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Stable PbS quantum dot ink for efficient solar cells by solution-phase ligand engineering†

Mengfan Gu, Yongjie Wang, Fan Yang, Kunyuan Lu, Ye Xue, Tian Wu, Honghua Fang, Sijie Zhou, Yannan Zhang, Xufeng Ling, Yalong Xu, Fangchao Li, Jianyu Yuan, Maria Antonietta Loi, Zeke Liu, and Wanli Ma

Surface passivation is essential to realize high photovoltaic performance for solar cells based on PbS quantum dots (QDs). The recently developed solution-phase ligand-exchange strategy can greatly simplify the device fabrication process compared with the traditional layer by layer method. However, the surface hydroxy ligand (OH) on the PbS QD surface, a main source of trap states, cannot be avoided in the solution-phase ligand-exchange process and has not been paid attention yet. Meanwhile, the unsatisfactory colloidal stability of current PbS QD ink is also a barrier for its industrial application and waiting for solutions. Here, we demonstrate a multiple-passivation strategy by solution-phase ligand engineering in lead halide exchanged QD ink. It was found that our facile approach can efficiently reduce the trap states of PbS QD ink by suppressing the amount of surface hydroxyl groups. Moreover, ligand engineering can also increase the interaction between QDs and solvent, which endows the QD ink with remarkably improved colloidal stability. As a result, a significant improvement of PCE from 9.99% to 11.18% and device stability were realized. Our results present a new passivation method for solution-phase ligand exchanged QD ink and the improved colloidal stability may help to boost the industrial application of PbS QD based solar cells.

1. Introduction

In the past decade, lead chalcogenide (PbX) colloidal quantum dots (QDs) have attracted substantial attention as promising photovoltaic materials for solar cells due to their tunable bandgap, low-cost solution processing, and capacity for multiple exciton generation. In addition, the infrared-harvesting capability makes PbX QDs good candidates for back cells to construct tandem solar cells. With the advances of QD surface passivation and device architecture optimization, rapid progress has been made in improving solar cell efficiency and stability simultaneously. Recently, the certified record power conversion efficiency (PCE) of PbS QD solar cells has reached 12.0%. Generally, the large surface trap density in PbS QD films gives rise to a major open-circuit voltage (Voc) deficit, which is one of the key factors limiting PbX QD solar cell performance. And the voltage loss in PbX QD solar cells is significantly inferior compared with most of the other widely studied high-efficiency photovoltaic materials. Even numerous strategies have been applied to increase passivation in traditional solid-state ligand-exchange methods. These methods, using short ligands to replace the initial long insulating ligands to increase the conductivity of QD films, are inevitably accompanied by inconsistent ligand exchange and nanocrystal fusion due to surface stripping in the repeated cycles (around 10 times). These issues have been well overcome by developing a solution-phase ligand-exchange method, which boosts the PCE of PbS QD solar cells to new heights. In the past few years, the existence of hydroxyl (OH) groups on PbS (111) facets has been revealed in the standard synthesis procedure (lead oxide as the precursor, and oleic acid as the ligand) which can help to stabilize the (111) face during synthesis, but will work as detrimental trap states for photovoltaic devices. Although some synthetic protocols of PbS QDs (lead chloride as the precursor, and oleylamine as the ligand) can avoid OH groups, their bandgap is too small to realize high photovoltaic device performance. Thus several methods have been developed to reduce OH groups in PbS QD solar cells based on solid-state ligand exchange. However, little attention has been paid to optimizing surface passivation during the solution-phase ligand-exchange process.

Solution-phase ligand exchange has the potential to simplify the production processes and lower the fabrication cost.
compared to the traditional layer-by-layer method. After substituting the original ligand (oleic acid) with halometallates in solution, the mechanism of colloidal stabilization has switched from steric to electrostatic stabilization. However, it remains a challenge to realize good colloidal stability for different solution-exchanged QD systems. The colloidal stability for the current PbS QD ink is still not satisfactory, which makes it difficult for relatively long-time storage and impeded its potential for practical implementation.

Here, we demonstrated a multiple-passivation strategy for solution-exchanged PbS QD ink, which was found to efficiently decrease the amount of OH groups on the PbS QD surface. Both optical and electrical characterization techniques proved that the QDs were well passivated with fewer trap states after reducing the OH groups. Moreover, the colloidal stability of QD ink was also significantly improved due to the interaction between mercaptopropionic acid (MPA) and the solvent (butylamine, BA), which resulted in PbS QD ink with significantly improved storage stability for around two months. In addition, PbS QD solar cells with a high PCE of 11.18% (vs. control PCE of 9.99%) and enhanced stability were obtained due to the reduced QD surface trap states.

2. Results and discussion

The engineering of conventional PbS QD ink with MPA is based on two expectations: (1) MPA with two functional groups (thiol and carboxylate) possesses large potential to passivate more types of surface states. (2) The acidic carboxyl group would have strong interaction with the amine group of the solvent (BA), which can lead to improved colloidal stability of PbS QD ink. The processing was implemented under ambient conditions by modifying the previously reported solution-phase ligand-exchange method. Briefly, lead iodide (PbI₂) and ammonium acetate (NH₄Ac) in DMF were used to replace the long chain ligand (oleic acid) on PbS QDs. After purification and drying, the lead iodide-passivated PbS QDs were then dispersed in BA to prepare PbS QD ink. Then a certain amount of MPA was added to the final PbS QD ink to tailor the surface of QDs (these MPA processed PbS QD inks and films are thus subsequently referred to as MPA-treated). Devices were then fabricated using the architecture (ITO/ZnO/PbS-lead halide/PbS-EDT (1,2-ethanediol)/Au), with the device schematic diagram and cross-sectional scanning electron microscopy (SEM) image shown in Fig. 1a and b. For the MPA engineered devices, the solution was stirred for 5 min at room temperature before spin-coating to ensure sufficient reaction between PbS QDs and MPA. The MPA concentration and film thickness were carefully optimized (Fig. S1 and S2†). It was shown that 0.7% (v/v) MPA in BA and 400 nm film thickness for the lead halide-exchanged PbS QD layer gave the best device performance. Current-voltage (J–V) characteristics of the optimized device together with the control device under simulated AM 1.5G illumination are shown in Fig. 1c. The best power conversion efficiency (PCE) of the MPA-treated device reaches 11.18%. In contrast, the control device without MPA only shows a highest PCE of 9.99%. To ensure the reproducibility of the results, 36 independent devices using different batches of QD materials were fabricated and tested. Histograms of the device-performance characteristics are shown in Fig. 1d, and the average and best device photovoltaic parameters are summarized in Table 1. All MPA-treated devices show superior performance compared to the control devices. We have to point out that the PCE of our control device is lower compared to the record device using almost the same processing conditions. However, it’s comparable to the PCE of the control device in other reports. The difference in the device efficiency may be caused by the different lab atmospheres and experimental skills. We noticed that the improvement mainly stems from the increase of open-circuit voltage (VOC) and fill factor (FF), while the short-circuit current density (JSC) almost remains identical, which can be confirmed from the EQE spectra of the devices (Fig. S3†). The calculated JSC values from the EQE spectra of the control and MPA-treated QD devices are 28.2 mA cm⁻² and 28.0 mA cm⁻² respectively, showing good agreement with the results directly measured from J–V curves. The improved VOC and FF indicate that the incorporation of MPA might help to decrease the trap density and then lead to reduced charge recombination and improved PCE.

To confirm the role of MPA in our strategy, X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) were performed to identify the surface chemistry after incorporating MPA. As shown in the high-resolution XPS core spectra of S 2p (Fig. 2a), the peaks at around 161.6 eV/162.2 eV and 163.1 eV/164.3 eV can be assigned to the bonded thiolates and free thiols with atomic ratios of 0.11 and 0.07 to Pb respectively (Table S1†), indicating that some of the thiol groups are chemically bonded to the PbS QD surface. Furthermore, the stronger peak at 532.8 eV and a new peak at 533.8 eV in high-resolution O 1s spectra (Fig. 2b) can be assigned to bonded (−COO⁻, CO₂) and free carboxyl (−COOH) respectively, indicating that some carboxylate groups from MPA are bound to the QD surface as well. This was further confirmed by FTIR testing. As shown in Fig. 2c, the peaks at ~1400 and ~1550 cm⁻¹, corresponding to the symmetric and antisymmetric carboxylate (COO⁻) stretching modes, appear after adding MPA to the PbS QD ink. Collectively, FTIR and XPS results show that both thiols and carboxyl moieties from MPA are bonded to the PbS QD surface. Moreover, the I/Pb ratio remains almost identical for MPA-treated and control films (Fig. S4 and Table S1†), which indicates that some other surface species are replaced by MPA. In O 1s spectra, the peak located at 531.7 eV shows only about one fifth intensity in the MPA treated film compared to the control sample (Fig. 2b and Table S1†). This peak has been assigned to OH groups on the PbS surface (Pb–OH) according to several reports, indicating that the amount of Pb–OH drops dramatically after MPA treatment. And it was found that the decreased amount of Pb–OH is roughly equal to the sum of bonded thiolate and carboxyl (Table S1†). It’s reasonable to conclude both thiol and carboxyl groups on MPA can efficiently replace OH on the PbS QD surface. Given that Pb–OH has been considered as one of the main sources causing sub-bandgap trap-states in PbS QDs, the suppression of Pb–OH by MPA
ligands can effectively reduce charge recombination and improve the device photovoltaic performance.

To investigate the effect of ligand engineering during solution-phase exchange, we investigated the optical properties of modified PbS QD inks. As shown by UV-vis absorption spectroscopy (Fig. 3a), the films show an almost identical exciton peak location. However, a narrower peak with a smaller full-width at half-maximum (FWHM) of 229 meV is observed for the MPA-treated film, compared to 241 meV for the control film. The small-angle X-ray scattering (SAXS) results show almost identical packing density and homogeneity of the QD film assembly (Fig. S5†). Then the narrower absorption peak can be attributed to reduced bandtails and then improved energetic homogeneity, which is favorable for photovoltaic performance.\(^9,19,27,31\) Moreover, the MPA-treated film displays a smaller Stokes shift (201 meV) than that of the control QD film (275 meV), which is likely an indication of a reduced band tail in the MPA-treated ink compared to control QDs.\(^32,37\)

The solution PL decay lifetime (Fig. 3c) of MPA-treated ink (39.0 ns) is also about two times longer than that of control ink (21.6 ns). Furthermore, the MPA-treated film shows a longer PL decay lifetime (1.68 ns) than that of the control film (0.75 ns) in 2D transient photoluminescence spectra (Fig. 3d), which suggests that the incorporation of MPA indeed suppresses sub-bandgap trap states.\(^38\)

To gain a deeper understanding of the improvement of photovoltaic properties, several electrical characterization

Table 1  Photovoltaic parameters of the control and MPA-treated devices. Statistics is based on 36 different devices

<table>
<thead>
<tr>
<th></th>
<th>(V_{oc} (V))</th>
<th>(J_{sc} (mA cm^{-2}))</th>
<th>FF(^a) (%)</th>
<th>PCE(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.554 ± 0.015</td>
<td>27.40 ± 0.52</td>
<td>62.60 ± 1.10</td>
<td>9.52 ± 0.27</td>
</tr>
<tr>
<td>Champion device</td>
<td>0.57</td>
<td>27.55</td>
<td>63.62</td>
<td>9.99</td>
</tr>
<tr>
<td>MPA-treated</td>
<td>0.593 ± 0.009</td>
<td>27.34 ± 0.51</td>
<td>64.90 ± 0.77</td>
<td>10.52 ± 0.23</td>
</tr>
<tr>
<td>Champion device</td>
<td>0.61</td>
<td>27.42</td>
<td>66.82</td>
<td>11.18</td>
</tr>
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\(^a\) Fill factor (FF). \(^b\) Power conversion efficiency (PCE).
techniques were performed. First, the light-intensity dependent \( J_{sc} \) and \( V_{oc} \) were studied to probe the charge recombination mechanism.\(^{39}\) The power law dependence of \( J_{sc} \) on the illumination intensity can be generally expressed as: \( J_{sc} \propto I^{\alpha} \), where \( I \) is the light intensity and \( \alpha \) is the exponential factor. The \( \alpha \) values of the control and MPA-treated devices are 1.00 and 0.99 (Fig. S6†) respectively. This result indicates that both devices have very little bimolecular recombination under the short-circuit conditions. The light intensity dependence of \( V_{oc} \) was also studied using the following relation:

\[
V_{oc} = \frac{n kT}{q} \ln(I) + C,
\]

where \( n \) is the diode ideality factor, \( k \) the Boltzmann constant, \( T \) the temperature in Kelvin, \( q \) the elementary charge, and \( C \) a fitting parameter collecting all the terms independent of light intensity. The slope of the plot for the MPA-treated devices is much lower (1.07\( kT/q \)) than that of the control QD devices (1.43\( kT/q \)), indicative of greatly reduced trap-assisted recombination (Fig. 4a), which should contribute to the improved \( V_{oc} \) and FF.\(^{40} \)

Transient photovoltage decay was also measured to uncover how MPA passivation modifies the carrier dynamics along the entire pathway in a complete cell.\(^{41} \) As shown in Fig. 4b, the decay times (\( \tau \)) are fitted and calculated to be 38.2 \( \mu \)s and 82.7 \( \mu \)s for the control and MPA-treated devices, respectively, which suggests an apparent decrease of charge-carrier recombination via MPA passivation.\(^{42} \) This result is also consistent with the decrease of diode ideality factor and longer PL decay lifetime. To quantify the trap-state density after MPA treatment, space charge limited current (SCLC) techniques were performed.
were performed by fabricating electron-only devices (ITO/ZnO/PbS-lead halide/ZnO/Au). The electron trap-state densities (Ntrap) were calculated from the logarithm of the J–V curve obtained in the dark. As shown in Fig. 4c, the current increases linearly as a function of voltage when the voltage is lower than the kink-point, which indicates ohmic conduction (n = 1). On further increasing the voltage beyond the kink-point, the current exhibits a rapid nonlinear rise (n > 3), which indicates that the trap states are fully filled by the injected carriers. The applied voltage at the kink point is known as the trap-filled limit voltage (VtrfL), which can be used to determine the trap density as follows: Ntrap = VtrfL (2εr/ε0)d where d is the film thickness, and ε and ε0 represent the elementary charge and vacuum permittivity respectively.41 The relative dielectric constant ε of PbS QDs is ≈18.7.44 After fitting and calculating, the corresponding trap density is 1.04 × 1016 cm−3 for the control films and 7.70 × 1015 cm−3 for the MPA-treated films. Meanwhile, the mobility extracted from SCLC reveals that the mobility of the PbS film is also improved by adding MPA (from 2.53 × 10−4 cm2 V−1 s−1 to 3.79 × 10−4 cm2 V−1 s−1, Fig. S7†). Collectively, both optical and electrical characterization techniques confirmed the reduction of trap states in the presence of MPA, resulting in enhanced photovoltaic performance. According to the above results, it can be concluded that lead halide cannot remove the hydroxyl group during the solution-state ligand-exchange process, whereas these hydroxyl groups can be efficiently replaced by thiols and carboxyl moieties from MPA, resulting in fewer trap states and improved photovoltaic device performance.

Ultraviolet photoelectron spectroscopy (UPS) was also applied to get insight into the effect of MPA on the energy levels of PbS QDs. As shown in Fig. 4d and e, the valence-band maximum (VBM) level does not substantially change upon MPA introduction, whereas the Fermi level (Ef) has moved from about −4.77 eV with respect to vacuum for the control film to −4.49 eV for the MPA-treated film, indicating more n-type behavior for MPA introduction. This is reasonable if we consider two aspects: (1) lead halogen, as the main surface ligand, will give n-type features.21 (2) The OH exchanged PbS QD film shows stronger p-type doping than the MPA doped one,43 which has been used to achieve a heavy p-type layer for p–n junction PbS QD solar cells.46,47 So it will show more n-type characteristic after replacing OH with milder p-type ligand MPA. We speculate that this can contribute to the Voc enhancement, which is confirmed by the increased built-in potential (Vbi) (Fig. S8†). The doping density of MPA-treated films, extracted from Mott–Schottky capacitance-voltage characterization (Fig. 4f), is more than twice higher in comparison to the control films (4.13 × 1017 cm−3 vs. 2.01 × 1017 cm−3), which also corresponds to the more n-type character after introducing MPA.

In addition to surface passivation, the colloidal stability also generates a significant effect on the corresponding device performance. As shown in Fig. S9,† the QD inks with different storage time were used to fabricate photovoltaic devices. The PCES of the device with control ink dropped to less than 70% after one day storage and 40% after two day storage compared to the device using fresh QD ink. Considering the unsatisfactory colloidal stability, the QD ink cannot sustain long time storage and transportation, which will be imperative for industrial application. It was observed that the colloidal stability of PbS QD ink was largely improved after the incorporation of MPA (Fig. 5a). The control PbS QD ink shows aggregation in BA within one day and almost all QDs precipitate after 15 days. In contrast, the MPA-treated ink still keeps stable for at least 50 days (Fig. S10a†). Meanwhile, we found that our MPA-treated

**Fig. 4** (a) Light intensity dependence of Voc (solid lines: logarithmic fits) of control and MPA-treated QD devices. (b) Voc decay of the corresponding solar cells as a function of time. (c) Logarithm of the J–V curve in the dark (a linear ohmic regime (n = 1) is followed by the trap-filled regime (n > 3)). At high voltages, the J–V curves show a trap-filled Child’s regime (n = 2)). (d) UPS spectra in the secondary cutoff region (left panel) and valence band region (right panel) for control and MPA-treated QDs. (e) Schematic band alignment diagram of control and MPA-treated QD regime (e1 and e2). (f) Mott–Schottky plots.
ink also shows better colloidal stability compared to the hybridamine method reported very recently, which was also able to increase colloidal stability (Fig. S10f). This can be rationalized by considering the strong interaction between free carboxyls with BA as schematically illustrated in Fig. 5b and c. As proven by 1H NMR spectroscopy, the hydrogen peaks from carboxyl disappear after mixing with BA (Fig. S11†). Benefiting from the improved colloidal stability, the PCEs of the device from MPA-treated ink can retain around 90% after one day storage and 80% after two day storage, which will largely facilitate practical manufacturing and transport of PbS QD ink. Meanwhile, this strong interaction between MPA and BA also increases the dispersibility of PbS QDs, which results in a smoother film with fewer pinholes, as shown in the scanning electron microscopy (SEM) images (Fig. S12†). The 3D topographic atomic force microscopy (AFM) analysis (Fig. S13†) gives a quantitative comparison. The MPA-treated film has a surface roughness (RMS) of 1.7 nm, which is less than half of the control film (3.5 nm). We believe that the better film quality may also contribute to the improved device performance and repeatability.

Finally, the air-stability of solar cells based on both control and MPA-treated inks was also tested, which is often used to evaluate the surface passivation of QDs. As shown in Fig. 6, after storage in an ambient atmosphere for 50 days, the devices based on MPA-treated ink retain around 93% of their initial PCE, while control devices only maintained around 80% of the original efficiency. The enhanced air-stability also confirmed the better surface conditions improved by MPA passivation.

3. Experimental

3.1. Synthesis of PbS QD inks

The olate-capped PbS QDs were synthesized via a modified procedure from a previous report. The solution-phase ligand-exchange process was conducted under ambient conditions in accordance with the literature procedure. It contains three steps: (1) ligand exchange: lead iodide (0.1 M) and NH₄Ac (0.04 M) are pre-dissolved in dimethylformamide (DMF). 5 mL PbS-OA QD hexane solution (~8 mg mL⁻¹) was added to 5 mL of precursor solution. The solution was mixed vigorously for 2–3 min until the QDs completely transferred to the DMF phase. (2) Puriﬁcation of the exchanged QDs: after ligand exchange, the DMF solution was ﬁrst washed four times with hexane and then precipitated via adding toluene (~50–60% in a volume ratio compared with DMF). After being separated through centrifugation, the PbS QDs were dried under vacuum for 30 min to yield QD powder. (3) Preparation of QD ink solution: the dried PbS QDs were then re-dispersed in butylamine with different ratios of MPA (0.7 vol%, 0.0804 mM as an example) to prepare concentrated PbS QD ink (200–400 mg mL⁻¹). During this process, lead iodide works as a new ligand to replace the...
original oleic acid and provides surface passivation. The addition of MPA in the last step can efficiently replace OH groups with its thiols and carboxyl moieties, providing additional surface passivation and improving ink colloidal stability.

3.2. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized according to the literature with some modification.7 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 left stirring at 63 °C for 3 h. ZnO nanocrystals were extracted by centrifugation and then washed twice with 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 μm filter.

3.3. Device fabrication

The ITO-coated glass substrate was ultrasonically cleaned with solvents and then treated with oxygen plasma. One layer of ZnO (80–100 nm) was fabricated by spin-coating a solution of ZnO nanoparticles (about 80 mg mL−1) onto ITO at 2500 revolutions per minute (rpm). QD ink-based active layers were fabricated by single-step spin-coating at 2500 rpm for 40 s to form the films with different thicknesses via changing the QD ink concentration (200–400 mg mL−1) (Table S2†), which were then heated at 90 °C for 1 min in air. For PbS-EDT layers, the oleate-capped PbS QD solution (20 mg mL−1) was spin-coated, followed by EDT solution (0.04 vol% in acetonitrile) and pure 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.

3.4. Measurement and characterization

UV-vis-NIR spectra were recorded on a PerkinElmer model Lambda 750. Photoluminescence measurements were performed on samples prepared on quartz substrates by spin-coating PbS QD inks. 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 using a cooled array detector (Andor, iDus 1.7 μm). Time-resolved PL spectra were recorded 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 a N2 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 MΩ. The intensity of white light, which is referred to henceforth as a “light bias”, was used to control the open-circuit voltage (Voc) of the devices. A laser with a wavelength of 532 nm was used for 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 (≪Voc). The frequency, light intensity and pulse duration were kept constant. XPS was carried out using a SPECDTM ultrahigh vacuum photoelectron spectroscopy system. SAXS experiments were performed using a high-flux X-ray instrument (SAXSess mc2, Anton Paar) equipped with a line collimation system and a 2200 W sealed-tube X-ray generator (Cu Kz, λ = 0.154 nm). PbS QD inks were spin-coated on aluminum foil (supported by glass). Then the PbS films on aluminum foil were carefully stripped for testing. The X-ray scattering patterns were recorded in a vacuum on an imaging-plate (IP). The scattering peak positions were calibrated with silver behenate. Current–voltage characteristics were recorded using a Keithley 2400 (J–V) digital source meter under simulated AM 1.5G solar irradiation at 100 mW cm−2 (Newport, Class AAA solar simulator, 94023A-U). The light intensity is calibrated using a certified Oriel Reference Cell (91150V) and verified with a NREL calibrated Hamamatsu S1787-04 diode. The SEM image was characterized on a Zeiss Supra 55 field in high vacuum mode at 20 kV accelerating voltage. The device cross-section was characterized by scanning electron microscopy (SEM) on a Zeiss Supra 55 field in high vacuum mode at 10 kV accelerating voltage. The capacitance–voltage measurements were acquired with a Keithley 4200-CVU semiconductor characterization system with the samples stored in a high vacuum (~10−6 Torr) probe station at a frequency of 50 kHz and an AC signal of 100 mV, scanning from −1 to 1 V. Electron only devices were fabricated using the device structure ZnO/PbS-ink/ZnO for the measurement of trap density and diffusion length. J–V curves of devices exhibiting space charge limited current (SCLC) in the presence of traps show three characteristic regions. At low bias, thermally generated charges outnumber the injected charge carriers, and the device follows Ohm’s law (J ∝ V). At a certain voltage (VTH), the injected charges exceed the thermally generated charges and injected charges fill the trap states leading to trap-filling SCLC behaviors.

4. Conclusions

In summary, we demonstrated a multiple-passivation strategy by simple solution-phase ligand engineering in conventional PbS QD ink. The presence of MPA can efficiently reduce the surface trap states of PbS QDs by replacing the OH groups. Moreover, the colloidal stability of QD ink is also significantly improved by the chemical bonding between MPA and BA. As a result, ligand engineering allows for the achievement of simultaneous enhancement of Voc and FF, and a remarkable PCE up to 11.18%. Our work demonstrates a simple approach to realize both improved passivation and colloidal stability of PbS QD ink. We believe that this study will facilitate scalable manufacturing of efficient photovoltaic devices based on QDs in the near future.

Author contributions

M. Gu conceived the idea and contributed to most experimental work. Z. Liu and W. Ma supervised the project. F. Yang, S. Zhou...
and Y. Xue assisted in the materials synthesis. Y. Wang, T. Wu, K. Lu, Y. Zhang and F. Li assisted in the solar cell fabrication and measurement. Y. Xu, X. Ling and J. Yuan assisted in the morphology and device characterization. H. Fang and M. A. Loi assisted in the 2D PL lifetime characterization. M. Gu, Z. Liu and W. Ma drafted and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

4 R. Saran and R. J. Curry, Nat. Photonics, 2016, 10, 81.