Supplementary Information

Understanding charge transfer and recombination by interface engineering for improving the efficiency of PbS quantum dot solar cells

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EXPERIMENTAL SECTION

Materials. Lead (II) oxide (Wako, 99.5%), oleic acid (OA, Wako, 60%), 1octadecene (ODE, Aldrich, 90%), and bis(trimethylsilyl) sulfide (TMS₂ sulfide, Aldrich, 99.999%), cadmium chloride (CdCl₂, Wako, 99.8%), oleylamine (OLA, Aldrich, 70%), tetradecylphosphonic acid (TDPA, Aldrich, 97%), zinc acetate dihydrate (Wako, 99.9%), magnesium acetate tetrahydrate (Wako, 99%), 2aminoethanol (TCI, 99%), and 2-methoxyethanol (Wako, 99%) were used as purchased without further purification.

PbS quantum dot synthesis

Colloidal PbS QDs were synthesized according to a modified literature method,¹ different-sized PbS QDs were prepared as described previously in literature.² In this work, PbS QDs were manipulated using the standard Schlenk line techniques.⁶ The mixed solution of 6 mmol PbO, 15 mmol OA, and 50 ml of ODE in a 100 mL threeneck flask was stirred and degassed at room temperature and 90 °C for 20 min and 40 min, respectively. The solution was then heated for 1 h up to the required temperatures of 90, 130°C, followed by the injection of TMS solution (3 mmol TMS mixed with 10 mL pre-degassed ODE). After injection, the heater was removed immediately and the solution was kept stirred. When the solution was cooled down to 75 °C, a CdCl₂-TDPA-OLA solution containing 1 mmol CdCl₂, 0.1 mmol TDPA, and 3 mL OLA was injected into the PbS colloidal solution. After cooling down to the room temperature, PbS QDs were precipitated from the growth mixture and re-dispersed into an organic solvent toluene. The resulting precipitate was isolated by centrifugation, washed twice with acetone and methanol to remove the unbound OA ligands in PbS colloidal solution, and then dispersed in octane. The concentration of the PbS colloidal solution was about 100 mg·ml⁻¹.

ZnO compact layer synthesis

Solution-processed ZnMgO thin films were fabricated on FTO glass by a modified sol-gel method according to previous reports.^{3, 4} The FTO-glass substrates were cleaned

by ultrasonication sequentially in water, acetone, and isopropyl alcohol for 30 min each and then by ozone treatment for 10 min. $Zn_{1-x}Mg_xO$ (x=0-0.20) precursor solutions were prepared using a fixed molar ratio of zinc acetate dihydrate and magnesium acetate tetrahydrate dissolved in a mixture of 2-methoxyethanol and 2-aminoethanol under stirring overnight, where the ratio of 2-aminoethanol to total metal acetate was 1.0 and the total concentration of metal acetate was 0.3 M. These transparent solutions were spin-coated on the top of the FTO-glasses, which were pretreated by oxygen plasma for 5 min. Then the films were pre-heated on a hot plate at 150 °C for 10 min, and further transferred into an oven for annealing at 290 °C for 30 min.

Device fabrication

To fabricate PbS heterojunction solar cells, PbS colloidal QDs were prepared on ZnMgO compact layer by a typical layer-by-layer method using a fully automatic spincoater under ambient conditions. Each PbS colloidal layer was deposited at 2500 rpm and ligand exchange briefly with Hexadecyltrimethylammonium bromide (CTAB) solution (30 mM in methanol) was conducted also by spin-cast at 2500 rpm. The ligand exchange step was conducted twice to ensure complete ligand exchange with the oleic acid ligand on PbS surface. Each layer was then rinsed three times with methanol while spinning at 2500 rpm to remove excess unbound ligands. Then the PbS QD spin-coating procedure was repeated until desired thickness was reached. For PbS-EDT layers, PbS QD solution (100 mg \cdot ml⁻¹) was spin coated, followed by an EDT solution (0.1 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. Contacts consisting of ~100 nm of gold were deposited on the PbS layer through a mask to create four identical cells on each substrate by thermal evaporation. The contact sizes were 0.16 cm².

Characterization

Current-voltage characterization was performed with a Keithley 2400 source measuring under AM 1.5 G with solar simulator PEC-L10. The IPCEs were measured

by monochromatic illumination (300 W xenon arc lamp through Nikon G250 monochromator). The transient photovoltage decay measurements were carried out using a 630-nm diode laser (without a background light bias) with 5 ns pulse duration and 4 Hz pulse frequency. The voltage responses from the devices were recorded using an Iwatsu digital oscilloscope DS-5554. X-ray photoelectron spectroscopy (XPS) data were accumulated on a photoelectron spectrometer, S4 JPS-90MX (JEOL, Ltd., Japan). Field-emission scanning electron microscopy (FESEM) was carried out on a JEOL JSM-6340 F instrument (Japan). UV-vis absorption spectra were recorded with a spectrophotometer (HITACHI, U-3900H, Japan). PL decay was measured using a NIR PL lifetime spectrometer (C12132, Hamamatsu Photonics). Transient absorption (TA) measurements were performed using a fs TA setup. The laser source was a titanium/sapphire laser (CPA-2010, Clark-MXR Inc.) with a wavelength of 775 nm, a repetition rate of 1KHz, and a pulse width of 150 fs. The light was separated into two parts. One part was incident on a sapphire plate to generate white light for the probe beam. The other part was used to pump an optical parametric amplifier (OPA) (a TOAPS from Quantronix) to generate light pulses with a wavelength tunable from 290 nm to 3 µm. In this study, a pump light with a wavelength of 470 nm was used to excite the QDs. The pump light intensity is $15 \,\mu$ J/cm². Time-resolved TA spectra at 1500 nm were obtained with a temporal resolution of 100 fs. The photoelectron yield spectrum (PYS) was collected using a BIP-KV205 ionization energy measurement system (Model BIP-KV205, Bunkoukeiki Co, Ltd).



Figure S1. (a) Schematic diagrams illustrate the band alignment and charge recombination in the cells without ZnO (Left) and with ZnO (Right). (b) J-V curves for the PbS QD solar cells with and without ZnO layer under illumination. (c) J-V curves measured under dark conditions.



Figure S2. Photoelectron yield spectroscopy (PYS) spectra of the as-prepared $Zn_{1-x}Mg_xO$ films (x = 0, 0.05, 0.10, 0.15 and 0.20). The VBM is determined from the intersection of the tangent line with the baseline of the spectra.



Figure S3. (a) Absorption spectrum of the PbS QDs (E_g =1.19 eV) in octane. (b) PYS spectrum of the PbS QD thin films. The inset shows the vacuum energy level diagram of the PbS QDs.



Figure S4. (a)TEM image of PbS QDs. Inset displays size histogram. (b) High-resolution TEM image of PbS QDs; Inset displays SAED patterns of the corresponding PbS QDs.



Figure S5. (a) Gaussian fitting curves of ultraviolet (UV), violet, blue, green and yellow emissions, exhibiting several sub-bands with similar peak positions to those observed in excitation-dependent PL spectra at room temperature. (b) Schematic illustration of PL emission process in ZnO. The Kröger Vink notation uses: CB = conduction band, VB = valance band, C = center, i = interstitial site, Zn = zinc, O = oxygen, and V = vacancy.



Figure S6. Carrier densities of $Zn_{1-x}Mg_xO$ and PbS QD at room temperature derived from Hall measurement.



Figure S7. The traditional equivalent circuit model for solar cells. The photocurrent source is simply the result of converting absorbed photons to free charge by the solar cell, the diode represents electron-hole recombination at the p-n junction, the series resistor accounts for the internal resistance of the cell to current flow, and the shunt resistor represents model's leakage current through the cells (e.g., via pinholes). Note that the diode represents recombination current.

Effective Carrier Lifetime

The effective carrier lifetime (τ_{eff}) in the PbS QDHSCs from the photovoltage decay can be evaluated as defined by the following equations:^{5, 6}

$$\tau_{eff} = -\left(\frac{kT}{q}\right) / \frac{dV_{oc}}{dt} = \frac{1}{\left(\tau_n^{-1} + \tau_p^{-1}\right)}$$

$$\tau_n^{-1} = \frac{(dn/dt)}{n}$$
(5)

$$\tau_p^{-1} = \frac{(ap/at)}{p} \tag{6}$$

where k is the Boltzmann constant, T is the temperature, q is the elementary charge, and n, p is the photoexcited electron and hole carrier densities in the PbS QDHSCs, respectively. τ_n and τ_p are the electron and hole lifetimes in the PbS QDHSCs. According to the above equations, the open-circuit photovoltage decay is dependent on both the electron and hole lifetimes in PbS QDHSCs.



Figure S8. (a) Absorption spectrum of the L-PbS QDs (E_g =1.11 eV) in octane. (b) PYS spectrum of the L-PbS QD thin films. The inset shows the vacuum energy level diagram of the L-PbS QDs.



Figure S9. (a)TEM image of L-PbS QDs. Inset displays size histogram. (b) Highresolution TEM image of L-PbS QDs; Inset displays SAED patterns of the corresponding L-PbS QDs.



Figure S10. Statistics of the device performance using two sizes of PbS QDs and $Zn_{1-x}Mg_xO$ electron transporting layer (x=0, 0.05, 0.10, 0.15, 0.20): (a) J_{sc} , b) V_{oc} , (c) *FF*, and (d) PCE. The solid data points represent the average values, and the error bars stand for the standard deviations.



Figure S11. PL decay curves of PbS QDs (oleic acid-passivated) of both sizes (i.e., M-PbS and L-PbS) at room temperature.



Figure S12. A schematic diagram of the TA setup, showing the concept of the pumpprobe experiments. The pump and probe pulses overlap in the heterojunctions, and the absorbance change in the probe pulse is detected at different time delays.



Figure S13. TA responses of (a) the free PbS QDs in solution and PbS QD layer deposited on glass substrate, and (b) glass/ZnO/PbS QDs and glass/Zn_{1-x}Mg_xO/PbS QD samples measured with a pump light wavelength of 470 nm and probe light wavelength of 1500 nm and pump light intensity of 15 μ J/cm².



Figure S14. *J-V* curves of the best performing photovoltaic devices under AM 1.5G illumination. The structure of the solar cell device is $FTO/Zn_{1-x}Mg_xO/M-PbS/EDT-PbS/Au$ (x=0, 0.05, 0.10, 0.15, 0.20).

Table S1.	. Statistical	Averages of	f the Photovol	taic Performan	ce Parameters	of 12 E	Devices for
Each Typ	oe of the QD	HSCs ^a .					

Sample	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}$	FF	PCE
		(mV)		(%)
x=0	26.58±0.89	578.2±4.4	0.529±0.012	8.11±0.27
	(27.37)	(571)	(0.534)	(8.35)
x=0.05	28.86±1.41	584.4±7.9	0.535±0.009	8.89±0.17
	(28.98)	(580)	(0.541)	(9.08)
x=0.10	30.35±1.48	591.6±10.8	0.549±0.013	9.96±0.11
	(30.41)	(590)	(0.563)	(10.10)
x=0.15	31.84±0.36	590.8±5.2	0.560±0.009	10.49±0.10
	(31.52)	(590)	(0.570)	(10.60)
x=0.20	32.04±0.76	585.5±3.7	0.535±0.012	9.77±0.14
	(31.81)	(585)	(0.532)	(9.92)

^aResults for the device with the highest PCE are shown in parentheses.

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