Electronic Supplementary Information

Design and development of highly efficient PbS quantum dot-sensitized solar cells working in an aqueous polysulfide electrolyte

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1. Experimental Procedures

Preparation of TiO_2 paste. The viscous TiO_2 paste, used for the preparation of nanoporous oxide electrode, was prepared by following procedure. 0.2 g ethyl cellulose (viscosity: 46 cP, Aldrich), 0.1 g lauric acid (Aldrich) and 4.0 g terpineol (Aldrich) were added to the 10 mL ethanol suspension of 1.0 g TiO_2 (20 nm-sized nanoparticle in the anatase phase), and the ethanol was removed from the solution by rotary evaporator in a water bath at 60^{o}C to obtain viscous paste. It was then blended at 1200 rpm for 90 min in a paste mixer (PDM-300, Dae-Wha Tech.).

Deposition of TiO_2 layer. The prepared TiO_2 paste was coated on the FTO layer with a doctor-blade method. 60 μm-thick 3M tape was used as spacer in coating the paste by doctor blade, and the coated film was dried at 150^{o}C for 30 min. In calcination, the temperature was elevated to 500^{o}C with a ramping speed of 5^{o}/min, and maintained for 15 min.

Deposition of PbS QDs. PbS QDs were deposited onto the TiO_2 layer by a typical (successive ionic layer adsorption and reaction) SILAR method. TiO_2 films were immersed in 0.02 M $Pb(NO_3)_2$ (Aldrich) methanol solution for 1 min, and washed several times by methanol. It was then immersed in 0.02 M Na_2S (Aldrich) in methanol/H_2O (1:1 in volume) solution for 1 min, and washed several times by methanol. This SILAR cycle was repeated three times for the deposition of PbS QDs. Afterwards, a thin ZnS layer was deposited to passivate the PbS surface. 0.05 M $Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich) ethanol solution and 0.05 M

Na_2S (Aldrich) in methanol/H_2O (1:1 in volume) solution were used for the deposition of ZnS layer by SILAR process.

HTR process. The as-prepared ZnS/PbS/TiO_2 films were post-treated by a heat-treatment and regeneration (HTR) process. That is, the as-prepared films were heat-treated at 250^{o}C in air for 30 min. For the regeneration of PbS phase, the heat-treated films were immersed in methanol/H_2O 7:3 solution of 0.125 M S/0.500 M Na_2S. Actually, in fabricating the PbS QDSCs, we omitted this regeneration step to simplify the process. The ZnS/PbS(3)/TiO_2 films after heat-treatment were directly used for the assembly of the cells, and they were then regenerated by the electrolyte filled in the cell. In this case, the composition of electrolyte was 0.125 M S, and 1.50 M Na_2S in deionized H_2O.

Preparation of CuS/FTO and Au/CuS/FTO

0.02 ml of 0.30 M $Cu(NO_3)_2 3H_2O$ in methanol solution was dropped on an FTO substrate (1.5×2.0 cm^2), and dried at ambient condition for 5 min. It was then inserted in a vacuum-tight tube furnace (Lindberg). Temperature was elevated to 100^{o}C with a ramping speed of 5^{o}C/min under pure Ar atmosphere. At 100^{o}C, flowing gas was changed to 1/99 H_2S/Ar to sulfurize the coated film. Typically, pure CuS/FTO was obtained by flowing 1/99 H_2S/Ar for 5 min at 100^{o}C. Photographic image of the prepared CuS/FTO film is shown in Figure S1.

Assembly of PbS QDSC. Au films deposited on the FTO substrate was used as counter electrode (CE). About 20 nm-thick Au layer was deposited on the FTO by a sputter (EXT75 DX, Edwards) operated at 40 mA for 1 min. The gap between the ZnS/PbS/TiO_2 films and the CE was adjusted to 60 μm by applying a Surlyn (Meltonix 1170-60, Solaronix). The composition of electrolyte was 0.125 M S, and 0.50–1.50 M Na_2S in deionized H_2O. The active area of the film, defined by a shadow mask, was 0.42 cm^2.

Characterizations. Transmission electron microscopy (TEM) images were obtained by a JEOL JEM2100F operated at 200 kV. One milligram of the particles, detached from the PbS/TiO_2 layer, was dispersed in 50 mL of ethanol, and a drop of the suspension was then spread on a holey amorphous carbon film deposited on the copper grid. X-ray photoelectron spectroscopy (XPS) analyses of the several PbS QDs were carried by a Sigma Probe Instrument (Thermo VG, U.K.) equipped with a standard monochromatic Al Kα excitation source ($h\nu$ = 1486.6 eV). The binding energy scale was calibrated by measuring a C 1s peak at 284.5 eV from the surface contamination.

Photocurrent-voltage (I-V) measurements were performed using a Keithley model 2400 source measurement unit. A 300 W Xenon lamp (Spectra-Physics) was used as the light source and the light intensity was adjusted using an NREL-calibrated Si solar cell equipped with a KG-5 filter for approximating AM 1.5G one sun light intensity. Incident photon to current efficiency (IPCE) was measured as a function of wavelength from 360 nm to 1100 nm using a specially designed IPCE system (PV Measurements, Inc.).

2. I-V characteristics of several QDSCs

Table S1. Photovoltaic properties of PbS QDSCs prepared with different conditions.

CE	HTR process	TiO_2 structure	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
Au/FTO	No	NP	337	14.21	20.1	0.96
CuS/FTO	No	NP	346	15.36	46.6	2.47
Au/CuS/FTO	No	NP	358	17.01	45.2	2.75
CuS/FTO	Yes	NP	404	16.29	58.9	3.87
Au/CuS/FTO	Yes	NP	414	18.76	56.7	4.40
Au/CuS/FTO	Yes	NP/SP	420	24.17	56.4	5.73

3. Characterization of CuS/FTO and Au/CuS/FTO

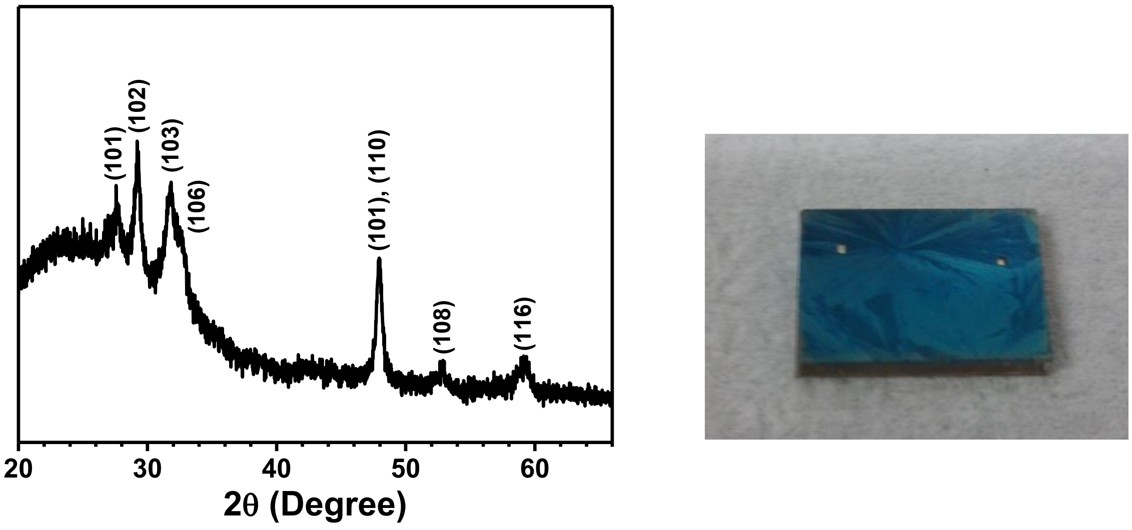

Fig. S1. XRD patterns and photographic image of the CuS film deposited on FTO substrate.

The SEM image in Fig. S2 shows the cross-sectional image of Au/CuS/FTO. The thickness of Au deposited on CuS/FTO was estimated to be ~20 nm. The Au in the fcc phase was identified from the XRD patterns in Fig. S3. The electrocatalytic activities of the CEs (Au/FTO, CuS/FTO, Au/CuS/FTO) were analyzed by electrochemical impedance spectra (EIS). The symmetrical dummy cells, consisting of the same CEs positioned in the WE and CE sides, were fabricated by filling the electrolyte (0.5M Na_2S and 0.125M S in water).[S1-S4] Based on the equivalent circuit in the inset of Figure S4, Nyquist plots of were obtained for these dummy cells by sweeping the frequency from 100 kHz to 0.1 Hz without applying bias voltage in close-circuit condition (See Fig. S4 and its inset.). In the equivalent circuit, R_S denotes to series resistance, R_{CT} charge transfer resistance of one electrode, and C capacitance of one electrode, while Z_N denotes to Nernst diffusion impedance in the pores of the electrode material. The determined R_S and R_{CT} by fitting the impedance plots using the Z-view software are listed in the Table S2. Compared to Au/FTO, CuS/FTO exhibited dramatically smaller R_{CT} value than Au/FTO, even though R_S was appreciably increased. By depositing Au on the CuS/FTO, both the R_S and R_{CT} were significantly decreased, inducing smaller series resistance as well as improved electrocatalytic activity.

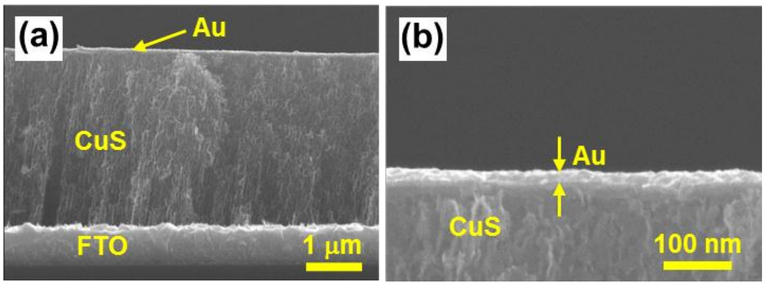

Fig. S2. Cross-sectional SEM images of the Au/CuS/FTO CE

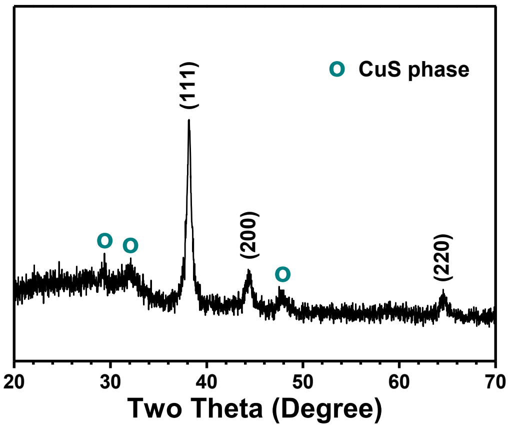

Fig. S3. XRD patterns of the Au/CuS/FTO CE. The peaks inherent from Au were indexed.

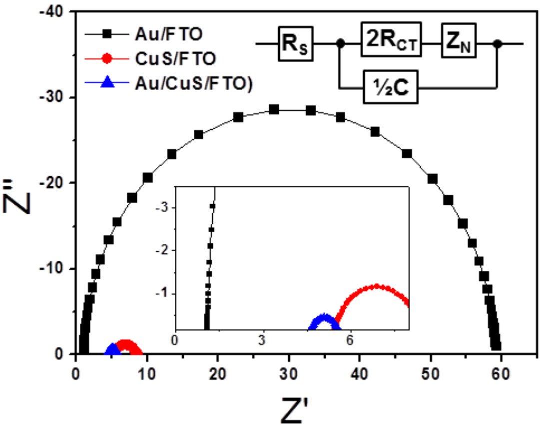

Fig. S4. Nyquist plots of electrochemical impedance spectra measured from 100 kHz to 0.1 Hz in closed circuit condition.

Table S2. Series resistance and charge transfer resistance of several CEs

Electrode	R_S (Ω)	R_{CT} (Ω)
Au	1.10	23.91
CuS	5.40	1.49
Au/CuS	4.56	0.63

4. Photostability of several PbS QDSCs

The stability test was performed under closed-circuit condition without applying bias voltage. Photocurrent of the PbS QDSCs was repeatedly measured at 0.1 sec interval under continuous illumination of 1 Sun (100 mW/cm^2). Au/FTO, CuS/FTO, Au/CuS/FTO and Cu_2S/brass have been applied as CE, and their stability was compared, as shown in Fig. S5. It was found that CuS/FTO exhibits relatively higher stability than Cu_2S/brass.

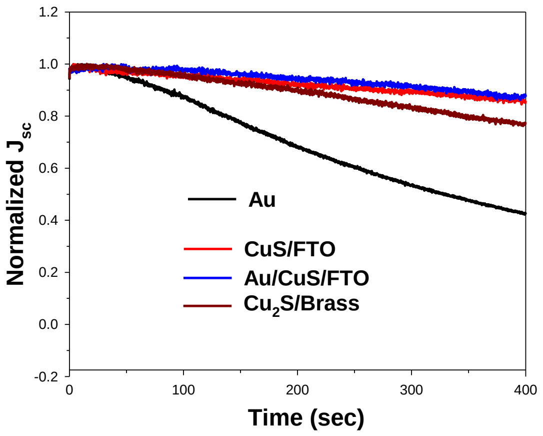

Fig. S5. Photostability of PbS QDSCs depending on CEs.

5. Temperature dependence for the HTR process

Temperature for the HTR process was varied up to 300°C. I-V curves of the cells, processed at different HTR temperatures, are shown in Fig. S6. It is indicated that 250°C is the optimized temperature for the HTR process. With HTR process at 150-250°C, both the V_{oc} and J_{sc} increased significantly. By elevating the temperature to 300°C, however, the V_{oc} and J_{sc} of PbS cells were rather decreased, suggesting that the oxidized lead sulfide at high temperature is difficult to return back to PbS phase by the regeneration process. The XRD patterns for the PbS/TiO_2 films, processed at different HTR temperatures, are shown in Fig. S7 and S8. The crystallite sizes of PbS QDs were increased by the HTR process, but they do not seem to be strongly dependent on the process temperature in the range of 150-300°C.

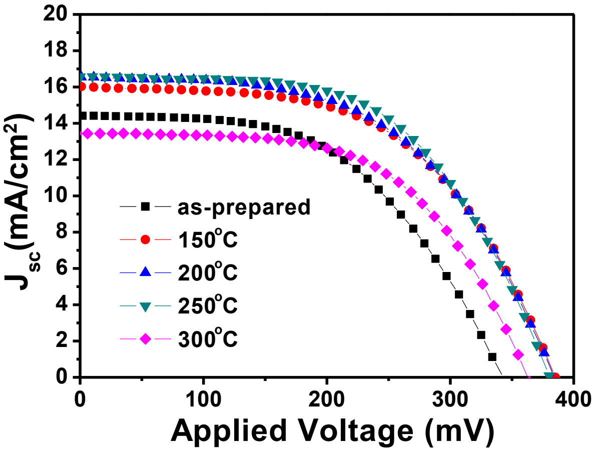

Fig. S6. I-V curves for the HTR-treated PbS QDSCs at different temperatures. CuS/FTO was used as CE.

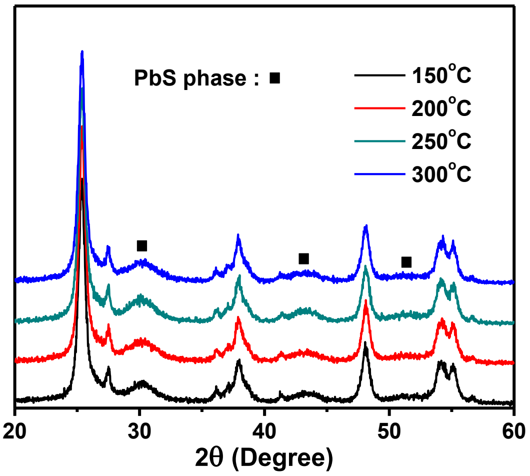

Fig. S7. XRD patterns of for the HTR-treated PbS QDSCs at several process temperatures.

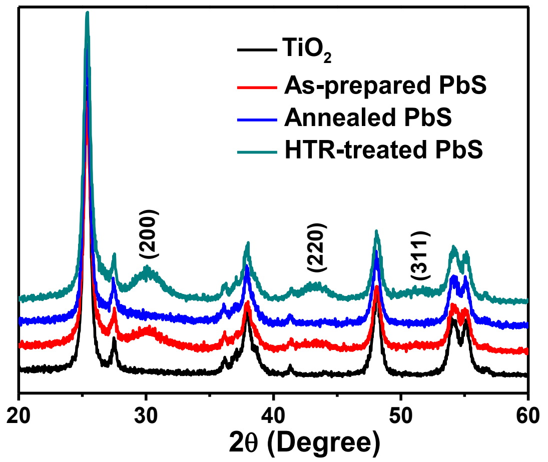

Fig. S8. XRD patterns of the bare TiO_2 and several PbS/TiO_2 photoelectrodes. The HTR treatment was performed at 250°C.

6. Absorbed photons to current efficiency (APCE) of the PbS QDSCs

APCE spectrum can be obtained from the corresponding IPCE and LHE spectra. Light harvesting efficiency (LHE) of the cell can be determined from the absorbance spectra by the equation (1).

$$\mathrm{LHE}(\%) = 1 - 10^{-\mathrm{Absorbance}} \qquad (1)$$

Then the absorbed photons to current efficiency (APCE) can be calculated according to the equation (2).

$$\mathrm{APCE}(\%) = \mathrm{IPCE}(\%) / \mathrm{LHE}(\%) \qquad (2)$$

Fig. S9 shows the APCE spectrum of the optimized PbS QDSC, determined by this method. In the short wavelength region, the APCE value was as high as 96%.

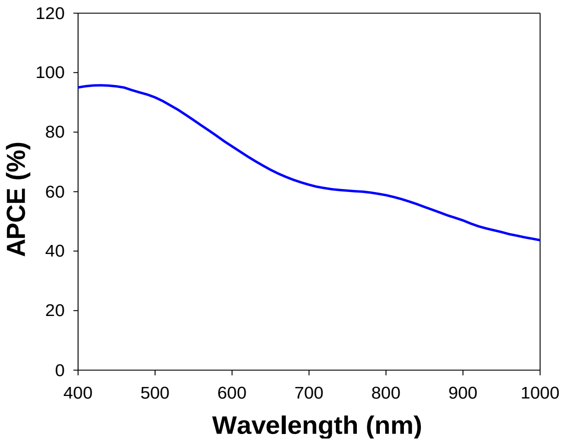

Fig. S9. Spectra for the APCE transformed from the corresponding IPCE and LHE spectra.

7. EIS analysis for the as-prepared and HTR-treated PbS QDSCs

Nyquist plots were obtained under dark condition, from 100 kHz to 0.1Hz with applying -0.3 V of bias voltage,[S5] as shown in Fig. S10. The HTR-treated PbS cell exhibited higher charge transport resistance (R_{CT}) and longer electron life time, as shown in Table S3.

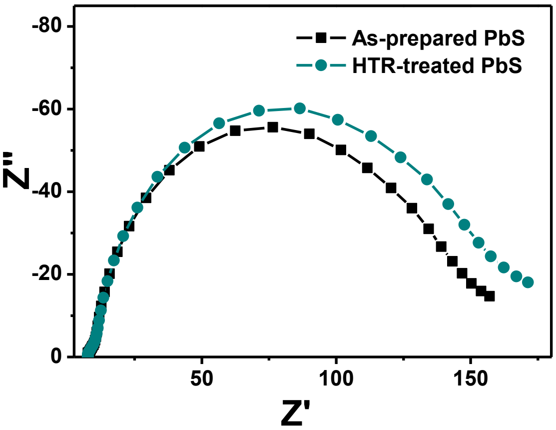

Fig. S10. Nyquist plots of EIS obtained from 100 kHz to 0.1Hz with applying -0.3 V of bias voltage for the as-prepared and HTR-treated PbS QDSCs.

Table S3. Determined RCT, capacitance and electron life time for the for the as-prepared and HTR-treated PbS QDSCs.

	R_{CT} (Ω)	Capacitance (mF/cm^2)	electron life time (ms)
As-prepared	126.7	1.61	48
HTR-treated	137.1	1.83	59

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