and obtained almost the same device parameters as those of PbAc-PbS QDs based ones (Figure S9, Supporting Information). Therefore, we can exclude the effect of hydrate water in the lead source. Next, we should consider the effect of acetate on the PbS surface, which always plays a crucial role in the performance of PbS QD solar cells.^[22,38] As acetate has capacity to exchange the original oleic acid on PbS QDs,^[39] we want to make sure the acetate from $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ will attach on the surface of PbS QDs during synthesis. ^1H NMR was performed on PbO-PbS QDs and PbAc-PbS QDs under the same condition. The nearly same ratio (16.1:1) of hydrogen atoms in saturated/unsaturated hydrocarbon suggests no acetate on the surface or the amount is too little to be detected by NMR (Figure S10, Supporting Information). Due to the small amount of acetate and its similar characteristic structure with oleate, it is extremely challenging to determine whether the acetate groups attach to PbS surface by using conventional technology. We then turned to substitute lead acetate with difluoroacetate lead (DFAcPb) to synthesize PbS QDs. Briefly, DFacPb was synthesized by adding lead oxide into difluoroacetate acid aqueous solution at 50°C under ambient atmosphere. After stirred for 2 h, the solution was vacuumed for 12 h at room temperature. White crystalline difluoroacetate lead trihydrate (DFAcPb) powder can be acquired. The DFacPb powder was then dissolved in OA and ODE for the synthesis of DFac-PbS QDs (scheme shown in Figure S11, Supporting Information). In this case, we could easily track the acetate by detecting the signal of fluorine using sensitive X-ray photoelectron spectroscopy. Prior to the measurement of XPS, photovoltaic devices based on DFacPb-PbS QDs were fabricated. Current-voltage characteristics (Figure S12, Supporting Information) show close photovoltaic parameters compared with PbAc-PbS QD based devices. The XPS spectra for as-synthesized, TBAI and EDT-treated DFacPb-PbS QDs are shown in Figure 3a. The F 1s peak centering at 688 eV confirms the existence of fluorine, which providing direct evidence for the covering of acetate ligands on

Figure 3. XPS spectra of PbO-PbS and PbAc-PbS QDs. a) F 1s spectra of as-synthesized, TBAI and EDT-treated PbS QDs synthesized from DFac-Pb. b) I 3d spectra of TBAI-treated PbO-PbS and PbAc-PbS QD films. The total peak areas of I 3d 5/2 are normalized to the Pb peak area of the corresponding sample. c) I/Pb ratio of TBAI-treated PbO-PbS and PbAc-PbS QD films. The O 1s spectra of PbO-PbS and PbAc-PbS QDs treated with d) TBAI and e) EDT. The total peak areas of O 1s spectra in (d) and (e) are normalized to the Pb peak area of the corresponding sample. For clarity of presentation and ease of comparison, the signal peaks are further normalized to the unity by the Pb–OH component in TBAI or EDT-treated PbO-PbS QDs.

the surface of as-synthesized PbS QDs. The amount of acetate ligands can be estimated from F 1s XPS spectrum, which is 19.1% compared to Pb. After PbS QDs are treated with TBAI or EDT, no apparent peak from F 1s can be detected in the XPS spectra. The results suggest that the acetate generated from the lead precursor can attach to the surface of resultant PbS QDs, while these acetate ligands can be further ligand exchanged by TBAI or EDT. To understand its profound impact on the surface chemistry of the synthesized PbS QDs in the subsequent device fabrication processing, we further characterized TBAI and EDT-treated PbS QDs with XPS. The narrow-scan I 3d spectra in Figure 3b indicate a higher iodide ions incorporation in the PbAc-PbS-TBAI QDs than in PbO based counterparts, as confirmed by the I/Pb ratio (0.74 vs 0.55) shown in Figure 3c. This difference of I/Pb ratio is very consistent with the acetate ligands on PbAc-PbS QDs. In addition, note that the high I/Pb ratio of 0.74 was almost the same as that of the optimal PbS QDs previously reported by the solution phase ligand exchange method.^[16] The evidence regarding the hydroxyl (OH) groups bound to the (111) facet of the rock-salt-structured PbS QDs is given by the O 1s spectra (Figure 3d,e). OH groups are considered as one of the sources causing sub-bandgap trap-states.^[22] The O 1s peaks can be deconvoluted into three species, which originate from Pb–OH (531.0 eV), Pb–O (529.5 eV), and C–O

(532.4 eV).^[21,22] The parameters of the deconvoluted peaks are summarized in Tables S1 and S2 in the Supporting Information. We can observe that the PbAc-PbS QDs (treated by TBAI or EDT) present much lower intensity of Pb–OH species peaks than PbO-PbS QDs, indicating better passivation, which is consistent with the aforementioned higher I/Pb ratio. Meanwhile, the OH groups on the (111) facet of PbS QDs is substantially suppressed in the PbAc-PbS QDs compared to that in PbO-PbS QDs, suggesting the effect of acetate and the reduction of sub-bandgap trap states. The C–O peak can be attributed to the residual OA after ligand exchange.^[22] Furthermore, in order to confirm the reduced OH ligands on as-synthesized PbAc-PbS QDs, we measured the O 1s XPS of oleic acid capped PbO-PbS QDs and PbAc-PbS QDs. As shown in Figure S13 in the Supporting Information, the Pb–OH peak in PbAc-PbS-OA sample shows a much lower intensity than PbO-PbS-OA, which is consistent with the corresponding Pb–OH peak intensity of the ligand exchanged QDs, confirming the reduction of OH capping ligands during the synthesis process. In order to confirm the defect reduction in as-synthesized PbAc-QDs, we also measured the photoluminescence quantum yield (PLQY) and time resolved PL decay (TRPL) of OA capped PbO-PbS and PbAc-PbS QDs (Figure S14, Supporting Information). The PLQY of PbS QDs synthesized from PbO is 10.05% in solution, while

the solution of PbAc-PbS QDs shows a higher PLQY (15.08%), which indicates the reduction of trap states in as-synthesized PbAc-PbS QDs. Furthermore, the solution of PbAc-PbS QDs shows a longer PL lifetime than that of PbO-PbS QDs (3.15 vs 2.32 μ s), which further confirms the defect reduction.

Based on the above results, we can conclude that the surface chemistry of the two PbS QDs is significantly different as a result of the lead precursor engineering. The evolution of the capping ligands on the (111) facet can be schematically described in **Figure 4**. During the synthesis procedure, OA, acetate, and OH in the solution are competing capping ligands. Without acetate, the PbS surface is covered by both OA and OH ligands. The latter cannot be ligand exchanged by iodide or EDT and will cause sub-bandgap trap states, resulting in lower device performance.^[22] By using PbAc₂·3H₂O as the lead source, acetate can play a role in the capping ligands. Since acetate has a smaller steric hindrance and higher binding energy to Pb than OA,^[40] it can help to better cover the surface of PbS QDs to avoid oxidation and replace some of the OH ligands during the synthesis. In the following ligand-exchange stage, the acetate on the surface will be exchanged by TBAI or EDT and lead to desired passivation, while the OH ligands remain on the QD surface, resulting in undesired sub-bandgap trap states, low FF and V_{oc} .

In summary, we have successfully synthesized PbS QDs with identical size using PbO or PbAc₂·3H₂O as the lead sources. The QD solar cells based on PbAc-PbS have demonstrated a high PCE of 10.82%, which is significantly higher than the PCE of 9.39% for PbO-PbS QDs based ones. For the first time, we carried out systematical investigations on the effect of lead

precursor engineering on the device performance. We revealed that by using PbAc₂·3H₂O as the lead source, acetate can act as an efficient capping ligands together with oleic acid, providing better surface coverage and replace some of the harmful OH ligands during the synthesis. In the following ligand-exchange stage, the acetate on the surface can be exchanged by iodide and lead to desired passivation. Meanwhile, the trap-states caused by the OH ligands will be largely reduced. Our work demonstrated that the precursor engineering has great potential in performance improvement. We also pointed out that the initial synthesis is an often neglected but critical stage and has abundant room for optimization to further improve the quality of the resultant QDs, leading to breakthrough efficiency.

Experimental Section

Synthesis of PbS QDs: The oleate-capped PbS QDs were synthesized via a rapid hot injection method by following a reported procedure.^[25] Briefly, 10 mmol of lead oxide or lead acetate trihydrate and 7 g of OA were dissolved in 60 g of ODE in a three-neck flask by heating the mixture to 100 °C under vacuum for 2 h. The sulfide precursor was prepared separately by mixing 1 mL of hexamethyldisilathiane and 9 mL of 1-octadecene. The reaction was initiated by rapid injection of the sulfide precursor into the lead precursor solution. After synthesis, the solution was transferred into a nitrogen-filled glovebox. QDs were purified by adding isopropanol, followed by centrifugation. The extracted QDs were redispersed in hexane and acetone was added to precipitate QDs, followed by centrifugation. Then the QDs were stored in the glovebox. For device fabrication, PbS QDs were redispersed in hexane (40 mg mL⁻¹).

Synthesis of DFAC-PbS QDs: Lead oxide (1 mmol) was added into 20 mL difluoroacetate acid aqueous solution (0.1 M) at 50 °C under ambient atmosphere. After stirred for 2 h, the solution was vacuumed for 12 h at room temperature. White crystalline difluoroacetate lead trihydrate (DFACPb) powder can be acquired. The DFACPb powder was then dissolved in 0.7 g OA and 6 g ODE for the synthesis of DFAC-PbS QDs, which is same as that of PbAc-PbS QDs described above.

Synthesis of ZnO Nanoparticles: ZnO nanoparticles were synthesized according to the literature with some modification.^[41] Zinc acetate dehydrate (2.95 g) was dissolved in 125 mL of methanol at 60 °C. Potassium hydroxide (1.48 g) was dissolved in 65 mL of methanol. The potassium hydroxide solution was slowly added to the zinc acetate solution and the solution was kept stirring at 63 °C for 3 h. ZnO nanocrystals were extracted by centrifugation and then washed twice by methanol followed by centrifugation. Finally, 10 mL of chloroform and 10 mL of methanol were added to the precipitates and the solution was filtered with a 0.45 μ m filter.

Device Fabrication and Testing: The ITO substrates were ultrasonically cleaned with solvents and then treated with oxygen plasma. The ZnO layer was fabricated by spin-coating the nanoparticle solution onto the ITO substrate. The PbS QDs layer was fabricated by layer-by-layer spin-coating methods in ambient air. For PbS-TBAI layers, $\approx 30 \mu$ L of PbS QD solution (40 mg mL⁻¹) was spin-cast onto the substrate at 2500 rpm for 20 s. A TBAI solution (10 mg mL⁻¹ in methanol) was then applied to the substrate for 30 s, followed by two rinse-spin steps with acetonitrile. For PbS-EDT layers, PbS QD solution (20 mg mL⁻¹) was spin coated, followed by an EDT solution (0.04 vol% in acetonitrile) and acetonitrile rinsing twice. The films were stored in air overnight and then transferred to a nitrogen-filled glovebox for electrode evaporation. Au electrodes (100 nm thick) were thermally evaporated onto the films through shadow masks at a base pressure of 10^{-6} mbar. The nominal device areas are defined by the overlap of the anode and cathode to be 0.0725 cm².

Measurement and Characterization: Current-voltage characteristics were recorded using a Keithley 2400 (I-V) digital source meter under a simulated AM 1.5G solar irradiation at 100 mW cm⁻² (Newport, Class AAA solar simulator, 94023A-U). The light intensity is calibrated by a certified

Figure 4. Schematic pictures of the (111) facet of as-synthesized, TBAI and EDT-treated PbS QDs synthesized from PbO and PbAc₂·3H₂O. During synthesis process, acetate ligands can partially substitute hydroxyl groups and then be ligand exchanged during TBAI or EDT treatment.

Oriel Reference Cell (91150V) and verified with an National Renewable Energy Laboratory calibrated Hamamatsu S1787-04 diode. The device cross-sectional image was characterized by SEM on a Zeiss Supra 55 field in high vacuum mode at 10 kV accelerating voltages. UV–vis–NIR spectra were recorded on a Perkin Elmer model Lambda 750. Photoluminescence measurements were performed on samples prepared on quartz substrates by spin-coating five layers of TBAI-treated PbS QDs or ten layers of EDT-treated PbS QDs. The second harmonic (400 nm) of a Ti:sapphire laser (Coherent, Mira 900, repetition rate 76 MHz) was used to excite the samples. The optical emission was recorded by a cooled array detector (Andor, iDus 1.7 μm). Time-resolved PL spectra were detected using a Hamamatsu streak camera with a cathode sensitive to near-IR radiation. The samples are prepared using the same method as the sample for steady state photoluminescence measurement. The samples were encapsulated in N_2 atmosphere to prevent photodegradation during the experiment. Regarding the transient electric output characteristic setup, the devices were connected to a digital oscilloscope with an input impedance of 1 M Ω . The intensity of white light, which is referred to henceforth as a “light bias,” was used to control the open-circuit voltage (V_{oc}) of the devices. A laser with a wavelength of 532 nm was used as optical perturbation, pulse duration was set to 1 μs and frequency to 100 Hz, which resulted in a voltage transient with a peak of 5 mV (V_{oc}). The frequency, light intensity, and pulse duration were kept constant. The oleic acid capped PbS QDs samples for XPS test were made by spin-coating low concentration PbS QDs onto glass/ITO substrate, in order to obtain a sub-monolayer film. After spin coating, the PbS QD films are washed with acetone to remove the unbound oleic acid ligands. The TBAI or EDT-treated sample was fabricated by spin coating 50–100 nm thick film on glass/ITO substrate. Electron only devices were fabricated using device structure Ag/PbS-TBAI/Ag for the measurement of trap density and diffusion length. J – V curves of devices exhibiting SCLC in the presence of traps show three characteristic regions.^[36] At low bias, thermally generated charges outnumber the injected charge carriers, and the device follows Ohm’s law ($J \propto V$). At a certain voltage V_{TFL} , the injected charges exceed the thermally generated charges and injected charges fill the trap states leading to trap-filling SCLC behaviors. The onset voltage V_{TFL} is linearly proportional to the density of trap states N_{traps}

$$V_{\text{TFL}} = \frac{eN_{\text{traps}}d^2}{2\epsilon\epsilon_0} \quad (1)$$

where ϵ_0 is the vacuum permittivity, ϵ is the material’s dielectric constant—here for PbS-TBAI, $\epsilon = 18.7$ is used.^[36] d is the thickness of exchanged PbS QD films, while e is the elementary charge. In Figure S15 in the Supporting Information, the V_{TFL} for PbO-PbS-TBAI and PbAc-PbS-TBAI are 2.31 and 1.45 V, respectively. Therefore, with a thickness of 200 nm, the trap density of PbO-PbS QD film is $1.2 \times 10^{17} \text{ cm}^{-3}$, while for PbAc-PbS QD film, it is $7.5 \times 10^{16} \text{ cm}^{-3}$, which confirms the reduction of trap states in PbAc-PbS QDs. Furthermore, mobility was calculated from the SCLC regime. For TBAI exchanged PbAc-PbS QD films, mobility is $5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while mobility of PbO-PbS QD films is $3.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Based on the mobility and carrier lifetime obtained above, diffusion length can be calculated according to the formula

$$L_D = \sqrt{\frac{k_B T}{e}} \mu \tau \quad (2)$$

where k_B is Boltzmann constant, T is temperature in Kelvin, e is elementary charge, μ is electron mobility, and τ is carrier lifetime.^[36] For PbAc-PbS QD films, the diffusion length is 95.1 nm, while the diffusion length of PbO-PbS QD films is 61.3 nm, indicating a reduction of trap states and improved surface passivation of PbAc-PbS QDs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

lead sources, PbS quantum dots, solar cells, surface passivation

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