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Highly efficient air-stable colloidal quantum dot solar cells by improved surface trap passivation

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ABSTRACT

While the power conversion efficiency (PCE) of colloidal quantum dot (CQD) solar cells can reach > 10%, the major obstacle for charge extraction and energy loss in such devices is the presence of surface trap sites within CQDs. In this work, highly trap-passivated PbS CQDs were developed using a novel iodide based ligand, 1-propyl-2,3-dimethylimidazolium iodide (PDMII). We examined the effects of PDMII on the surface quality of PbS-CQDs and compared them with TBAI, which is the best-selling iodide based ligand. By using PDMII, improved surface passivation with reduced sub-bandgap trap-states compared to TBAI was achieved. The reduced trap density resulted in enhanced charge extraction with diminished energy loss (0.447 eV) in the devices. Solar cell devices using our PDMII based CQDs displayed high PCE and air stability. The certified PCE of our PDMII based devices reached 10.89% and was maintained at 90% after 210 days of air storage.

1. Introduction

Colloidal quantum dots (CQDs) have emerged as promising materials for next-generation solar cells because of solution processability, size-dependent bandgap tunability infrared (IR) absorption, and capability for multiple exciton generation [1,2]. The performance of PbS-CQD based photovoltaic devices has rapidly improved during last decade via development in materials chemistry and device architectures. Power conversion efficiency (PCE) of > 10% was achieved by optimizing optical absorption and charge collection properties [3,4]. Conventional solution processing techniques are readily applicable for device fabrication, thus further improving in performance promises a great potential for low-cost portable power sources [5,6].

The solution processability of CQDs is offered by surface ligands that are incorporated during synthetic procedure. In case of PbS-CQD, the as-synthesized CQDs are typically capped by long-chain oleate ligands affording dispersability in organic media. However, to acquire desired optoelectronic properties, the long oleate ligands are replaced to shorter ligands that can reduce dot-to-dot distance. Short organic bidentated molecules such as 3-mercaptopropionic acid (MPA) [1],

1,2-ethanedithiol (EDT) [7], 1,3-propanedithiol (PDT) [8], 1,4-benzenedithiol (BDT) [9], or inorganic ligands [10–13], have been regularly used. The types of exchanging ligands and their coverage determine the key properties of CQDs such as energy levels, sub-bandgap trap-states, charge transport, and air-stability [11,13–17]. Typically, the ligand exchange step is performed by solid-state exchange (SSE) method, in which the exchanging ligand solutions are coated on CQD layers followed by washing [18]. However, the SSE method is intrinsically prone to generate additional trap-states due to imperfect repassivation. The resulting trap-states can cause charge recombination and energy loss curtailing device performance.

A range of strategies have been investigated to passivate the surface traps of CQDs that are formed during synthesis and film fabrication processes [10,13,19]. The detailed surface chemistry of PbS-CQD during synthesis and ligand exchange was recently revealed [20]. In as-synthesized oleate-capped PbS-CQD, nonpolar (001) surface facets are passivated by covalent bonding of carboxylic acid group (–COOH), whereas the Pb terminated polar (111) surface facets are passivated by deprotonated carboxylic acid group (COO[–]) along with a hydroxyl group (–OH) (Fig. S1). Especially, the OH groups bound on (111)

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surface facets of PbS-CQD are the main cause of sub-bandgap trap-states [21]. Development of new strategies to improve surface passivation, especially the (111) facets of PbS-CQD, promises further enhancement in device performance and stability. In previous reports, the improvement of the device performance by enhanced surface passivation has been reported [11,22–24].

Herein, we prepared surface trap-passivated PbS-CQDs using a novel iodide source, 1-propyl-2,3-dimethylimidazolium iodides (PDMII), coupled with dual-exchange method. The resulting PbS-CQDs exhibited near quantitative exchange from oleate-ligand to iodide. Particularly, the OH groups on (111) surface facet, which are the major cause of trap states, were effectively removed. The surface passivation and trap-state reduction by using PDMII were superior to the best-selling iodide-based-ligand, tetrabutylammonium iodide (TBAI). The effects of the ligand types and exchanging methods on the surface quality of PbS-CQDs and the device performance were investigated in detail. The solar cell devices using dual-PDMII-exchanged CQDs achieved high PCEs of 10.99% (certified PCE of 10.89%). Notably, the resulting devices showed unprecedentedly low energy loss (0.447 eV) and high air storage stability.

2. Material and methods

2.1. Synthesis of PbS-CQDs

The oleate-capped PbS-CQDs (o-PbS) were synthesized via a rapid hot injection method by following a reported procedure with slight modifications [25]. Briefly, 4 mmol of PbO and 8 mmol of oleic acid (OA) were dissolved in 20 mL of 1-octadecene (ODE) in a three-neck flask by heating the mixture to 100 °C under vacuum overnight. Then, 360 μ L of TMS₂S in ODE was injected into the lead oleate solution under a N₂ atmosphere. After purify, it was diluted in octane to 50 mg/mL (o-PbS).

2.2. Solution-phase treatment (SPT)

Tetrabutylammonium iodide (TBAI) or 1-propyl-2,3-dimethylimidazolium iodide (PDMII) were dissolved in oleylamine (OLA) and heated at 200 °C for 2 h under a N₂ atmosphere. In addition, TBAI or PDMII (0.6 M in 5 mL OLA) were then heated at 120 °C for 2 h under vacuum before use [17]. 0.6 mL of halide solution was added into 2 mL o-PbS type sample (150 mg/mL in toluene) under a N₂ atmosphere for 1 h while stirring. Methanol was added to the precipitate and then dilute in octane to 50 mg/mL (TBAI-PbS and PDMII-PbS, respectively).

2.3. Preparation of ZnO-SG

ZnO layers were prepared by using an in-situ sol-gel conversion method. A precursor solution was prepared by mixing a 0.45 M solution of zinc acetate dehydrate ([Zn(CH₃COO)₂·2H₂O], Sigma Aldrich, 99.9%, 5 g) and ethanolamine (NH₂CH₂CH₂OH, Sigma Aldrich, 99.5%, 1.35 mL) dissolved in 2-methoxyethanol (CH₃OCH₂CH₂OH, Sigma Aldrich, 99.8%, 50 mL).

2.4. Photovoltaic device fabrication

The ZnO-SG solution (100 μ L) was spin-coated (2000 rpm, 15 s) on top of the ITO/glass to obtain 40 nm thick layer and then annealed at 150 °C for 10 min. The PbS-CQD active layers were deposited using a conventional layer-by-layer (LBL) spin coating process under ambient atmosphere (thickness of 170–320 nm). A PbS-CQD solution (30 μ L in octane) was dropped and spin-coated at 2000 rpm (10 s). Typically, three different kinds of CQDs o-PbS, TBAI-PbS and PDMII-PbS were treated with solid-state exchange (SSE) following spin-coating (27 mM of TBAI or PDMII in methanol) until the desired thickness. Two wash

cycles were done for each layer with methanol solvent to remove unbound ligands at 2000 rpm for 10 s.

For the optimized devices, we fabricated PbS-CQD photovoltaic devices with an n-i-p architecture. To improve the performance of the ZnO EAL, we used a conjugated polyelectrolyte, WPF-6-oxy-F, as an interfacial modifying layer. Briefly, 0.07 wt% of WPF-6-oxy-F in ethanol was coated on top of the ZnO layers, following our previous report [8]. After the SSE process with TBAI/PDMII, thin layers (70 nm-thick) of PDT-exchanged (2 mM in acetonitrile) p-type PbS-CQD (PbS-PDT) were used as hole-accepting layers (HAL). Two wash cycles were done also with acetonitrile solvent at 2000 rpm for 10 s. Au was deposited as the anode (80 nm) by thermal evaporation at low pressure ($< 10^{-6}$ Torr).

2.5. Characterizations

UV-vis spectra were obtained using a S-3100 (Scinco Co., Ltd.) instrument. Photoluminescence (PL) measurements were carried out using an SPEX Nanolog 3–211 (Horriba). The signal was analyzed using an NIR spectrometer equipped with an InGaAs array detector (Symphony II). Fourier transform infrared spectroscopy (FTIR) The measurements were done using a Shimadzu IRTracer100-ATR averaging 50 scans. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a MultiLab 2000 (THERMO VG SCIENCE) system equipped with monochromatized Mg K α radiation at $h\nu = 1253.6$ eV. The base pressure was 1×10^{-9} Pa. Current density-voltage profiles were measured by using a Keithley 2401 source unit with a 150 W xenon lamp (Newport). The light intensity (AM 1.5 G one sunlight; 100 mW cm⁻²) was calibrated using a KG-5 filter covered monosilicon detector. Devices were measured under ambient air conditions. We used a metal aperture to define the device area to be 0.0518 cm² (the area of the aperture was also confirmed by an accredited institute, Newport). External quantum efficiency (EQE) spectra were obtained by passing the output of a 400 W Xenon lamp through a monochromator. The collimated output of the monochromator was measured through a 1 mm aperture with calibrated Newport 818-UV and 818-IR power meters (McScience, K3100 IQX). Calibration was performed by using a calibrated silicon photodiode as a standard. Intensity modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) methods were carried out using impedance analyzer. Both the DC and AC components of the illumination were provided by a green-emitting LED ($\lambda = 535$ nm). IMPS and IMVS values were obtained under short-circuit and open-circuit conditions, respectively. Drive-level capacitance profiling (DLCP) measurements were performed using an IVIUM Tech. IviumStat under ambient conditions for frequencies ranging from 0.1 to 1000 kHz. Transient photovoltage/photocurrent (TPV/TPC) measurements were performed using a nanosecond laser (10 Hz, NT342A-10, EKSPLA) as a small perturbation light source and a Xe lamp (150 W, Zolix) as a bias light source. The device was directly connected to a digital oscilloscope (500 MHz, DSO-X 3054A, Agilent), and the input impedance of the oscilloscope was set to 1 M Ω and a 50 Ω resistor for TPV and TPC measurements, respectively. The space charge limited current (SCLC) were performed to extract the carrier mobility. Hole mobility devices were fabricated using the device structure ITO/PEDOT/PbS/MoO₃/Au, while the Ag/PbS/Ag structure was used for electron mobility. Diffusion length calculation used an analytical model from the charge collection efficiency [24,26]. The collection efficiency (η) was calculated as Eq. (1):

$$(V) = \text{IQE}(\lambda, V = 0) \frac{J_H(V, \lambda) - J_L(V, \lambda)}{J_H(V = 0, \lambda) - J_L(V = 0, \lambda)} \quad (1)$$

where J_H and J_L are the current density values for higher (0.05 mW) and lower (0.004 mW) power under 680 nm (λ) monochromatic illumination (see Supporting information for detail). Capacitance-voltage (C_p -V) measurements were carried out using an impedance

analyzer under dark conditions with an AC signal set to 1 kHz frequency and 50 mV amplitude.

3. Results and discussion

The preparation schemes of our dual-PDMII-exchanged PbS-CQDs (PDMII-PbS-PDMII) and other CQDs used in this study are shown in Fig. 1. The dual exchange consisted of a solution-phase treatment (SPT) followed by SSE [17]. In SPT step, as-synthesized oleate-capped PbS-CQDs (o-PbS) [25] in toluene were treated with a PDMII solution in oleic amine to yield PDMII-PbS. The PDMII-PbS was dispersible in octane indicating that the oleate-ligand is still the major surface-covering ligands. We chose PDMII as an iodide-based ligand because it has been demonstrated as an excellent iodide source for solid-state electrolyte of dye-sensitized solar cells [27]. We also prepared the PbS-CQDs using state-of-the-art iodide based ligand, TBAI, to fairly judge the performance of PDMII. The TBAI treated PbS-CQDs (TBAI-PbS) were also prepared by the SPT procedure [17]. By SPT, optical absorption and excitonic features of CQDs were persistent as indicated in ultraviolet-visible (UV-vis) absorption spectra (Fig. 2a). These results suggest that the introduction of iodide passivation by SPT does not influence the CQD sizes, whereas the mono-dispersity remained unchanged. Furthermore, the HR-TEM images in Fig. S2 confirm the mono-dispersity of CQD without fusion. The incorporation iodide by SPT was indicated by the I 3d peaks from X-ray photoelectron spectroscopy (XPS) analysis (Fig. 2b). The higher I 3d peak intensity in Fig. 2b and the atomic ratio determined from the wide-scan survey spectra (Fig. S3a) demonstrated that higher iodide incorporation by PDMII than TBAI. The atomic ratios of CQDs from XPS analysis are summarized Fig. S3. Partial removal of oleate-ligand by SPT was indicated by the decrease of characteristic peaks (C-H, C=C, C=O) in Fourier transform infrared (FT-IR) spectra (Fig. 2c). The photoluminescence quantum yield (PLQY) of the pristine o-PbS was considerably enhanced by SPT. The PLQY values of o-PbS, TBAI-PbS, and PDMII-PbS solutions in octane were calculated to be 19%, 23%, and 27% respectively. This result confirmed that the surface passivation of CQDs were improved by SPT, and more efficiently using PDMII than TBAI

[13,17].

The dual-exchanged CQDs, PDMII-PbS-PDMII and TBAI-PbS-TBAI, were prepared by SSE of PDMII-PbS and TBAI-PbS (Fig. 1). Dramatic removal of the oleate-ligands by additional SSE was indicated from the FT-IR spectra (Fig. 2c). Notably, the PDMII-PbS-PDMII showed near quantitative removal of oleate-ligands, whereas the counterpart, TBAI-PbS-TBAI, was not. To elucidate the effects of dual-exchange, we also prepared PbS-CQD samples by conventional SSE method (without SPT), o-PbS-PDMII and o-PbS-TBAI. The FT-IR spectra (Fig. 2c) and XPS analysis results (Fig. S3a) revealed that the exchange is more efficient by our dual-exchange than conventional SSE. The PDMII-PbS-PDMII showed the highest iodide incorporation (I/Pb ratio of 0.70) with lowest O/Pb ratio (0.04) among all studied CQDs (Fig. S3c). The I/Pb ratio of 0.70 was even higher than that of PbS CQDs prepared by the current state-of-the-art passivation method [22,23]. Considered that the I/Pb ratio of TBAI-PbS-TBAI was 0.64 with O/Pb ratio of 0.11, the PDMII is the more effective iodide source than TBAI. This superior exchanging property of PDMII to TBAI was consistent in the CQDs prepared by conventional SSE (o-PbS-PDMII vs. o-PbS-TBAI).

It is known that the OH groups on the (111) facet in PbS-CQDs are the major source of sub-bandgap trap-states [20]. Fig. 3 shows the O 1s spectra from XPS analysis. The O 1s spectra, shown in 528–533 eV, can be deconvoluted as three species, which is originated from the hydroxyl (OH) group bound to the Pb on the (111) facet in rock-salt-structure PbS-CQDs (Pb-OH), 530.8 eV and other functional groups of the remained oleate-ligands (Pb-O, 528.8 eV and COO-Pb, 532.4 eV) [20,28]. The suppression of Pb-OH peak was more prominent in dual-exchanged CQDs (Fig. 3b vs. d), while it was more efficient by PDMII than TBAI (Fig. 3c vs. d). The results of deconvoluted O 1s spectra are summarized in Table S1.

To elucidate the effects of surface passivation on radiative sub-bandgap trap-states of CQDs, we measured PL emission spectra of PbS-CQD films [24,29]. As shown in Fig. 4a, all CQD films fabricated including SSE process showed sub-bandgap emission at 1300–1600 nm in addition to band-edge emission peak at ~ 1100 nm. Considering that the films of TBAI-PbS and PDMII-PbS showed single

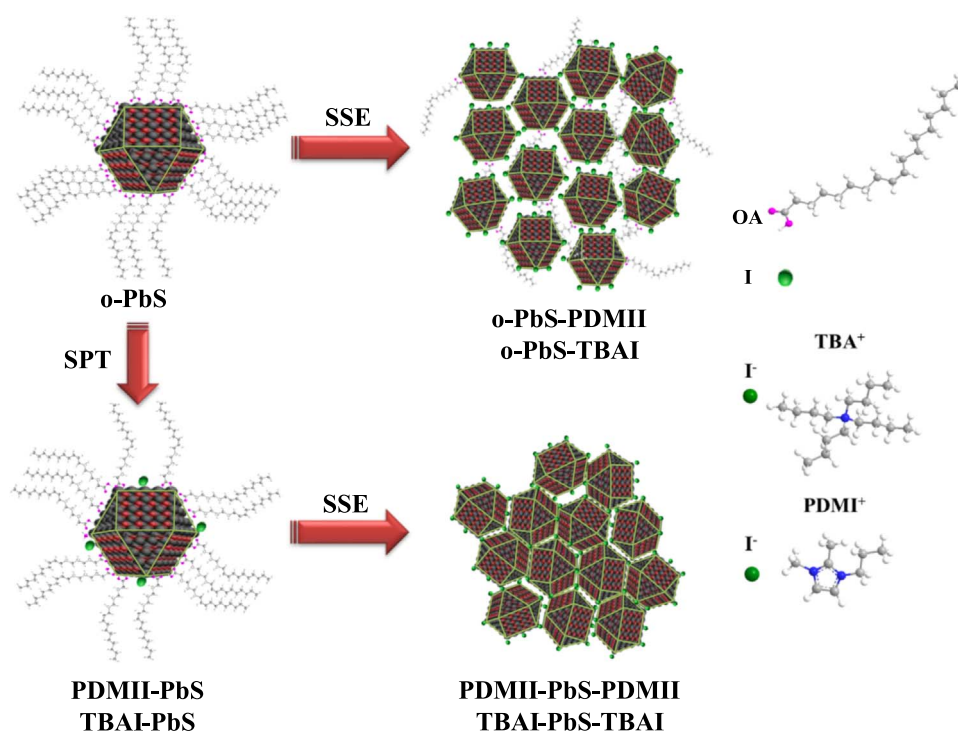


Fig. 1. Schematic illustration of the preparation of dual-exchanged CQDs and solid-state exchanged CQDs.

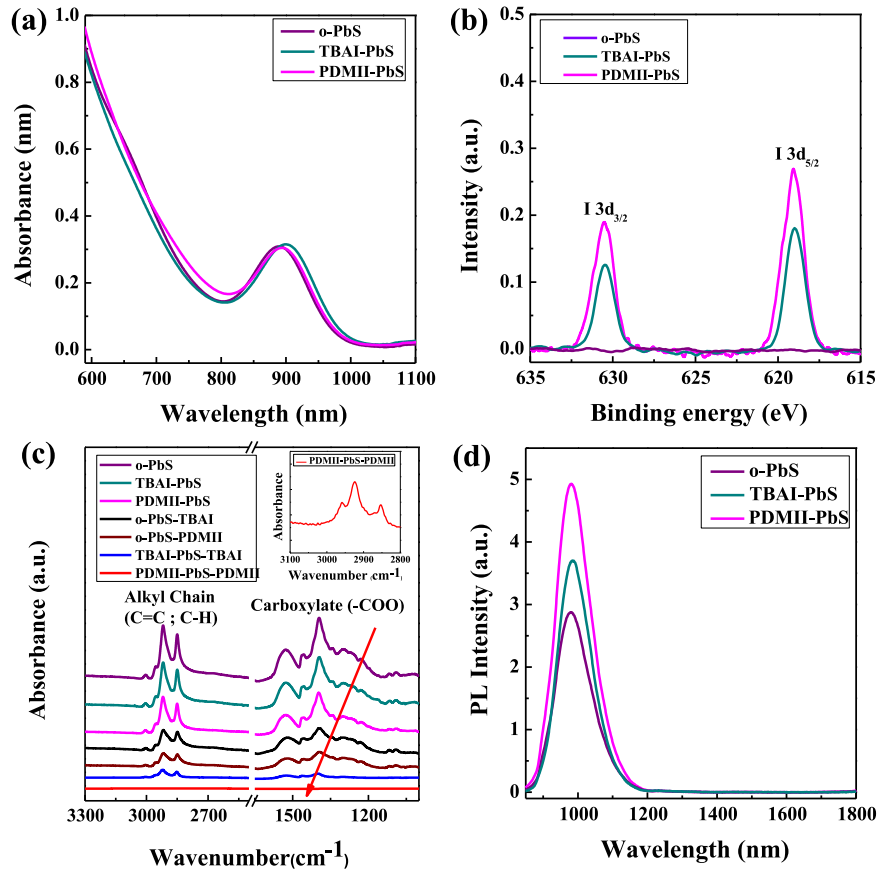


Fig. 2. Properties of CQDs by SPT; (a) UV-vis absorption spectra, (b) I 3d peaks from XPS analysis, (c) FT-IR analysis results, and (d) PL emission spectra. The excitation wavelengths for PL measurement was 650 nm.

band-edge emission (Fig. S4), the trap-states are mainly due to imperfect repassivation during SSE. Notably, PDMII-PbS-PDMII displayed only band-edge emission, whereas the TBAI-PbS-TBAI still exhibited sub-bandgap emission (Fig. 4a). This result indicates that the dual-exchange using PDMII can achieve exceptionally high surface passivation of PbS-CQD with much reduced sub-bandgap trap-states.

The trap density was further investigated by transient photovoltage (TPV) combined with transient photocurrent (TPC) spectroscopy [24,31]. The CQD devices with structure of ITO/ZnO/CQD/Au were fabricated and the density of states (DOS) were measured with respect to V_{OC} . As indicated in Fig. 4b, the DOS trends of CQD layers were consistent to the results by PL emission spectra. The DOS of PDMII-PbS-PDMII ($1.2 \times 10^{17} \text{ cm}^{-3}/\text{eV}$) at was much lower than that of o-PbS-TBAI ($5.2 \times 10^{17} \text{ cm}^{-3}/\text{eV}$) at maximum power voltage (V_{MPP}). The DOS is also determined using drive-level capacitance profiling (DLCP) measurement, which is developed for materials containing a relatively large number of defects, such as amorphous silicon, polycrystalline $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}$, and PbS-CQDs [24,32]. In DLCP measurements, the capacitance responses are measured as a function of frequency. At high modulation frequency, only the intrinsic free carriers contribute to DOS, whereas at low modulation frequency, both intrinsic free carriers and trap states contribute to DOS. As indicated from Fig. 4c, the DOS values of CQDs prepared by dual-exchange were lower at all frequencies of measurement. The resulting DOS values of PDMII-PbS-PDMII ($0.37 \times 10^{17} \text{ cm}^{-3}$) was one order of magnitude lower than that of o-PbS-TBAI ($5.3 \times 10^{17} \text{ cm}^{-3}$) at 0.1 kHz. The results from TPV/TPC and DLCP analyses are summarized in Table S2, and the detailed DOS calculation procedures are shown in the experimental section in the Supporting information (SI).

Photovoltaic devices using PbS-CQDs were fabricated with an architecture of ITO/ZnO/CQD/Au (Fig. S5a). Thin ZnO electron-

accepting layers (EAL, 40 nm-thick) were prepared by in-situ sol-gel conversion, and the charge generating CQD active layers were prepared by conventional layer-by-layer spin-coating method (thickness of 170–320 nm) [1]. The Au anodes were prepared by thermal evaporation. The device fabrication is performed under air ambient conditions. Fig. 5a shows the current density-voltage (J - V) characteristics of the CQD devices under simulated AM 1.5 G one sun illumination, and the results are summarized in Table 1. The PDMII-PbS-PDMII based devices (dual-exchange using PDMII) showed the highest PCE of 8.23% with $V_{OC} = 0.61 \text{ V}$, $J_{SC} = 21.04 \text{ mA cm}^{-2}$, and $FF = 0.63$, whereas the o-PbS-TBAI based devices (SSE using TBAI) showed the PCE of 5.20% with $V_{OC} = 0.55 \text{ V}$, $J_{SC} = 18.05 \text{ mA cm}^{-2}$, and $FF = 0.53$. The higher J_{SC} of PDMII-PbS-PDMII devices compared to other devices was confirmed in the EQE spectra (Fig. 5b). The mismatch of the J_{SC} values from the J - V characteristics and those estimated from the EQE spectra was $< 3\%$ (Table 1). The PDMII-PbS-PDMII devices also showed improved charge selectivity (Fig. S7a) compared to other devices. The performance trend was confirmed by statistical analysis of 50 devices (Fig. S6a).

The optimum CQD active layer thickness of devices were altered by the types of CQDs. The dual-exchanged CQD based devices showed the optimum performance at a thickness of 270 nm, whereas the CQDs by SSE showed at 230 nm (Fig. S6b). This result implies that the charge extraction in dual-exchanged CQD layers is more efficient than CQDs by SSE due to improved passivation, thus the higher J_{SC} can be attained without much sacrificing FF at thicker active layers. To investigate charge extraction properties, charge recombination times (τ_{rec}) of devices were determined. Fig. 5c shows the (τ_{rec}) values determined by TPV spectroscopy [8,33]. The τ_{rec} values with respect to the applied voltage were determined by mono-exponential function of the voltage decay curves (Fig. S7b). The τ_{rec} of PDMII-PbS-PDMII

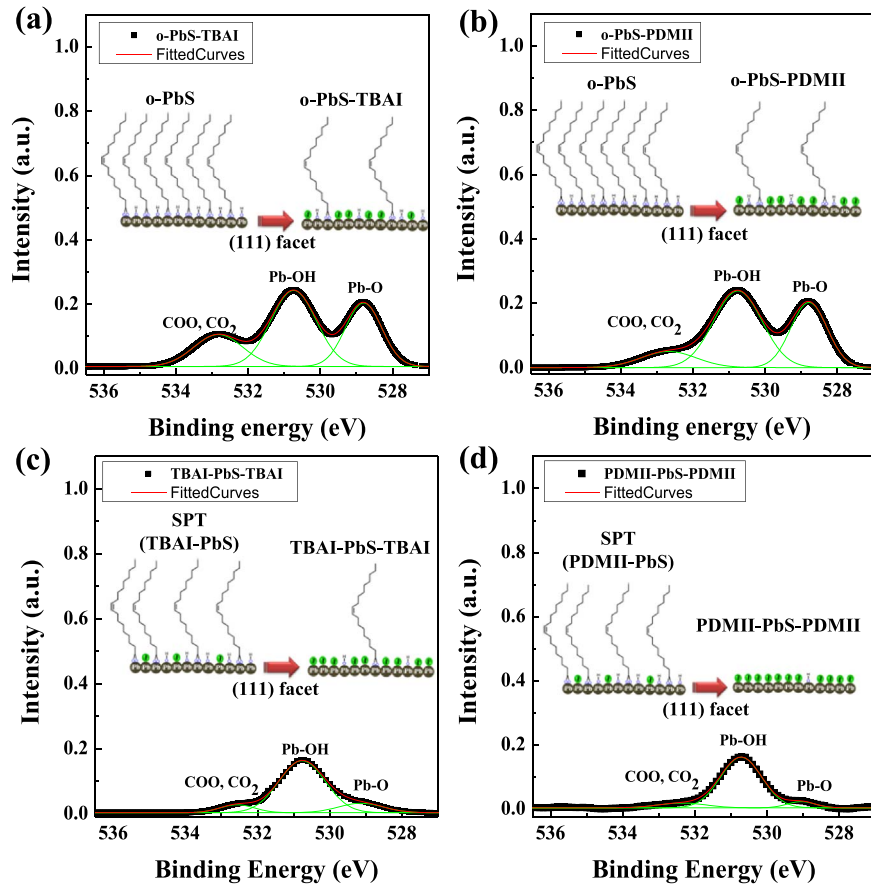


Fig. 3. O 1s spectra of PbS-CQDs from XPS analysis; (a) o-PbS-TBAI, (b) o-PbS-PDMII, (c) TBAI-PbS-TBAI, and (d) PDMII-PbS-PDMII. The green lines indicate the deconvoluted curves. The inset schemes illustrate the surface chemistry of (111) facet on PbS-CQD.

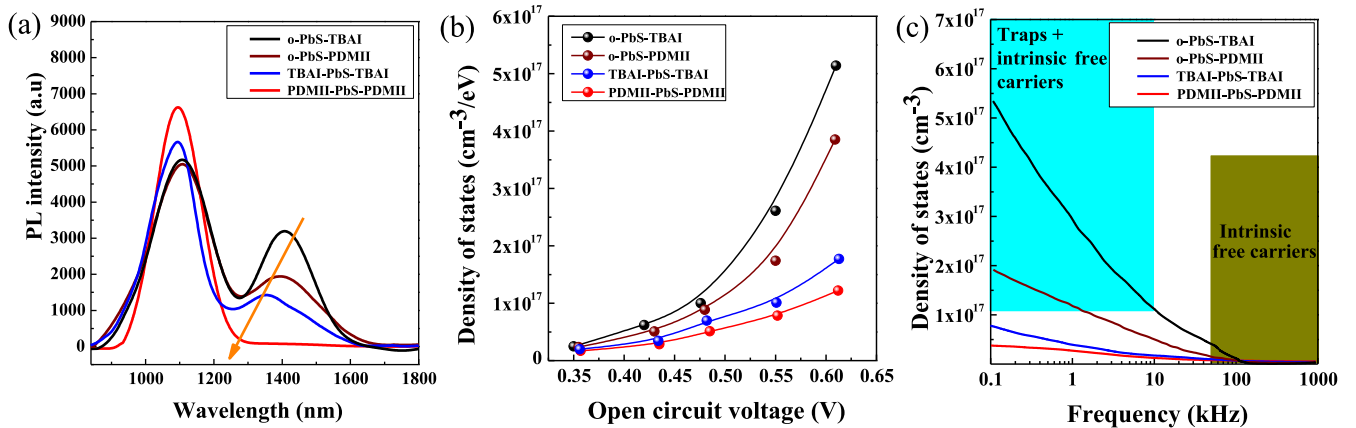


Fig. 4. Trap state density analysis of PbS-CQDs. (a) PL spectra of CQD films. DOS measurement by (b) TPV/TPC analysis and (c) DLCP analysis. The device structure for TPV/TPC analysis is ITO/ZnO/CQD/Au, and for DLCP is Au/CQD/Ag.

based devices ($7.4 \mu\text{s}$) was much longer than that in o-PbS-TBAI based devices ($5.5 \mu\text{s}$) at V_{MPP} . We also measured τ_{rec} by intensity-modulated photovoltage spectroscopy (IMVS) analysis using the relation, $\tau_{\text{rec}} = 1/2\pi f_{\text{min}}$, in which f_{min} is the minimum voltage in the imaginary part of the low-frequency range of the IMVS spectra (Fig. S7e). The trend of τ_{rec} determined by IMVS was consistent to TPV results (Table S3). The charge transport time (τ_{ct}) from intensity-modulated photocurrent spectroscopy (IMPS) analysis (Fig. S7d), and the transit time (τ_t) from TPC spectroscopy (Fig. S7c) showed that the improved surface passivation can also leverage charge transport. The charge extraction properties are summarized in Table S3 and the detailed measurement

and calculation procedures are shown in the experimental section in [Supporting information](#).

The effects of trap density on carrier mobility were studied by measuring space-charge-limited current (SCLC). Fig. S8 shows the J - V curves of electron-only (Ag/CQD/Ag) and hole-only (ITO/PEDOT/CQD/MoOx/Au) devices. Both the electron mobility (μ_e) and hole mobility (μ_h) were enhanced in the CQDs with lower trap densities. PDMII-PbS-PDMII devices showed μ_e and μ_h higher values than o-PbS-TBAI devices (Table S4). Charge diffusion length (L_D) of devices was estimated by measuring collection efficiency (η) with respect to the applied voltage (Fig. 5d) [12,24,26]. L_D is determined by fitting the

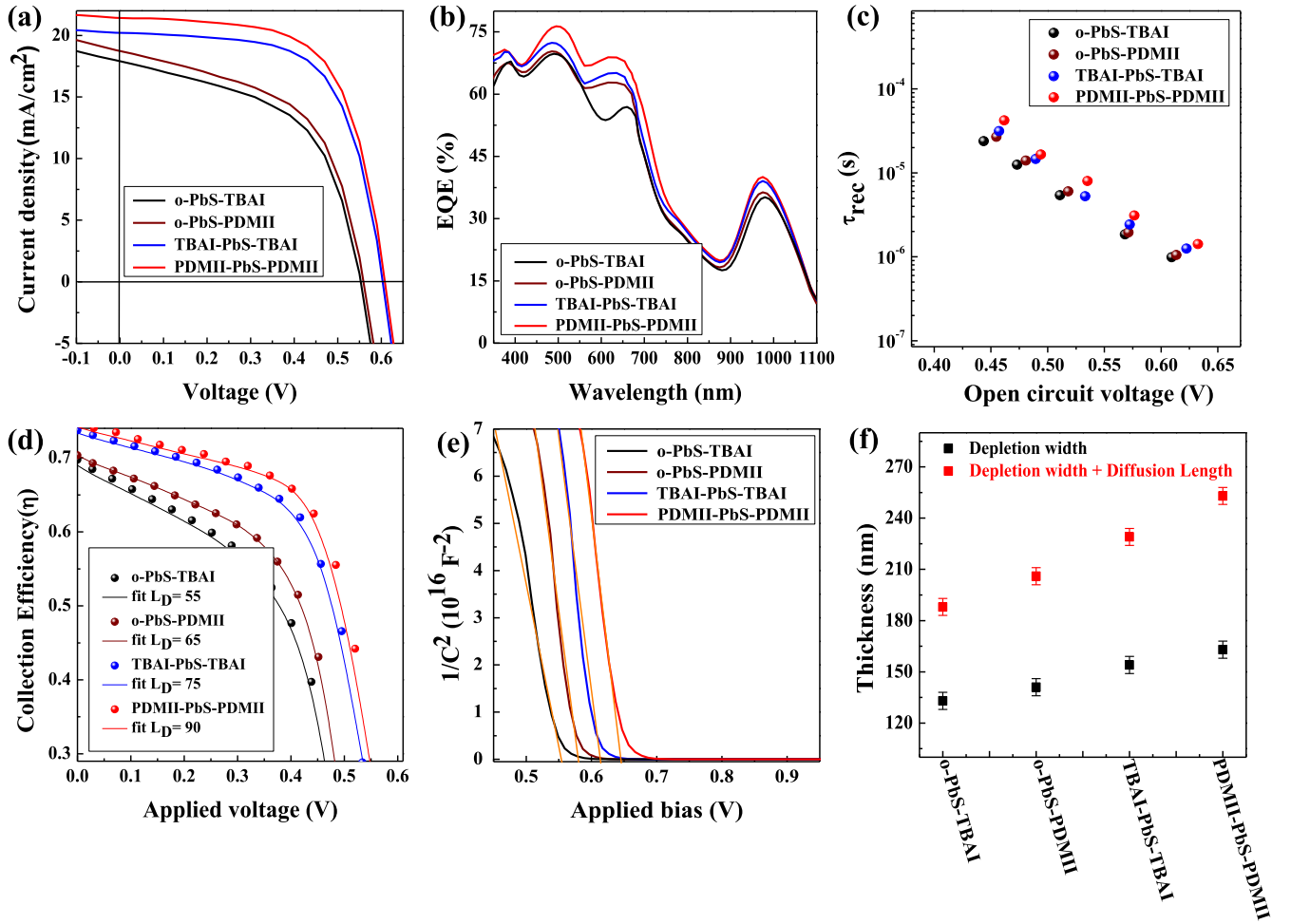


Fig. 5. Device characterization results; (a) $J-V$ characteristics under AM 1.5G one-sun illumination (100 mW cm⁻²), (b) EQE spectra, (c) τ_{rec} vs. V_{OC} plots by TPV analysis, (d) collection efficiency plot, (e) Mott-Schottky plot (f) estimated combined charge-transport-length (charge diffusion plus drift) of devices at short-circuit condition.

Table 1

Summary of device performance. The devices without HAL have a structure of ITO/ZnO/CQD/Au and the devices with HAL have a structure of ITO/ZnO/CQD/HAL/Au. The HAL is a p-type CQD, PbS-PDT.

Device structure	CQD	PCE (%)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	R_S (Ω cm ²)	R_{SH} (Ω cm ²)	Calculated J_{SC} (mA cm ⁻²)
ITO/ZnO/CQD/Au	o-PbS-TBAI	5.20	0.55	18.05	0.53	25.14	320	17.01
	o-PbS-PDMII	5.87	0.56	18.98	0.54	23.64	374	18.35
	TBAI-PbS-TBAI	7.65	0.60	20.42	0.62	21.76	728	19.78
	PDMII-PbS-PDMII	8.23	0.61	21.04	0.63	19.82	785	20.46
ITO/ZnO/CQD/HAL/Au	o-PbS-TBAI	9.14	0.65	22.29	0.63	15.76	763	21.86
	o-PbS-PDMII	9.72	0.66	22.67	0.64	14.25	862	22.06
	TBAI-PbS-TBAI	10.14	0.67	23.15	0.65	13.17	973	23.11
	PDMII-PbS-PDMII	10.99	0.68	24.11	0.67	11.68	1084	23.55
	PDMII-PbS-PDMII ^a	10.89	0.68	23.55	0.68	—	—	—

^a Results from an accredited institute, Korea Institute of Energy Research.

experimental results based on the drift-limited p-n junction model, which is a previously proposed model. The L_D for PDMII-PbS-PDMII devices is determined to be ~ 90 nm, which is > 60% longer than that for o-PbS-TBAI devices (~ 55 nm). These results are summarized in Table S4.

The effects of trap density the widths of depleted region (W_D) were investigated by capacitance-voltage (C_p-V) analysis. As shown in Mott-Schottky plot of devices (Fig. 5e), the built-in potential (V_{bi}) of PDMII-PbS-PDMII devices was 0.65 V, whereas that of the o-PbS-TBAI devices was 0.55 V. The calculated carrier number (N_a), V_{bi} , and W_D

of the devices were plotted in Fig. S9. Under short-circuit conditions, the W_D of PDMII-PbS-PDMII devices is determined to be 163 nm, while that of o-PbS-TBAI devices is 133 nm. From the results for W_D and L_D , the combined charge-transport length by drift and diffusion can be obtained. The estimated combined length of charge diffusion and drift at short-circuit condition was 253 nm (163 + 90 nm) for PDMII-PbS-PDMII devices and 188 nm (133 + 55 nm) for o-PbS-TBAI devices. This result clarifies the reasons of different optimum active layer thickness (270 nm vs. 230 nm) among the studied devices. The decreased trap density of dual-PDMII-exchanged CQDs is the origin of

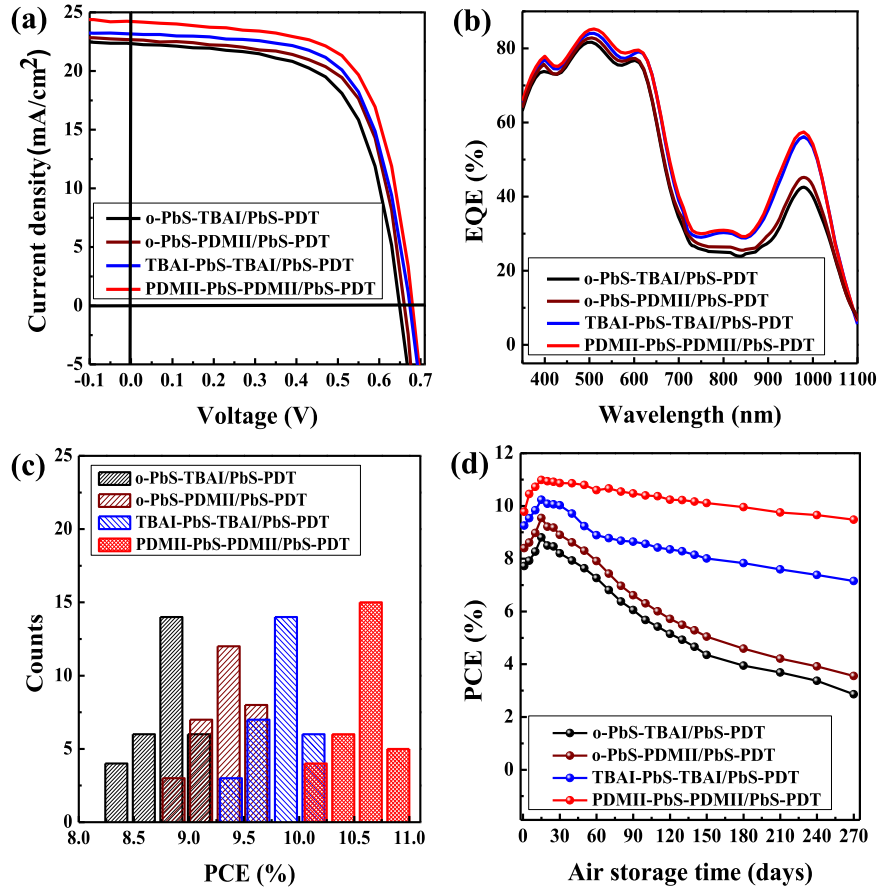


Fig. 6. Performance of CQD devices with HAL; (a) *J-V* characteristics under AM 1.5G one-sun illumination (100 mW cm^{-2}), (b) EQE spectra, (c) statistics of device PCE, (d) stability trend in air ambient storage. For statistical analysis, 30 devices are used for each type of CQD.

improved charge diffusion/drift. Detailed experimental conditions and the calculations used to determine W_D are given in [Supporting information](#), and the results are summarized in [Table S4](#).

To optimize device performance, we fabricated CQD photovoltaic devices with n-i-p architecture containing hole-accepting layers (HAL) (ITO/ZnO/CQD/HAL/Au) as shown in [Fig. S5b](#). Thin layers (70 nm-thick) of PDT-exchanged p-type PbS-CQD (PbS-PDT) were used as the HAL [8,13,17,24,33]. The performance of all devices was enhanced compared to those without HAL as shown in *J-V* curves and EQE spectra ([Fig. 6a](#) and [b](#)). The PCE of PDMII-PbS-PDMII devices was 10.99% with $V_{OC} = 0.68 \text{ V}$, $J_{SC} = 23.55 \text{ mA cm}^{-2}$, and $FF = 0.68$, while that of o-PbS-TBAI devices was 9.14% with $V_{OC} = 0.65 \text{ V}$, $J_{SC} = 22.29 \text{ mA cm}^{-2}$, and $FF = 0.63$. The parameters from all types of devices are summarized in [Table 1](#). The trend of performance was confirmed by statistical analysis ([Fig. 6c](#)). Notably, the PCE of 10.99% was one of highest values among reported results. This performance was higher than that of the reported devices using the state-of-the-art CQD passivation method (PCE of 10.6%) [22]. Furthermore, the PDMII-PbS-PDMII devices exhibit 90% of their original PCE after storage for 210 days in air ambient atmosphere, which is considerably better than the o-PbS-TBAI based devices which shows only 32% of retention. After 25 days of storage under ambient conditions, we shipped a PDMII-PbS-PDMII device to an accredited institute in Korea (Korea Institute of Energy Research, KIER) for certification. The certified PCE is 10.89% ($V_{OC} = 0.675 \text{ V}$, $I_{SC} = 1.220 \text{ mA}$, and $FF = 0.685$) over an active area of 0.0518 cm^2 ([Fig. S10](#)) [33]. The result corroborates that the enhanced surface passivation of our PDMII-PbS-PDMII achieved high device performance and air stability simultaneously.

It is an intriguing fact that our optimized PDMII-PbS-PDMII devices achieved particularly high V_{OC} (0.68 V) values considering the bandgap of CQDs. The energy loss ($E_{loss} = E_g - qV_{OC}$) of our PDMII-PbS-PDMII devices was remarkably low (0.447 eV) compared to other reported state-of-the-art CQD devices (0.47–0.48 eV) [3,4,11–13,22–24,30,34,35]. We estimated the E_g based on the onset of EQE values following a reported conventional method [24,29]. The E_{loss} values of o-PbS-TBAI and o-PbS-PDMII devices were 0.497 eV and 0.487 eV, which are similar to other reported values. Considered that the trap-states of CQDs are the crucial factor to determined energy loss [11,29], the unprecedentedly low E_{loss} of our devices is due to the improved surface passivation of our dual-PDMII-exchanged CQDs, PDMII-PbS-PDMII.

4. Conclusion

In summary, we developed CQD solar cells, which can achieve state-of-the-art efficiency and air stability. It is achieved by developing highly trap-passivated PbS-CQDs using a novel iodide source, PDMII. The effects of PDMII on surface quality of PbS-CQDs were investigated in detail that were compared in cases with TBAI. The improved surface passivation by PDMII effectively reduced the sub-bandgap trap-states, which is the major obstacle for charge collection and energy loss in the CQD devices. The reduced trap density enhanced charge extraction properties and reduced energy loss (0.447 eV) in devices. Using our dual-PDMII-exchanged CQDs, the devices with PCE of 10.99% (certified PCE of 10.89%) was achieved. Furthermore, the devices maintained 90% of their original performance after storing in air for 210 days. This result was unprecedentedly high efficiency and air stability.

Further performance enhancement might be feasible by additional optimization in device architecture such as optical management and interfacial controls.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2017.06.040>.

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Supporting Information

Highly Efficient Air-Stable Colloidal Quantum Dot Solar Cells by Improved Surface Trap Passivation

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Sang-Yong Ju,^c Jin-Won Lee,^d Tae-Wook Kim,^d Seung-Hwan Oh,^e Sung-Yeon Jang^{a*}*

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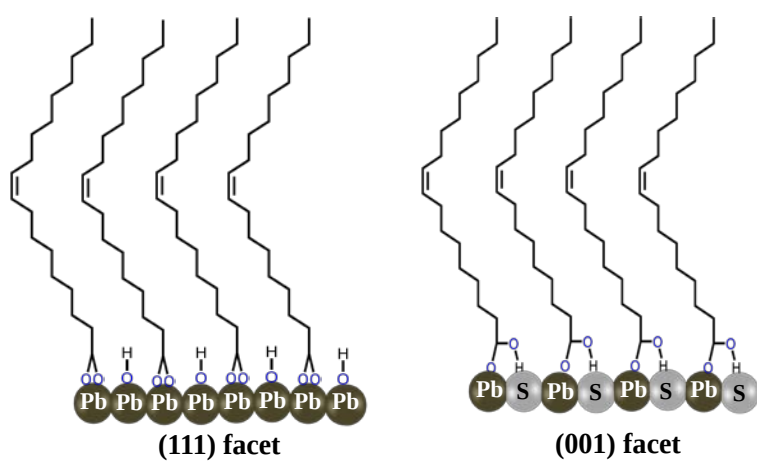


Figure S1. Surface passivation in oleate-capped PbS-CQDs: (111) and (001) facet.

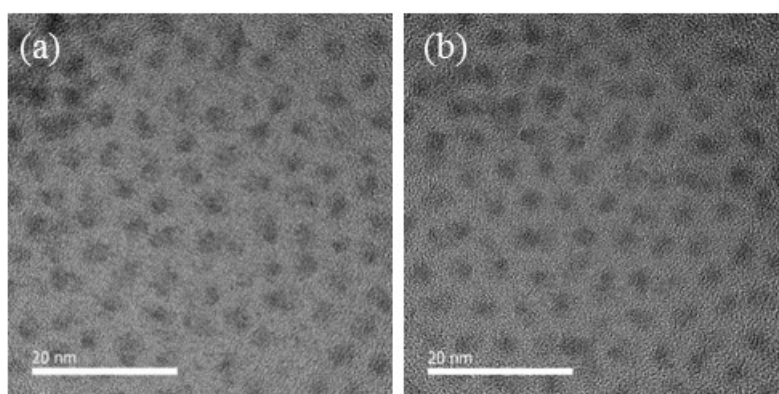


Figure S2. HR-TEM images of CQDs. (a) o-PbS and (b) PDMII-PbS.

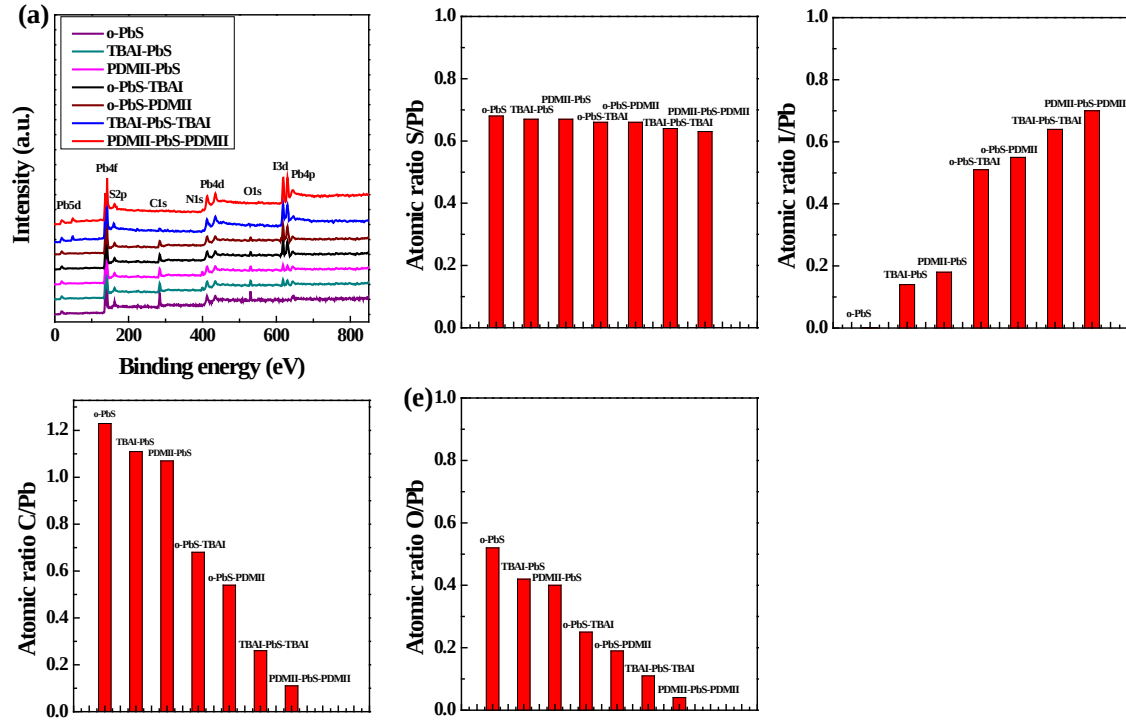


Figure S3. XPS analysis results of CQDs by SPT: (a) Wide scan survey spectra, (b) S/Pb atomic ratio, (c) I/Pb atomic ratio, (d) C/Pb atomic ratio, and (e) O/Pb atomic ratio.

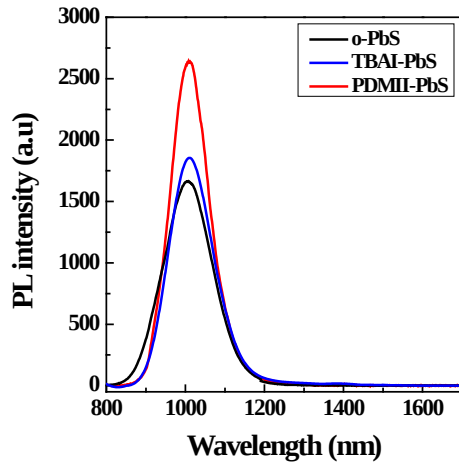


Figure S4. PL spectra of the CQD films (o-PbS, TBAI-PbS, and PDMII-PbS).

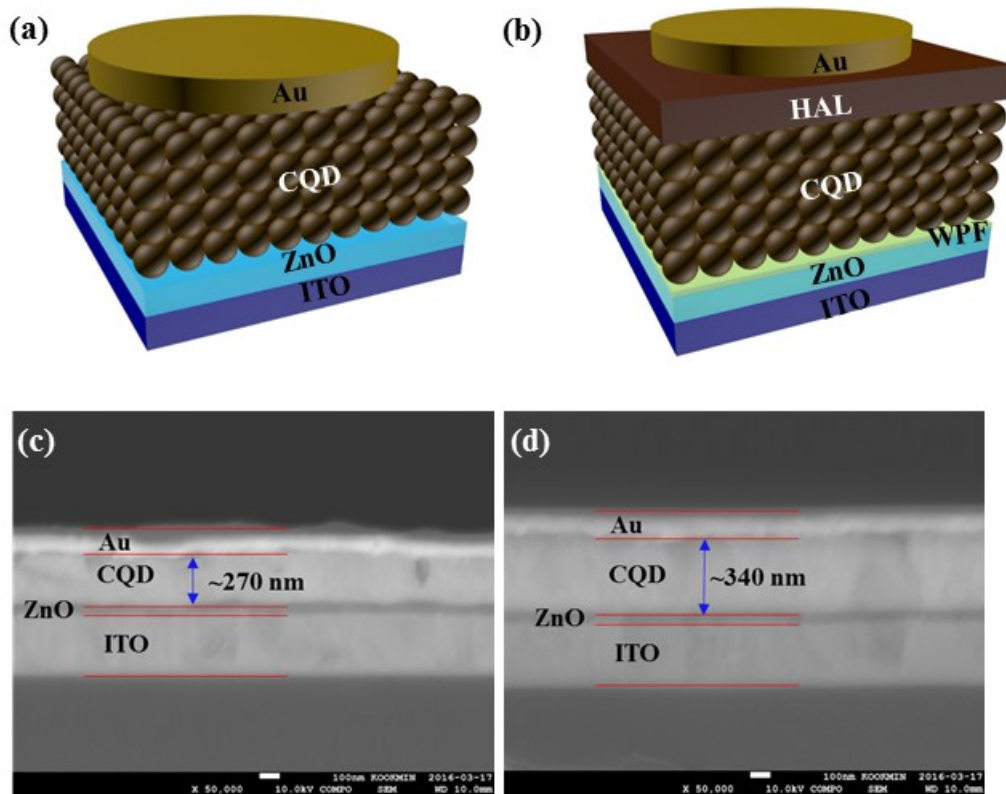


Figure S5. Schematic illustration of device structures used in this study. (a) The devices without HAL have a structure of ITO/ZnO/CQD/Au. (b) The devices with HAL have a structure of ITO/ZnO/CQD/HAL/Au. The HAL is a p-type CQD, PbS-PDT. The cross-sectional SEM images of devices without (c) and with (d) HAL layers.

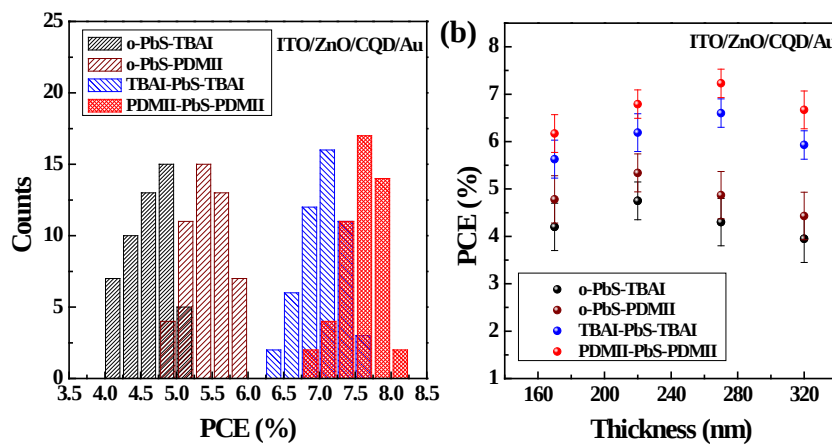


Figure S6. Statistical analysis of the PCE and the alteration of PCE with respect to the active layer thickness. For statistical analysis, 50 devices were used for each type of CQD.

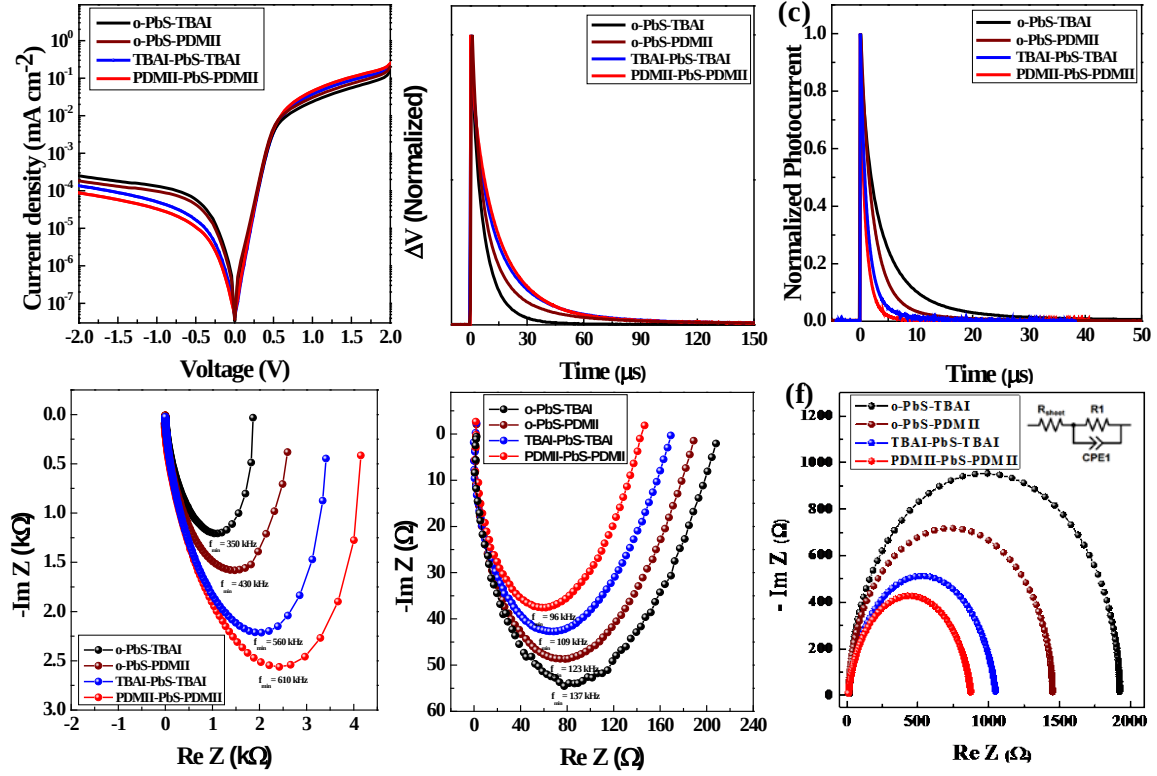


Figure S7. Charge collection properties analysis results; (a) dark J-V curves, (b) TPV spectroscopy, (c) TPC spectroscopy, (d) intensity-modulated photocurrent spectroscopy (IMPS), (e) intensity-modulated photovoltage spectroscopy (IMVS) and (f) Nyquist plot.

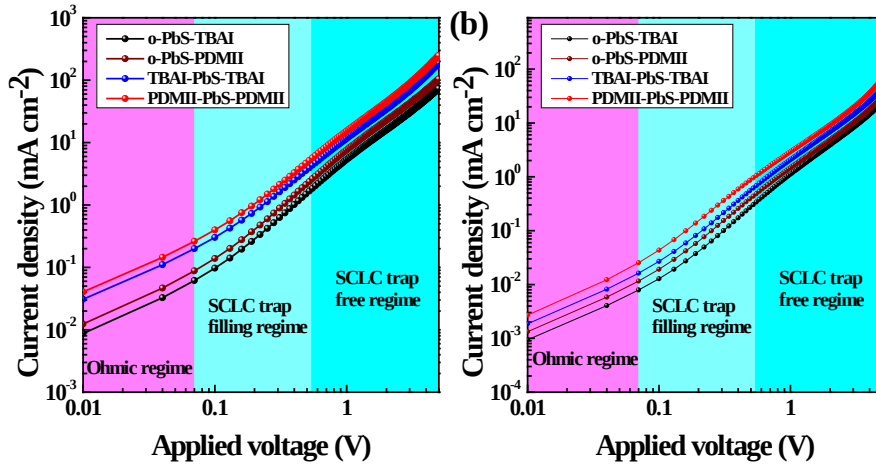


Figure S8. Space charge limited current using (a) electron-only (Ag/CQD/Ag) and (b) hole-only (ITO/PEDOT/CQD/MoOx/Au) devices.

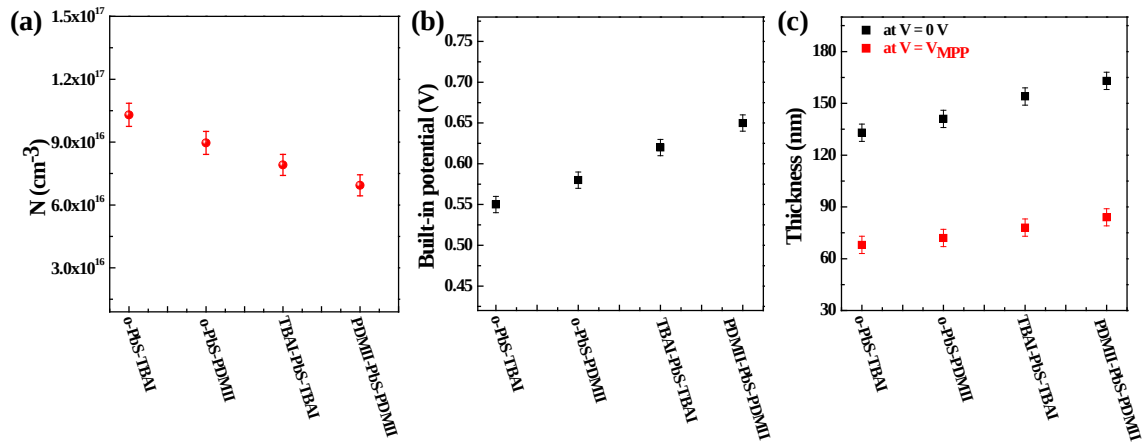


Figure S9. Results from the C_p -V analysis: (a) the calculated carrier number (N_a), (b) V_{bi} values, and (c) depletion width (W_D) at short-circuit and V_{MPP} conditions.



Test Results

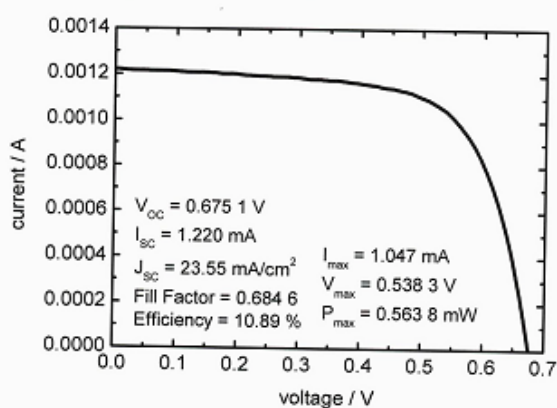
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KIER-16-0176

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[Appendix 3]

Kookmin University Quantum dot solar cell

Device ID : PbS QD-#3
Date of Test : March 29, 2016
Simulator : WACOM, WXS-155S-L2 (Class-AAA)
Spectrum : AM1.5 Global
Irradiance : 100 mW/cm²
Sample Type : Quantum dot solar cell
Device Area : 0.0518 cm² (designated illumination area)
Device Temperature : 25.0 °C



Operator: YoungJoo Eo

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Figure S10. The certification of the device performance from an accredited institute in Korea (Korea Institute of Energy Research, KIER).

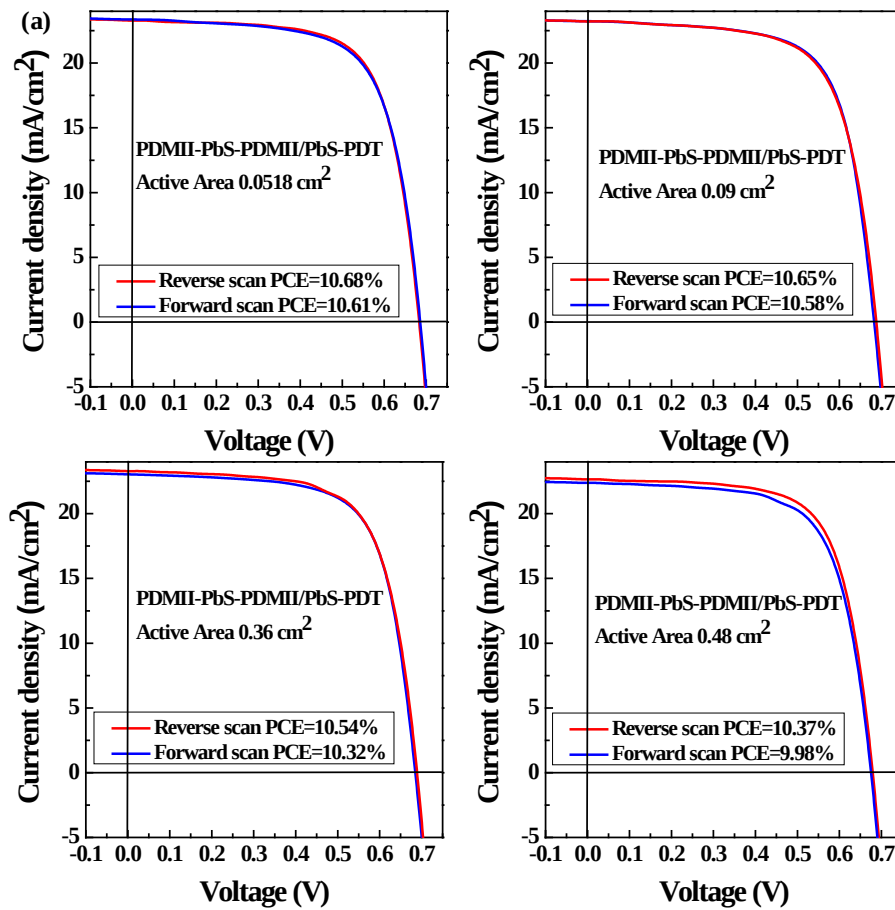


Figure S11. *J-V* characteristics under AM 1.5 G one-sun illumination (100 mW·cm⁻²) for reverse scan and forward scan with the following different active areas: (a) 0.0518 cm², (b) 0.09 cm², (c) 0.36 cm² and (d) 0.48 cm².

Table S1. Summary of the deconvoluted peaks of the O 1s spectra in Figure 3.

PbS-CQD	Component	Peak (eV)	FWHM	Area
o-PbS-TBAI	Pb-O	528.83	1.01	0.21
	Pb-OH	530.84	1.25	0.39
	COO, CO ₂	532.70	1.45	0.30
o-PbS-PDMII	Pb-O	528.80	0.99	0.20
	Pb-OH	530.81	1.36	0.38
	COO, CO ₂	532.65	1.52	0.17
TBAI-PbS-TBAI	Pb-O	529.13	1.35	0.09
	Pb-OH	530.85	0.87	0.20
	COO, CO ₂	532.40	1.87	0.11
PDMII-PbS-PDMII	Pb-O	529.10	1.49	0.05
	Pb-OH	530.79	1.42	0.18
	COO, CO ₂	532.42	1.90	0.06

Table S2. Summary of the DOS analysis. The DOS values from the TPV/TPC analysis were obtained at V_{MPP} , and those from the DLCP were obtained at 0.1 kHz.

Type	Density of states cm ⁻³ /eV (TPV/TPC)	Density of states cm ⁻³ (DLCP)
o-PbS-TBAI	5.2×10^{17}	5.3×10^{17}
o-PbS-PDMII	3.8×10^{17}	2.0×10^{17}
TBAI-PbS-TBAI	1.9×10^{17}	0.76×10^{17}
PDMII-PbS-PDMII	1.2×10^{17}	0.37×10^{17}

Table S3. Summary of charge collection properties of the devices by TPV, TPC, IMPS, IMVS, and collection efficiency. The light intensity for TPV is 0.5 mW.cm⁻².

CQD	τ_{rec} from TPV (μs)	τ_{rec} from IMVS (μs)	τ_{t} from TPC (μs)	τ_{ct} from IMPS (μs)
o-PbS-TBAI	5.5	1.16	2.1	0.46
o-PbS-PDMII	6.2	1.29	1.9	0.37
TBAI-PbS-TBAI	6.8	1.46	1.6	0.29
PDMII-PbS-PDMII	7.4	1.66	1.4	0.26

Table S4. Summary of the charge mobility and charge-diffusion length determined by TPV/TPC, SCLC and collection efficiency analyses. The detailed calculations are shown in the experimental section.

Type	μ_{t} from TPC ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_{e} from SCLC ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_{h} from SCLC ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	L_{D} from η (nm)
o-PbS-TBAI	$0.78 \cdot 10^{-3}$	$0.31 \cdot 10^{-4}$	$0.87 \cdot 10^{-5}$	55
o-PbS-PDMII	$0.81 \cdot 10^{-3}$	$0.36 \cdot 10^{-4}$	$0.11 \cdot 10^{-4}$	65
TBAI-PbS-TBAI	$0.92 \cdot 10^{-3}$	$0.45 \cdot 10^{-4}$	$0.16 \cdot 10^{-4}$	75
PDMII-PbS-PDMII	$0.97 \cdot 10^{-3}$	$0.49 \cdot 10^{-4}$	$0.20 \cdot 10^{-4}$	90

Transient photovoltage/photocurrent (TPV/TPC)

To determine the charge density, we also measured the photocurrent transient for an identical pulse at short circuit conditions, following the procedure described by Shuttle et al.[1] The V_{OC} perturbation transient was induced by a short change in the incident power at a given light bias. Subsequently, the change of charge density was obtained by integrating the short circuit current transient induced by only the laser pulse. This charge corresponds to the stored charge in the bulk of the film by assuming exciton generation was independent of an applied bias and recombination at the short circuit current was small. The density of states (DOS) for each open circuit voltage was obtained by integrating the capacitance over the voltage (see equation 1):

$$DOS = \frac{1}{Aed} \int_0^{V_{OC}} C dV \quad (1)$$

where A is the device area, e is the elementary charge of an electron and d is the film thickness. Here, DOS is related to the number of mid-gap states that need to be filled.

Drive-level capacitance profiling (DLCP)

The density of states (DOS) values were calculated following a reported model.[2] The capacitance with varying amplitude was obtained, and in order to achieve the correct capacitance value at a higher order, equation 2 was used.

$$C = C_0 + C_1 dV + C_2 (dV)^2 + \dots \quad (2)$$

After calculating C_0 and C_1 values, the DOS was obtained by equation 3:

$$DOS = \frac{C_0^2}{2e^2 A^2 C_1} \quad (3)$$

where A is the device area, e is the elementary charge of an electron and ϵ_r is the dielectric constant of PbS-CQDs.

Mobility calculations from the space charge limited current (SCLC)

The Mott-Gurney formula was used to extract the carrier mobility as follows:

$$J = \frac{9 \mu \epsilon_0 \epsilon_r V^2}{8 L^3} \quad (4)$$

where J is the current density, μ is the carrier mobility, ϵ_0 is the permittivity under vacuum, ϵ_r is the dielectric constant of PbS-CQDs, L is the film thickness of the active layer and V is the applied voltage.

Mobility calculation from the transient photocurrent (TPC) method

The carrier mobility can be extracted from TPC results following equation 5.[3]

$$\mu_t = \frac{L^2}{\tau_t \cdot V_{bi}} \quad (5)$$

where μ_t is the transit mobility, L is the thickness of the device, τ_t is the transit time from the photocurrent decay curve and V_{bi} is the built-in voltage.

Diffusion length calculation from the charge collection efficiency

We also used an analytical model employed in prior reports to fit the experimental data.[4]

The collection efficiency (η) was calculated as equation 6:

$$\eta(V) = \text{IQE}(\lambda, V = 0) \frac{J_H(V, \lambda) - J_L(V, \lambda)}{J_H(V = 0, \lambda) - J_L(V = 0, \lambda)} \quad (6)$$

where J_H and J_L are the current density values for higher (0.05 mW) and lower (0.004 mW) power under 680 nm (λ) monochromatic illumination. The IQE was calculated from the EQE

at short-circuit conditions and the absorption at this wavelength. The diffusion length was estimated by fitting the experimental data by the following analytical model equation 7:

$$\eta(V) = \left(\frac{1}{\kappa}\right)^{\gamma} \frac{1}{\gamma+1} [(\kappa)^{\gamma} - (\kappa - 1)^{\gamma}] \quad (7)$$

Where, κ and γ follow in equations 8 and 9:

$$\kappa = 1 + \frac{W(V) \sqrt{\frac{kT}{e\mu\tau_{rec}}}}{2(V_{bi}-V)} \quad (8)$$

$$\gamma = \frac{W(V)^2}{2(V_{bi}-V)\mu\tau_{rec}} \quad (9)$$

where $W(V)$ is adjusted to be the fully depleted device condition, T is the temperature (300 K), e is the elementary charge of an electron, V_{bi} is the built-in potential, μ is the mobility and τ_{rec} is the recombination time. Fitting the experimental data using this analytical method was performed with equation 7 to obtain the diffusion length value. This model works particularly well for drift-limited p-n junction models.

Depletion width calculation.

The depletion width was calculated following to equation 10:

$$W(V) = \frac{1}{N_a} \sqrt{\frac{2\epsilon_r\epsilon_0(V_{bi}-V)}{e\left(\frac{1}{N_a} + \frac{1}{N_b}\right)}} \quad (10)$$

where ϵ_r is the PbS-CQDs dielectric constant, N_a is the PbS-CQDs doping density, N_b is the ZnO doping density, e is the elementary charge of an electron and V_{bi} is the built-in potential of our devices. The ZnO doping density is 10^{17} cm^{-3} from a reference.[5]

To obtain the doping density of each PbS-CQD type, the dielectric constant was constructed using a parallel plate capacitor Au/PbS/Au following equation 11.

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (11)$$

The dielectric constant (ϵ_r) exhibited values of 17.51, 17.66, 17.82 and 17.98 for the o-PbS-TBAI, o-PbS-PDMII, TBAI-PbS-TBAI and PDMII-PbS-PDMII active layers, respectively. This shows that the dielectric constants for each different treatment of the PbS-CQDs were relatively the same.

The built-in potentials (V_{bi}) and doping density (N_a) of the PbS-CQDs active layers were obtained from a Mott–Schottky plot following equation 12.

$$\frac{1}{C^2} = \frac{2 (V_{bi} - V)}{A^2 e \epsilon_r \epsilon_0 N_a} \quad (12)$$

PLQY value were estimated by comparison with IR-26 dye, following the literature, using equation 13.[6]

$$\phi_{PL} = \frac{\int I_{sample}(\lambda) - r I_{ref}(\lambda)}{\int E_{sample}(\lambda) - E_{ref}(\lambda)} \quad (13)$$

where I indicates the measured intensity of the emitted light, E indicates the measured intensity of the excitation light, “sample” indicates measurements of the PbS-CQD samples, and “ref” indicates measurements of the reference IR-26.

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