Supporting Information

Integration of Photoelectrochemical Device and Luminescent Solar Concentrator based on Giant Quantum Dots for Highly Stable Hydrogen Generation†

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S1. Experimental Section

Materials

Cadmium oxide (CdO, 99%), selenium pellet (Se,99.999%), sulphur (S, 100%), oleyamine (OLA), oleic acid (OA), octadecene (ODE), trioctyl phosphine oxide (TOPO), trioctyl phosphine (TOP), zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$, 98%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, ≥ 99.9%), sodium sulfite (Na_2SO_3, ≥ 98%), lauryl methacrylate (LMA), ethylene glycol dimethacrylate (EGDM), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, hexane, toluene, methanol, and ethanol were obtained from Sigma-Aldrich Incorporation. TiO_2 pastes (18NR-AO, mixture of 20 nm and 450 nm) were purchased from Greatcell Solar, Australia. Solution Ti-nanoxide was brought from Sunlaite Co., Ltd., China. Transparent fluorine doped tin oxide (FTO) coated conducting glass substrates were purchased from Pilkington.

Synthesis of CdSe QDs

Cd-oleate ($Cd(OA)_2$, 0.38 mmol, 1 mL) and TOPO (1 g) in 8 mL of ODE were purged by nitrogen at 110 °C for 30 min. Then the temperature was raised to 300 °C. The mixture of TOP-Se (4 mmol, 4 mL), 3 mL of OLA and 1 mL of ODE at room temperature was quickly injected into the Cd-oleate suspension under vigorous stirring. Subsequently, the reaction temperature dropped to 240 °C. After 5-min reaction, the reaction cell was quenched with cold water. Ethanol was added,

and then the suspension was centrifuged and the supernatant was removed. The QDs were dispersed in toluene or hexane for further characterization or shell coating.

Synthesis of CdSe/CdS QDs and CdSe/CdSSe/CdS QDs

In a 100 mL round-bottom flask, OLA (5 mL), ODE (5 mL) and CdSe QDs (~ 2×10^{-7} mol in hexane) were degassed at 110 °C for 30 min. The reaction flask was re-stored with N_2 and the temperature was further raised to 240 °C under stirring. The $Cd(OA)_2$ dispersed in ODE (0.25 mL, 0.2 M) was added dropwise and the mixture was allowed to react for 1 h, followed by dropwise addition of 0.2 M S or $S_{0.5}Se_{0.5}$ in ODE with same volume. The shell was further annealed for 10 min. For CdSe/CdS QDs, the addition volumes of S/$Cd(OA)_2$ for shell addition cycles 1-15 were as follows: 0.25, 0.36, 0.49, 0.63, 0.80, 0.98, 1.18, 1.41, 1.66, 1.92, 2.20, 2.51, 2.80, 3.25 and 3.6 mL, respectively. For CdSe/CdSSe/CdS QDs, the addition volumes of $S_{0.5}Se_{0.5}$/$Cd(OA)_2$ for shell addition cycles 1-5 were as follows: 0.25, 0.36, 0.49, 0.63, 0.80 mL, respectively. After 5-cycle growth of CdSSe alloyed layer, the S/$Cd(OA)_2$ precursors were used for further growth of 1-cycle CdS layer with the addition volume of 0.98 mL. Then the reaction flask was cooled down to room temperature. Ethanol was added, and then the suspension was centrifuged and the supernatant was removed. The QDs were then dispersed in toluene for further characterization and device fabrication.

SII. Characterizations and Mathematical Analysis

Materials characterization

XRD analysis was performed by a Rigaku Smartlab XRD using a Cu-Kα radiation source (λ = 0.15418 nm) with a step scan of 2°/min. TEM examination of the QDs was carried out using a JEOL JEM2100F TEM equipped with an EDS. Absorption spectra were recorded using a TU-1901

double beam UV-Vis spectrophotometer. PL spectra were performed by a Cary Eclipse fluorescence spectrophotometer.

Calculation of H_2 evolution based on the photocurrent

The theoretical number of moles of H_2 evolution was obtained by Faraday's law[1]:

$$Mole\ of\ H_2 = \frac{q}{zF} = \frac{I \times t}{zF} = \frac{\int_0^t Idt}{zF} \quad (4)$$

where z is the number of transferred electrons per mole of water, q is the electric charge in coulombs (C), F is the Faraday's constant (C/mole), I is the photocurrent in Ampere and t is the time in seconds.

SIII. Supporting Figures and Tables

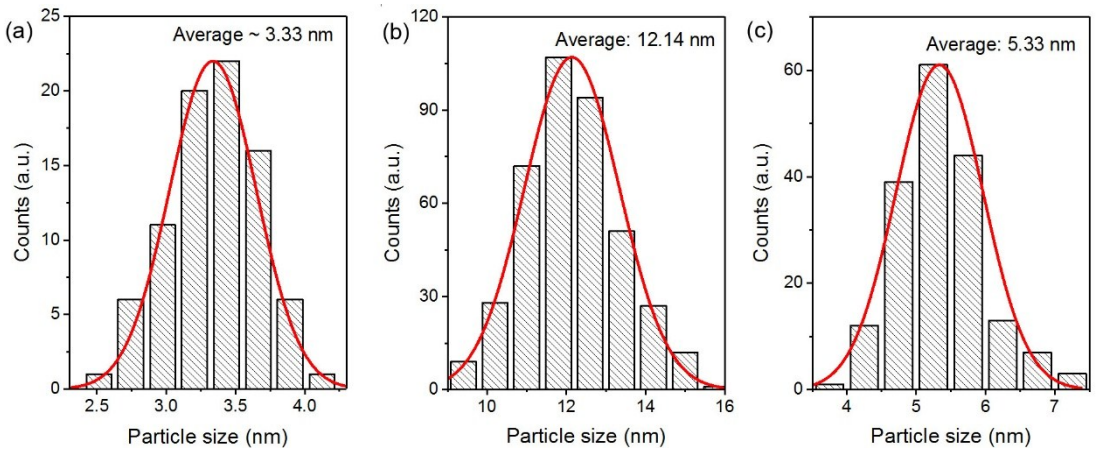

Fig. S1 Size distributions of CdSe core QDs (a), CdSe/$(CdS)_{15}$ core/shell QDs (b) and CdSe/$(CdSSe)_5$/CdS core//multi-shell QDs c), respectively.

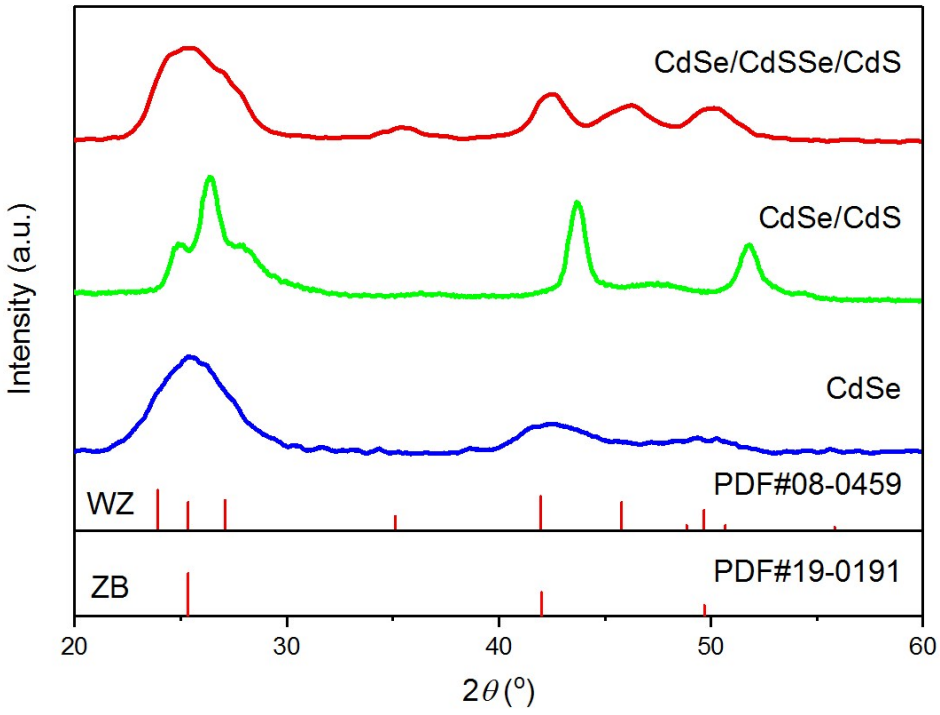

Fig. S2 XRD patterns of CdSe QDs, CdSe/CdS core/shell QDs and CdSe/CdSSe/CdS core//multi-shell QDs, respectively.

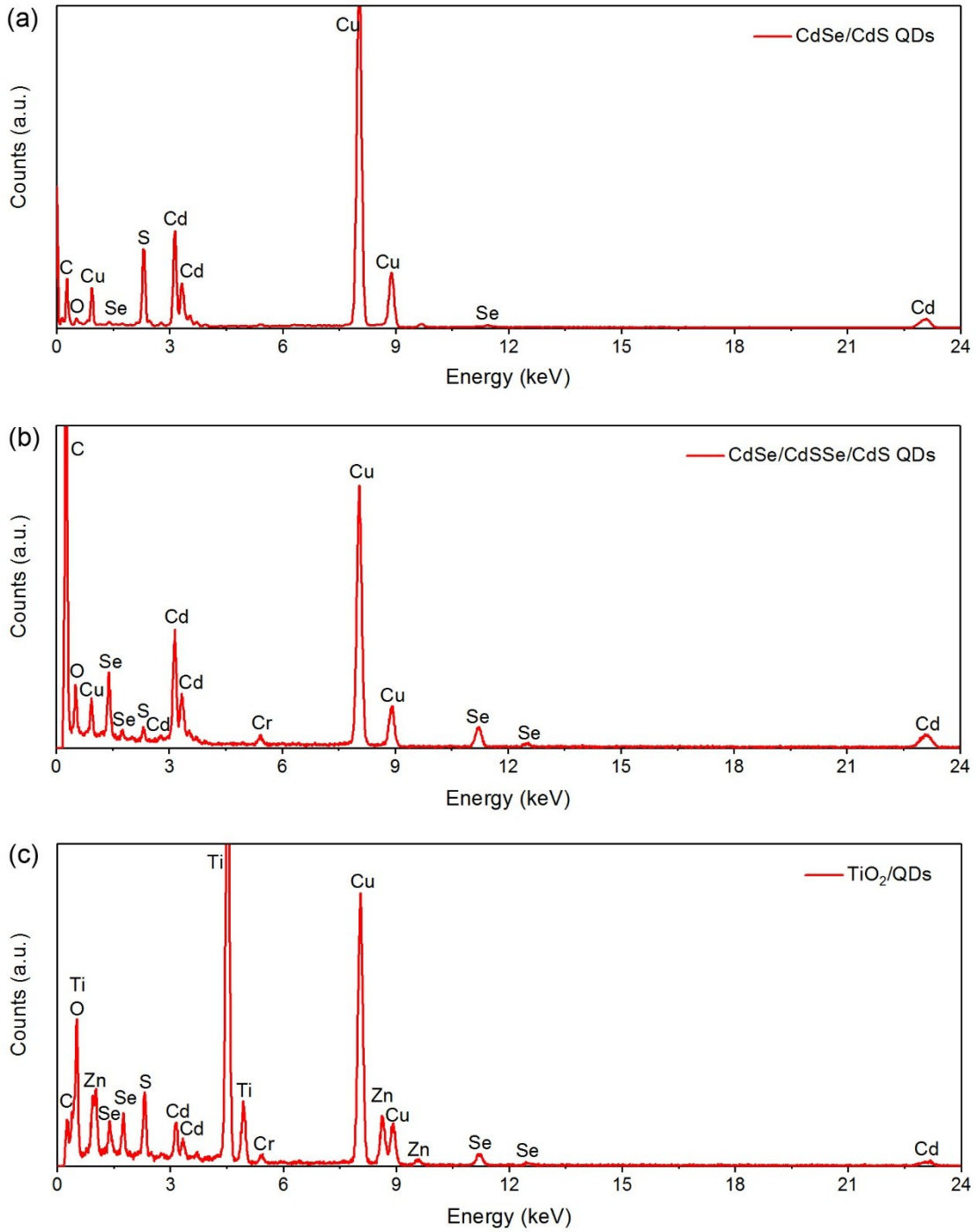

Fig. S3 EDS spectra of CdSe/CdS core/shell QDs (a), CdSe/CdSSe/CdS core/multi-shell QDs (b) and CdSe/CdSSe/CdS QDs dispersing in TiO_2 films after ZnS coated process (c).

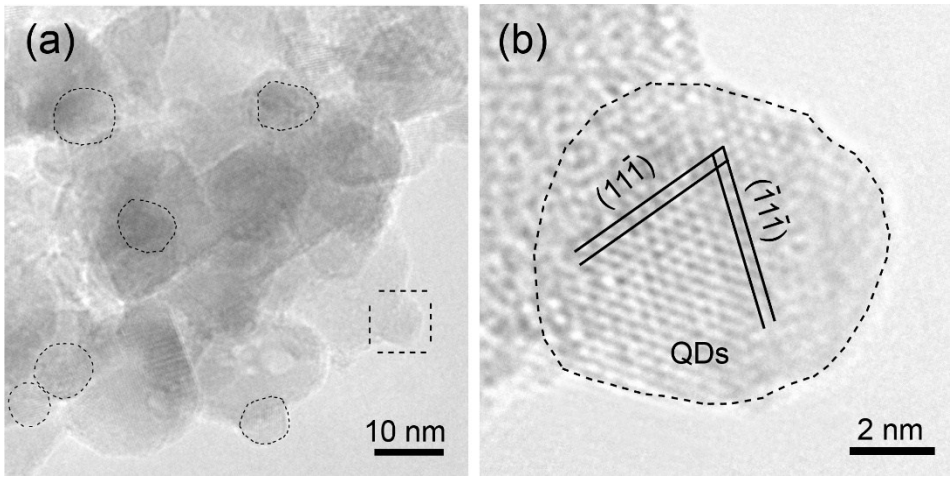

Fig. S4 TEM (a) and HRTEM (b) images of CdSe/CdSSe/CdS QDs dispersed on TiO_2.

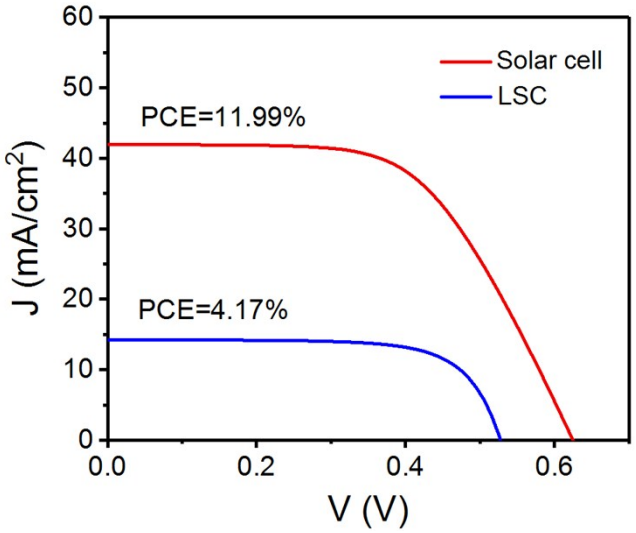

Fig. S5 *J-V* characteristics of the silicon solar cells and the same solar cell attached to the edge of the LSC under 128 mW/cm^2 sunlight illumination.

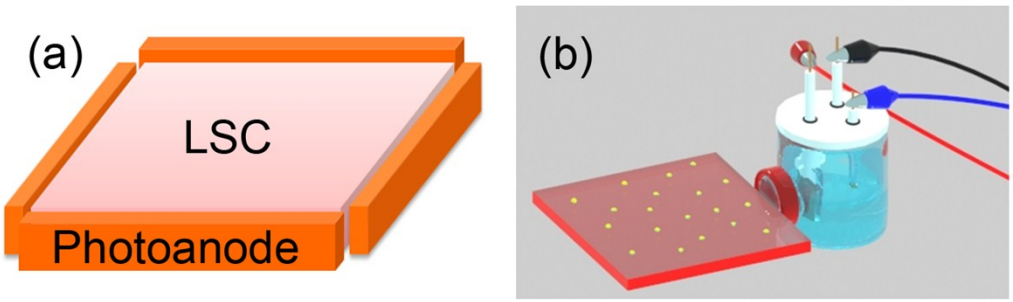

Fig. S6 (a) Expected combination of LSC-PEC system. (b) The actual combination of LSC and PEC in measurement process.

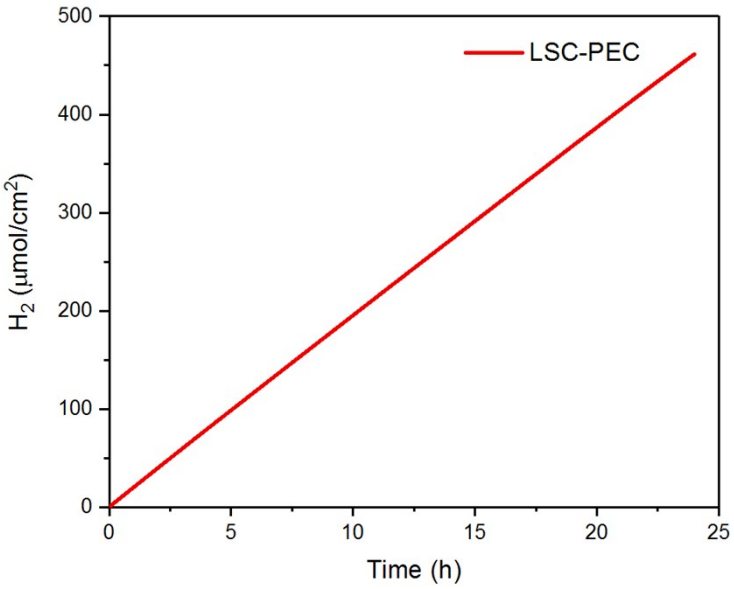

Fig. S7 Time dependent H_2 evolution of CdSe/CdSSe/CdS QDs based PEC device coupled with CdSe/CdS QDs based LSC under one sun illumination (100 mW/cm^2).

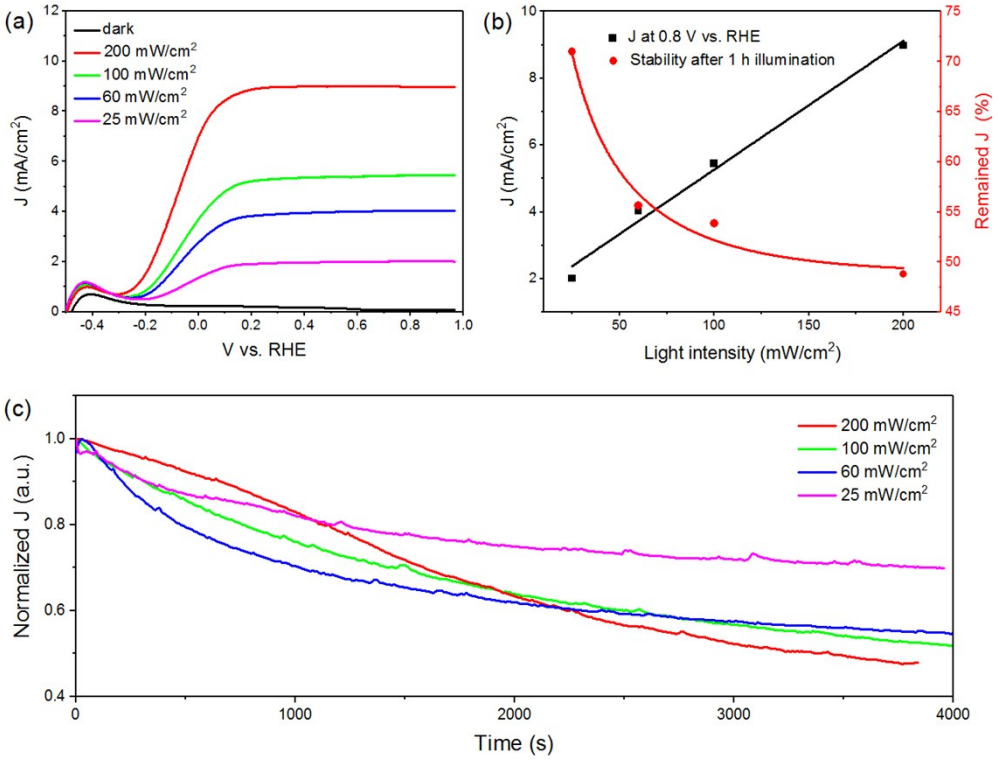

Fig. S8 (a) *J-V* curves of the PEC device using CdSe/CdSSe/CdS QDs-TiO_2 photoanode in dark and under illumination with different light intensities. (b) Saturated photocurrent density of the PEC device under different light intensities illumination and the percentage of saturated photocurrent density retained after 1 hour continuous illumination with different light intensities. (c) Normalized *J-t* curve for the CdSe/CdSSe/CdS QDs-TiO_2 photoanode at 0.6 V *vs.* RHE under illumination with different sunlight intensities.

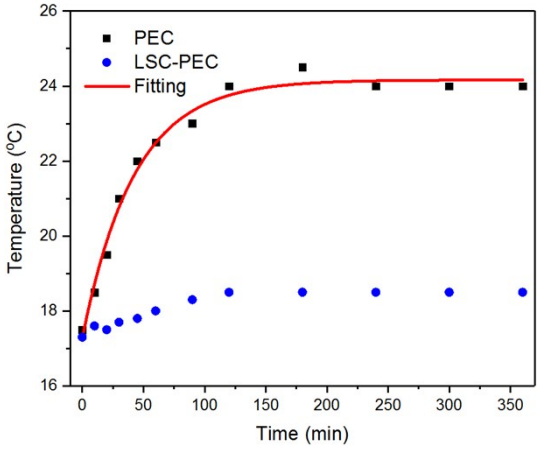

Fig. S9 The change of temperature during PEC measurements under one sun illumination for PEC and LSC-PEC systems, respectively. The room temperature is 17 °C.

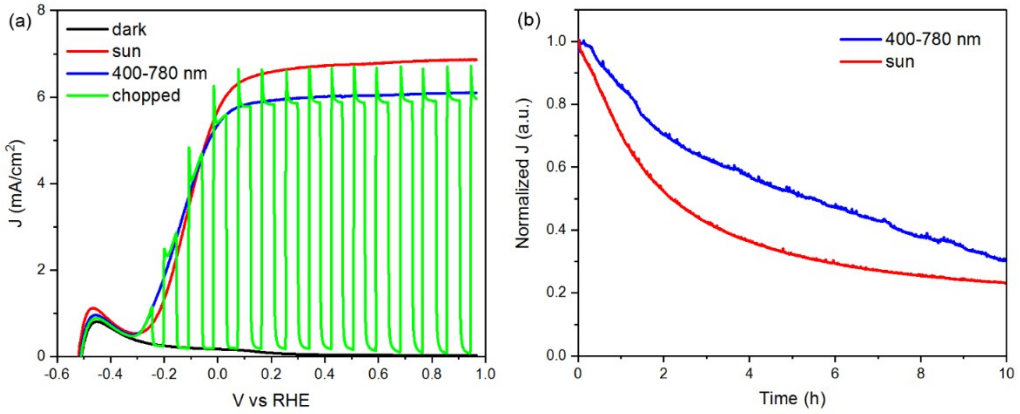

Fig. S10 *J-V* (a) and *J-t* (b) curves of the PEC device under sunlight illumination (100 mW/cm^2) with a long pass filter (400-780 nm).

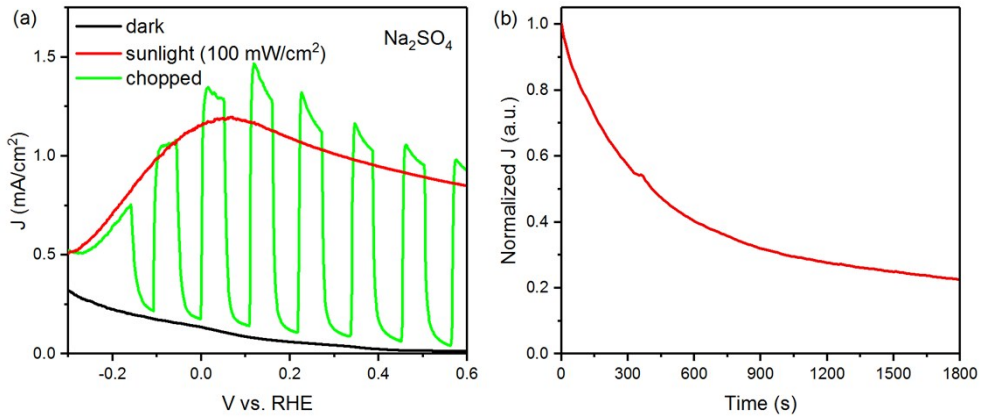

Fig. S11 (a) *J-V* curves of the PEC device using CdSe/CdSSe/CdS QDs-TiO_2 photoanode in 0.2 M Na_2SO_4 electrolyte in dark, under chopped and one sun illumination (100 mW/cm^2). (b) Normalized *J-t* curve for the CdSe/CdSSe/CdS QDs-TiO_2 photoanode at 0.6 V *vs.* RHE under one sun illumination.

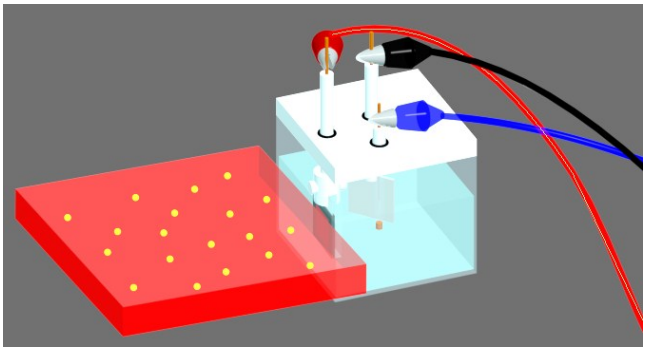

Fig. S12 The combination of the LSC and PEC in measurement process. In the geometry, the anode (glass side) was taped to the quartz window to decrease the distance between the LSC and anode.

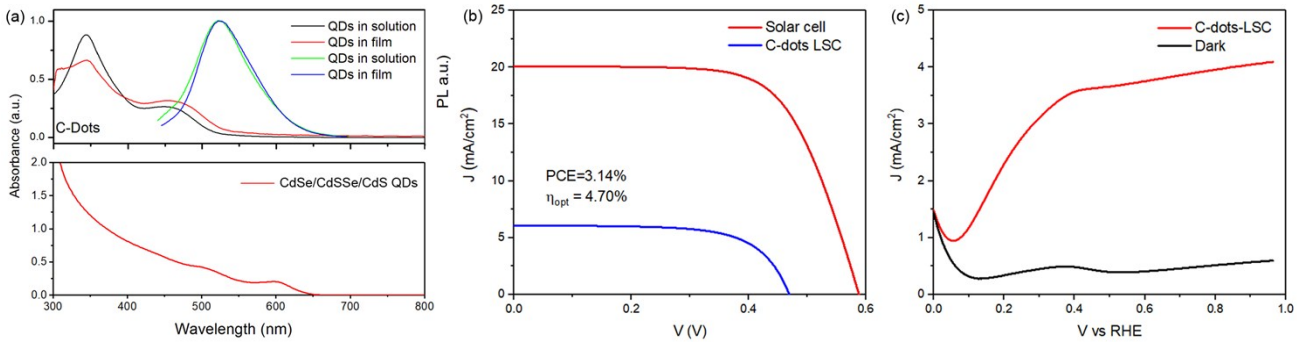

Fig. S13 (a) Absorption and emission spectra of C-dot based LSC and QDs used in PEC. (b) *J-V* characteristics of the silicon solar cells and the same solar cell attached to the edge of the LSC under natural sunlight illumination. (c) *J-V* curves of the PEC device using CdSe/CdSSe/CdS QDs-TiO_2 photoanode in dark and under C-dot based LSC emitted light illumination (18.2 mW/cm^2).

Table S1. Cost of chemicals for lab-scale production.

Chemical	Batch size	Price per batch ($)	Price $ per g or mL	Source link
CdO	500 g	139	0.278/g	https://www.sigmaaldrich.com/catalog/product/aldrich/244783?lang=en&region=US
Se	250 g	134	0.536/g	https://www.sigmaaldrich.com/catalog/product/aldrich/209651?lang=en&region=US
S	1000 g	37.6	0.0376/g	https://www.sigmaaldrich.com/catalog/product/sigald/13825?lang=en&region=US
OLA	500 g	132	0.264/g	https://www.sigmaaldrich.com/catalog/substance/oleylamine2674911290311?lang=en&region=US
OA	4000 mL	144	0.036/mL	https://www.sigmaaldrich.com/catalog/substance/oleicacid2824611280111?lang=en&region=US
ODE	1000 mL	37.4	0.0374/mL	https://www.sigmaaldrich.com/catalog/product/aldrich/o806?lang=en&region=US
LMA	4000 mL	144	0.036/mL	https://www.sigmaaldrich.com/catalog/pro

				duct/aldrich/364525?lang=en&region=US
EGDM	500 mL	120	0.24/mL	https://www.sigmaaldrich.com/catalog/substance/ethyleneglycoldimethacrylate198229790511?lang=en&region=US
TOPO	500 g	232	0.464/g	https://www.sigmaaldrich.com/catalog/substance/trioctylphosphineoxide386637850211?lang=en&region=US
TOP	2000 mL	1320	0.66/mL	https://www.sigmaaldrich.com/catalog/substance/trioctylphosphine37064473153711?lang=en&region=US
hexane	4000 mL	294	0.0735/mL	https://www.sigmaaldrich.com/catalog/product/sigald/650552?lang=en&region=US
TPO	50 g	141	2.82/g	https://www.sigmaaldrich.com/catalog/product/aldrich/415952?lang=en&region=US
$Zn(Ac)_2 \cdot 2H_2O$	1000 g	83.4	0.0834/g	https://www.sigmaaldrich.com/catalog/product/sigald/z0625?lang=en&region=US
$Na_2S \cdot 9H_2O$	500 g	86.9	0.1738/g	https://www.sigmaaldrich.com/catalog/product/sigald/s2006?lang=en&region=US
TiO_2 paste (18NR-AO)	20 g	185.28	9.264/g	http://www.greatcellsolar.com/shop/18nr-ao-active-opaque-titania-paste.html?tdsourcetag=s_pcqq_aiomsg

Table S2. Cost calculations for CdSe/CdS QDs.

Chemicals	unit-price	one-batch usage	Cost ($)
CdO	$0.28/g	0.67 g	0.19
Se	$0.54/g	0.32 g	0.17
S	$0.038/g	0.15g	0.0057
OLA	$0.26/g	8.00 mL	1.69
OA	$0.036/mL	5.00 mL	0.18
ODE	$0.037/mL	58.00 mL	2.17
TOPO	$0.46/g	1.00 g	0.46
TOP	$0.66/mL	4.00 mL	2.64
Solvent cost for cleaning and processing			5.04
Total cost of chemicals			12.55
Chemical yield of QDs		1.06 g	
Cost of chemicals per gram of QDs			11.84

Table S3. Cost calculations for CdSe/CdSSe/CdS QDs.

Chemicals	unit-price	one-batch usage	Cost ($)
CdO	$0.28/g	0.14 g	0.039
Se	$0.54/g	0.33 g	0.18
S	$0.038/g	0.02 g	0.00076
OLA	$0.26/g	8.00 mL	1.69
OA	$0.036/mL	1.59 mL	0.057
ODE	$0.037/mL	19.46 mL	0.73
TOPO	$0.46/g	1.00 g	0.46
TOP	$0.66/mL	4.35 mL	2.87
Solvent cost for cleaning and processing			2.52
Total cost of chemicals			8.55
Chemical yield of QDs		0.47 g	
Cost of chemicals per gram of QDs			18.19

Table S4. Per-m^2 cost comparison of QD-photoanode.

Component	Cost ($)
QDs	3.20
TiO_2 paste	185.28
$Zn(Ac)_2$	4.17
$Na_2S \cdot 9H_2O$	9.04
FTO	147.06
Total cost	348.75

Table S5. Cost comparison of 1 m^2 QD-LSC connected with 320 cm^2 QD-photoanode.

Component	QD-LSC	QD-photoanode
QDs	$2.13	$0.12
PLMA	$7.11	/
TiO_2 paste	/	$5.93
glass	$3.00	/

FTO	/	\$4.71
$Zn(Ac)_2$	/	\$0.13
$Na_2S \cdot 9H_2O$	/	\$0.29
Total cost	\$23.42	

Table S6. Cost of PEC device standalone and 1 m×1 m×0.8 cm LSC-PEC system at the same H_2 production. (η_{opt}: external optical efficiency of LSC, I: photocurrent of PEC device for LSC-PEC system.)

η_{opt} (%)	I (A)	H_2 yield (L/day)	LSC-PEC cost (\$)	PEC standalone cost (\$)
2%	1.97	19.78	23.42	5.99
3%	2.96	29.67	23.42	8.98
4%	3.94	39.55	23.42	11.98
5%	4.93	49.44	23.42	14.97
6%	5.92	59.33	23.42	17.96
7%	6.90	69.22	23.42	20.96
8%	7.89	79.11	23.42	23.95
9%	8.87	89.00	23.42	26.94
10%	9.86	98.89	23.42	29.94

Table S7. Considering photo-stability, the cost of PEC device standalone and 1 m×1 m×0.8 cm LSC-PEC system at the same H_2 production. (η_{opt}: external optical efficiency of LSC, I: photocurrent of PEC device for LSC-PEC system.)

η_{opt} (%)	I (A)	H_2 yield (L/day)	LSC-PEC cost (\$)	PEC standalone cost (\$)
2%	1.62	16.22	23.42	11.42
3%	2.43	24.33	23.42	17.13
4%	3.23	32.43	23.42	22.84
4.5%	3.64	36.49	23.42	25.69
5%	4.04	40.54	23.42	28.55

6%	4.85	48.65	23.42	34.25
7%	5.66	56.76	23.42	39.96
8%	6.47	64.87	23.42	45.67
9%	7.28	72.98	23.42	51.38
10%	8.08	81.09	23.42	57.09

Table S8 Photoelectrochemical properties of various QDs based photoanode, compared with that of the prepared CdSe/CdSSe/CdS QDs based photoanode in LSC-PEC system.

Ref.	Photoanodes	Electrolyte	Bias	Current density (mA/cm^2)
[2] Adv. Energy Mater. 2018	TiO_2/Zn-$CuInSe_2$ /$CuInS_2$ g-QDs	Na_2S/Na_2SO_3 (0.25M/0.35M)	0.8 V vs. RHE	3.1
[3] Adv. Sci. 2018	$TiO_2/CuInSe_xS_{2-x}$ /CdSeS/CdS QDs	Na_2S/Na_2SO_3 (0.25M/0.35M)	0.3 V vs. RHE	5.5
[4] Nano Energy 2017	TiO_2/CISeS/ZnS QDs	Na_2S/Na_2SO_3 (0.25M/0.35M)	0.8 V vs. RHE	5.3
[5] Nano Energy 2016	TiO_2/PbS/CdS QDs	Na_2S/Na_2SO_3 (0.25M/0.35M)	0.2 V vs. RHE	5.3
[6] Nat. Commun. 2015	FeOOH/N_2-$BiVO_4$	$NiSO_4$ (0.1M)	0.6 V vs. RHE	3.47
[7] J. Phys. Chem. Lett. 2013	TiO_2/PbS/CdS QDs	Na_2S/Na_2SO_3 (0.25M/0.35M)	0.4 V vs. RHE	6.0
This work	TiO_2/CdSe/CdSSe/CdS QDs	Na_2S/Na_2SO_3 (0.25M/0.35M)	0.6 V vs. RHE	4.5

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