Electronic Supplementary Materials

Suppression of Hydroxylation on Surface of Colloidal Quantum Dots to Enhance Open-Circuit Voltage of Photovoltaics

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Experimental

Synthesis of PbS CQDs: Lead acetate (II) trihydrate (Sigma–Aldrich, 99.999%), OA (Alfa Aesar, 99%), 1-octadecence (Sigma–Aldrich, 90%), and bis(trimethylsilyl) sulfide (Sigma–Aldrich) were used as purchased, without further purification. OA-capped PbS CQDs were prepared as previously described.[1]

Precipitation-redispersion Purifications of PbS CQDs: The first precipitation was conducted by injecting acetone into the crude solution. After the first precipitation was dispersed with toluene, the second precipitation was conducted by injecting a mixture of acetone and methanol into PbS CQDs in toluene. The final precipitation was conducted by injecting methanol into the PbS CQDs dissolved in toluene. The anhydrous solvents were used and the purification occurred in nitrogen glove-box condition.

Surface Modification of PbS CQDs for Ink Powders: Methylammonium iodide (0.174 g) and lead iodide (0.552 g) were dissolved in dimethylformamide (DMF) (10 mL) for the CQD-ink process (iodide solution).
1. OH-poor PbS CQD-ink: The crude solution of PbS CQDs (2 mL) was mixed with octane (8 mL). This mixture was directly injected into the iodide solution, followed by blending for 2 min. After ligand exchange, PbS CQDs were precipitated by toluene and redispersed in butylamine.
2. OH-rich PbS CQD-ink: Purified PbS CQDs were prepared (10 mg/mL, 10 mL). They were mixed with the iodide solution, followed by blending for 2 min. After ligand exchange, PbS CQDs were precipitated by toluene and redispersed in butylamine.

Device Fabrication: Patterned ITO was washed with methanol and acetone. ZnO nanoparticles were spin-coated onto the ITO substrates at 3000 rpm for 30 s. PbS CQD-ink (200 mg/mL) was spin-coated to form a PbS CQD layer 300 nm thick. 1,2-Ethanedithiol (EDT)-treated PbS CQDs were fabricated using a previously reported method. An Au electrode of 100 nm thick was thermally evaporated onto the EDT-treated CQD films.

Characterization of PbS CQDs: The absorption spectra were measured using an ultraviolet/visible/near-infrared spectrophotometer (Shimadzu, UV3600). The PL spectra were measured using a PL spectrometer (Fluorolog, Horiba Jobin Yvon). Each OA-capped PbS CQD and PbS CQD-ink was dissolved in tetrachloroethylene and DMF for absorption and PL

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measurements. To measure the XPS spectra, a PHI Quantera-II spectrometer with an Al anode (Al Kα = 1486.7 eV) was used. The XPS samples were spin-coated onto a Si wafer. UPS was performed using a hemispherical electron energy analyzer with a charge-coupled device camera (SES-100, VG-Scineta) with He I (21.22 eV) under 10^{-9} Torr. To prevent the charging effect of the CQDs, ITO glass was used as a substrate.

Characterization of PbS CQD Solar Cells: The *J–V* and light intensity–voltage characteristics were measured using a solar simulator (Sol3A Class-94043A, Newport). A 450-W Xe short-arc lamp filtered by an AM 1.5G filter and a 4.9-mm^2 mask were used to measure the current density. The light intensity was calibrated by reference cell (Newport Oriel 91150V). The EQE was recorded using a spectral measurement system (IQE-200, Newport). The TPV and TPC were measured using an oscilloscope (TDS3012B, Tektronix) and a function generator (332550A, Agilent). All characterization of solar cells was measured in the air condition, 27℃.

DOS Calculation: The DOS was calculated using the TPV and TPC, via the "differential charging" procedure reported by Shuttle et al.[2] The differential capacitance was determined according to the change of the charge density (integral of the photocurrent) with respect to the voltage. Then, the density of midgap trap states (n) was expressed as a function of the V_{OC}:

$$n = \frac{1}{eAd}\int_0^{V_{OC}} CdV,$$

where *e* represents the electron change, *A* represents the device area, and *d* represents the film thickness.
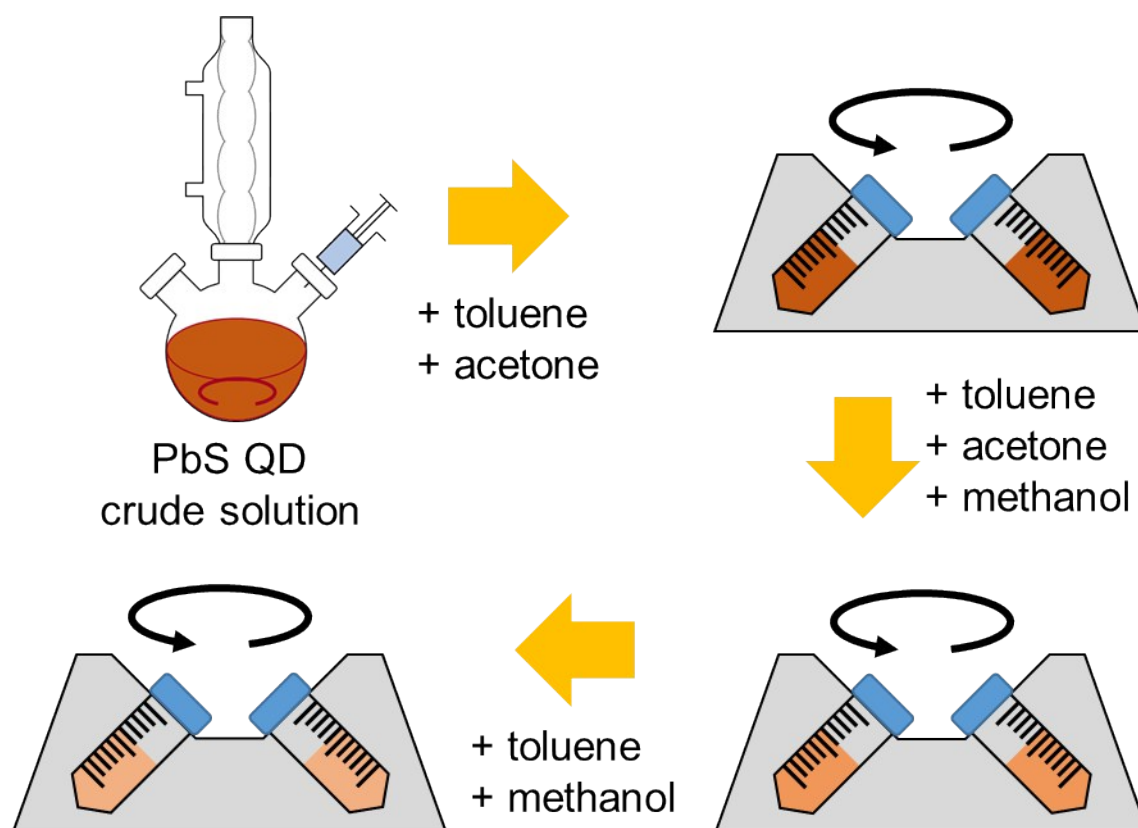
Scheme S1 Detailed purification steps for the PbS CQDs. To remove the byproduct, methanol was used more than two times, commonly believed.
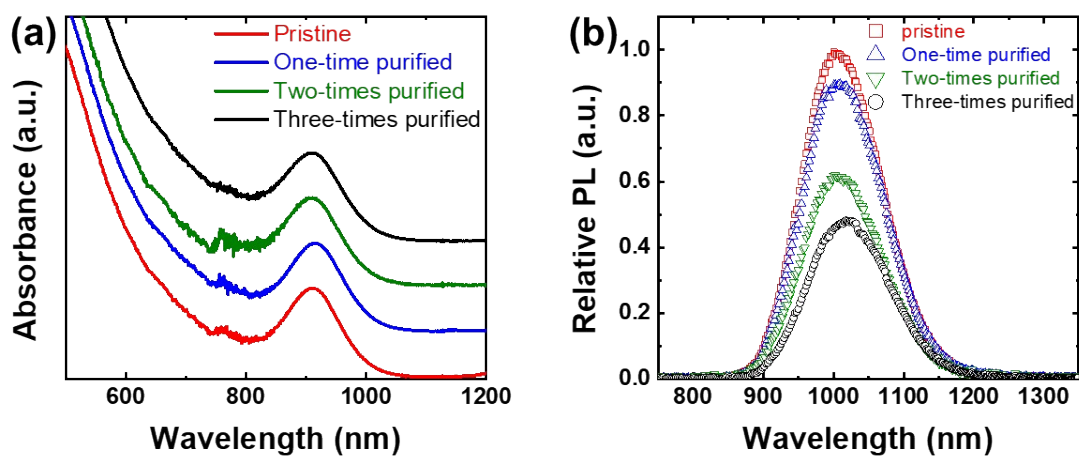
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Fig. S1 Absorption and PL spectra of PbS CQDs purified different numbers of times. The solution used for each step matches Scheme S1. The methanol-based purification was the main reason for the reduced PL intensity.
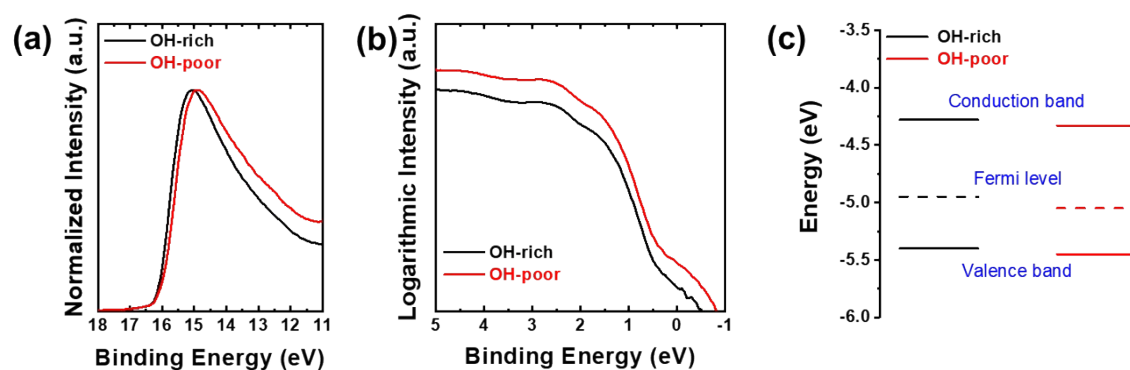

Fig. S2 Ultraviolet photoelectron spectra of OH-rich and OH-poor PbS CQDs. a) Secondary cutoff region of the ultraviolet photoelectron spectra. b) Valence band region of the ultraviolet photoelectron spectra. c) Energy-level diagram based on the ultraviolet photoelectron spectra and optical absorption bandgap.
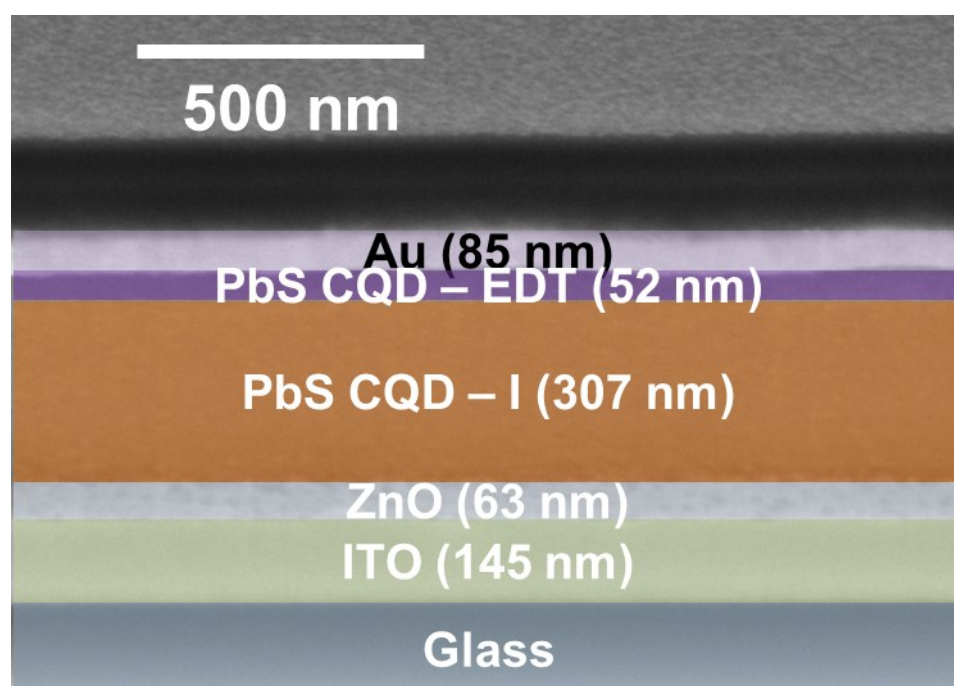

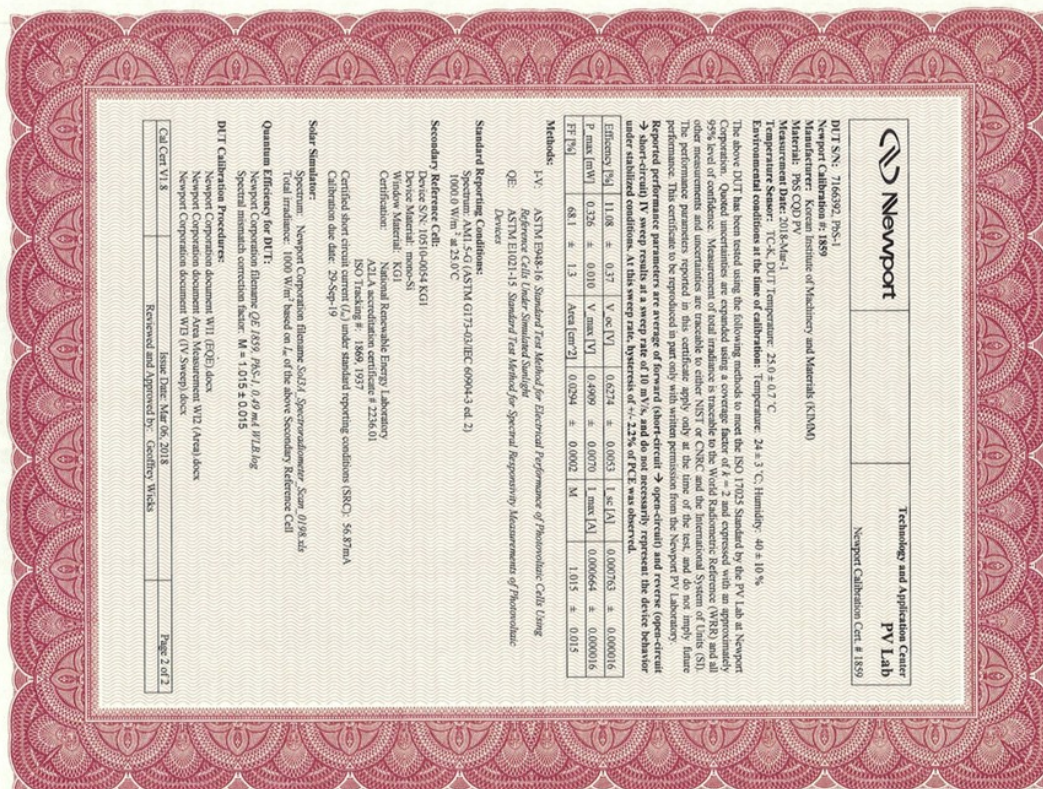**Fig. S3** Cross-sectional SEM topographic image of the PbS CQD solar cells.

Fig. S4 Certificates for PbS CQD solar cells based on a) OH-rich and b) OH-poor CQDs
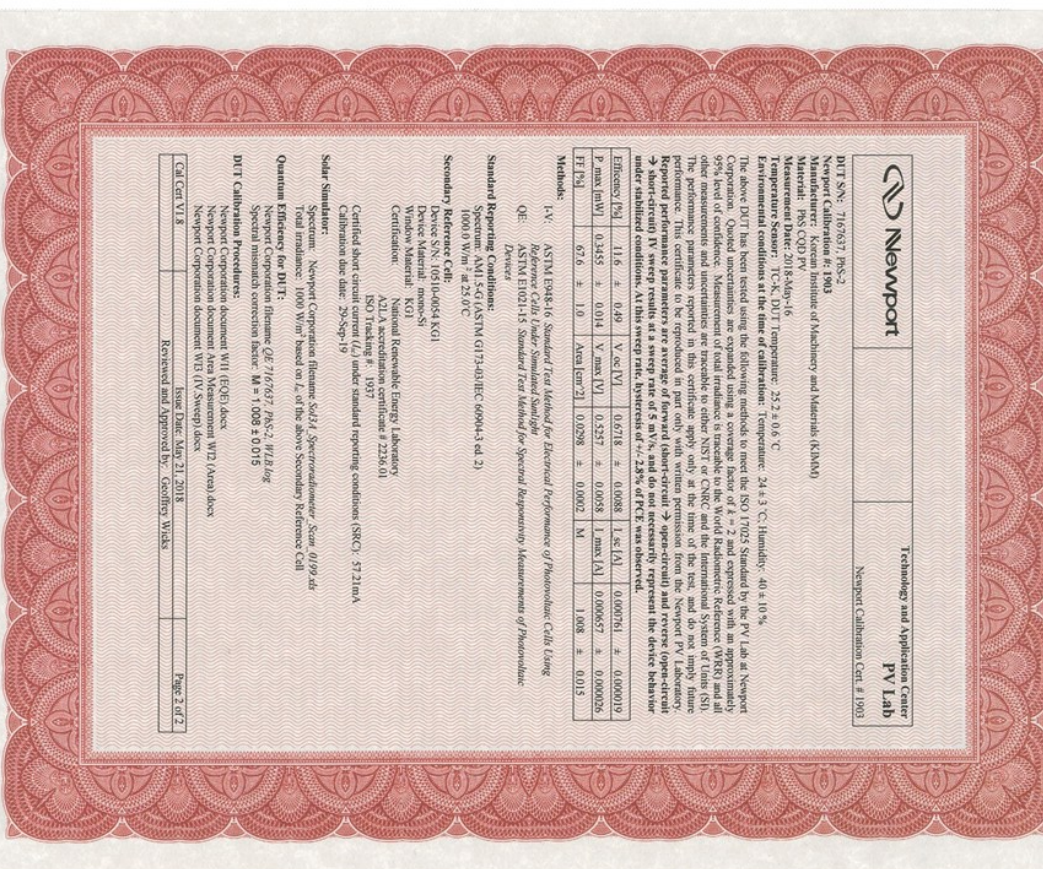
Table S1 Peak

PbS CQDs
OH-poor CQD (OA)
OH-rich CQD (OA)

(a)

(b)

OH-poor CQD (I)	
OH-rich CQD (I)	

a)Absorption; b)

Table S2 XPS

| PbS CQDs a) | O(total)/Pb | OH b)/Pb | COO c)/Pb |

OH-rich	1.14 ± 0.02	0.31 ± 0.12	0.17 ± 0.07	0.14 ± 0.05
OH-poor	1.16 ± 0.01	0.29 ± 0.11	0.09 ± 0.03	0.20 ± 0.08

[a]Iodide-treated CQDs; [b]hydroxyl group; [c]carboxyl group

1   J. H. Song, H. Choi, Y. H. Kim and S. Jeong, *Adv. Energy Mater.*, 2017, **7**, 1700301.

2   C. G. Shuttle, B. O'Regan, A. M. Ballantyne, J. Nelson, D. D. C. Bradley, J. De Mello and J. R. Durrant, *Appl. Phys. Lett.*, 2008, **92**, 93311.