Supporting Information

Near Infrared heavy-metal-free SnSe/ZnSe Quantum Dots for Efficient Photoelectrochemical Hydrogen Generation

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Experimental section

1.1 Materials: $SnCl_2$ (98%), Selenourea (99.9%), oleylamine (OLA) (technical grade 70%), oleic acid (OA) (technical grade 90%), octadecene (ODE), Ti-Nanoxide BL/SC were bought from Sigma-Aldrich Inc. and Zinc acetate dihydrate (98%) were purchased from Sigma-Aldrich. Sodium sulfide (Na_2S), sodium sulfite (Na_2SO_3), toluene, methanol, and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. Titania paste (code18NR-AO) was supplied by Dyesol. FTO coated glass substrates with sheet resistance of 10 Ω $square^{-1}$ were purchased from Pilkington glasses. All chemicals were used as-received.

1.2 TiO_2 film preparation: Briefly a thin blocking layer was first spin-coated on the FTO glass. TiO_x solution (50 ul) was dropped on the UV-cleaned FTO glass at spinning rate of 6000 r.p.m. for 30 s. Then, the film was annealed at 500 °C for 30 min under ambient atmosphere with a ramp rate of 2 °C/min. Then the commercial TiO_2 paste (18NRAO) composed of 20 and 450 nm anatase particles were deposited on top of the blocking layer by tape casting. The as-prepared thin film was first dried at 25 °C for 15 min at ambient conditions and then placed on a hot plate for 6 min at 110 °C. Subsequently, the thin films were sintered according to the following temperature profile: 325 °C /5 min, 375 °C/5 min, 450 °C/15 min and 500 °C 30 min with a ramp rate of 2 °C/minute. After cooling to room temperature, a TiO_2 mesoporous film was achieved.

Supporting figures and tables

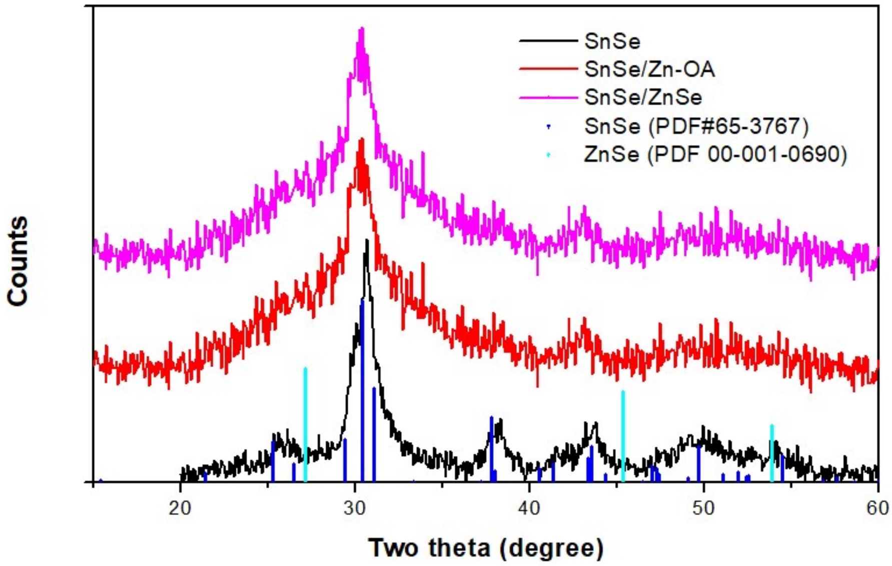

Fig. S1 XRD patterns of SnSe QDs, SnSe-ZnOA QDs and SnSe/ZnSe QDs. The QDs were synthesized at 100 °C with Sn/Se ratio of 4:1. The XRD peaks locate between the peak of orthorhombic crystal structured SnSe (blue) and zinc blend ZnSe (light green).

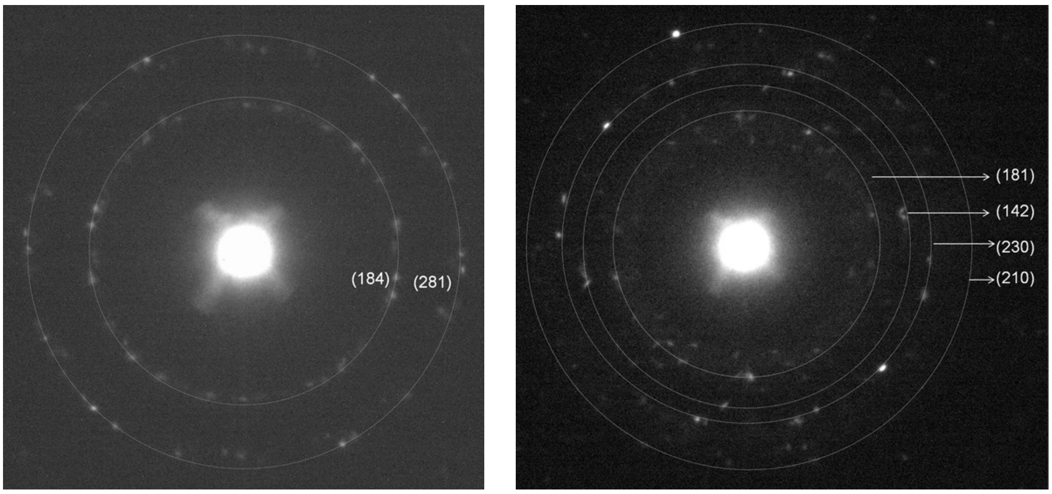

Fig. S2 (Left) SAED patterns of SnSe/ZnSe QDs. The SnSe QDs before cation exchange were synthesized at 90 °C with Sn/Se ratio of 2 and $SnCl_2$ contrition of 0.2 M. (Right) SAED patterns of SnSe/ZnSe QDs. The SnSe QDs before cation exchange were synthesized at 125 °C with Sn/Se ratio of 2 and $SnCl_2$ contrition of 0.1 M.

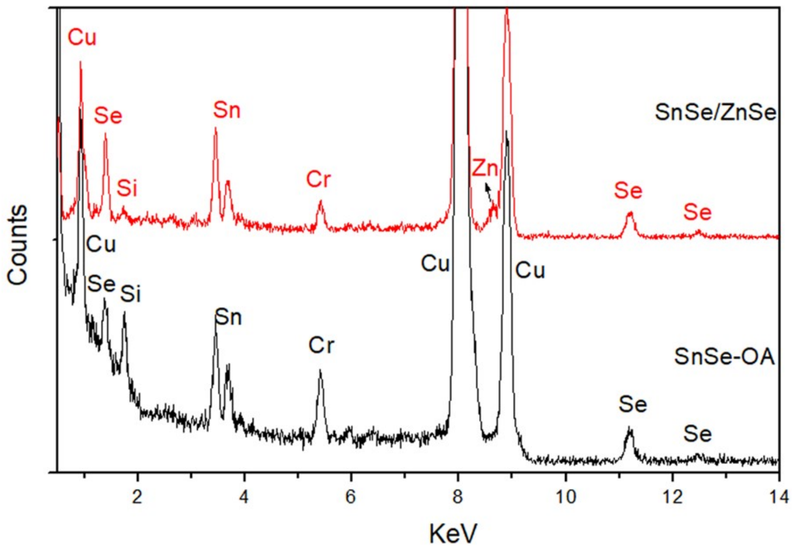

Fig. S3 EDS spectra of as-obtained SnSe QDs and SnSe/ZnSe QDs. The SnSe QDs were synthesized at 100 °C with Sn/Se ratio of 4 and $SnCl_2$ contrition of 0.4 M.

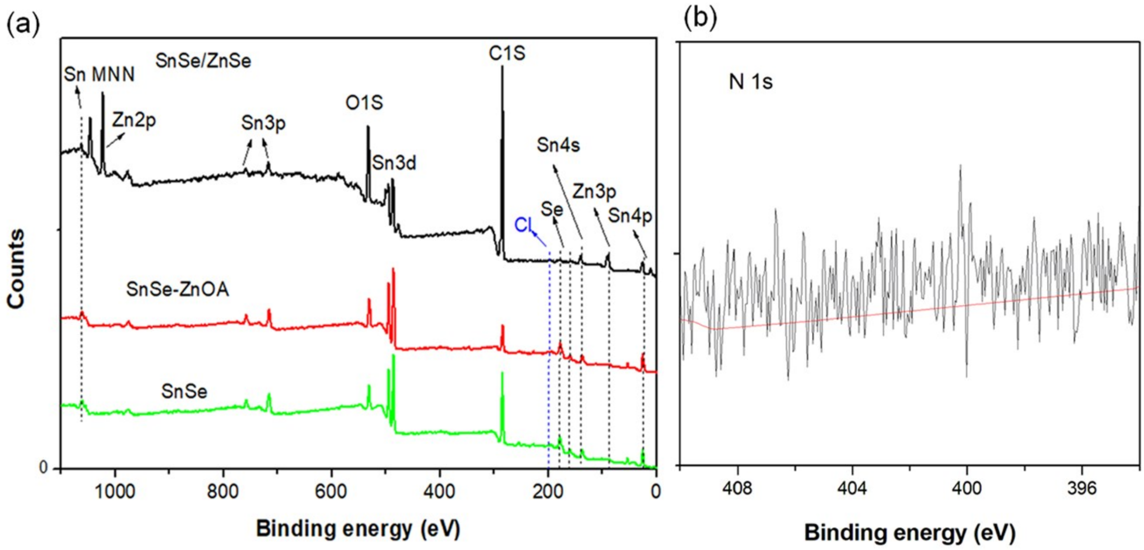

Fig. S4 (a) XPS spectra of SnSe QDs, SnSe-ZnOA, and SnSe/ZnSe QDs. (b) High resolution XPS N1s spectrum of SnSe/ZnSe QDs. The SnSe QDs seed were syntheszied with Sn/Se ratio of 4 and concentration of $SnCl_2$ of 0.4 M at 100 °C.

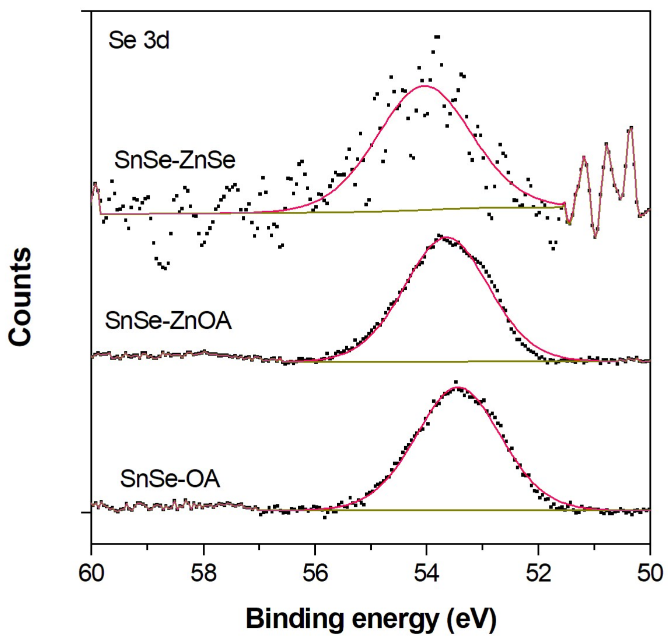

Fig. S5 High resolution XPS Se 3d spectra of SnSe QDs, SnSe-ZnOA, and SnSe/ZnSe QDs. The SnSe QDs seed were syntheszied with Sn/Se ratio of 4 and concentration of $SnCl_2$ of 0.4 M at 100 °C.

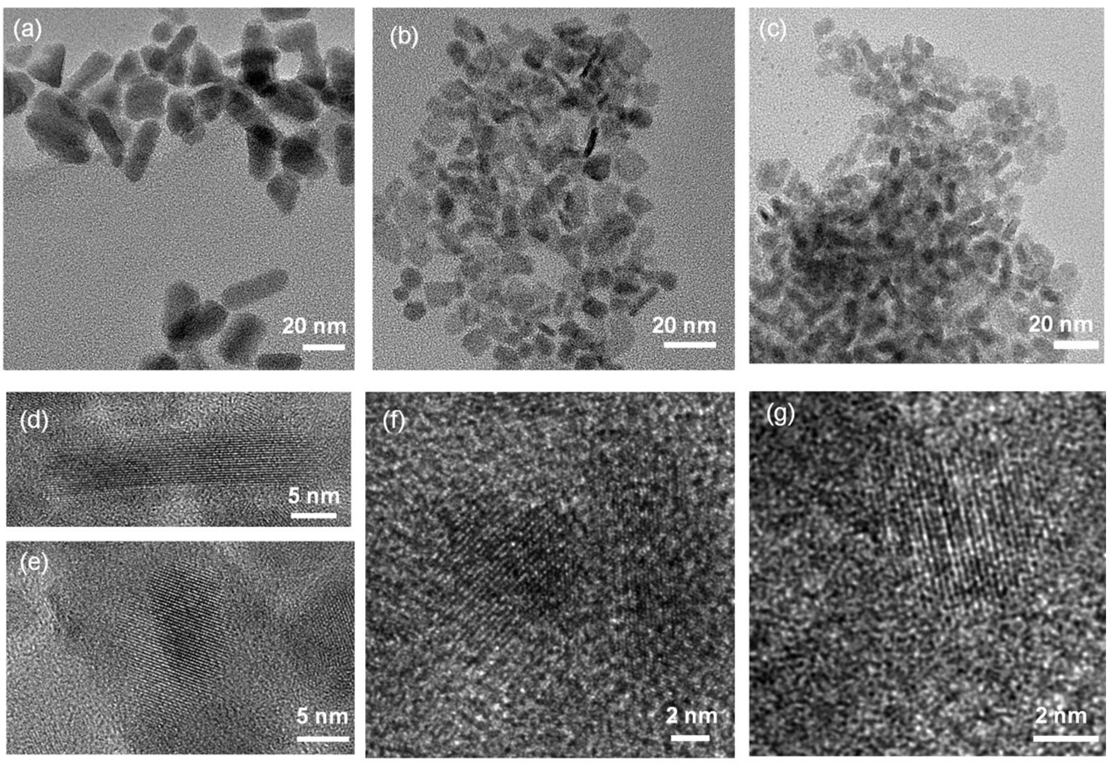

Fig. S6 TEM and HR-TEM of as-synthesized SnSe-ZnOA nanocrystals using the concentration of $SnCl_2$ of 0.05 M at different temperatures: (a, d, e) 125 °C; (b, f) 100 °C and (c, g) 80 °C.

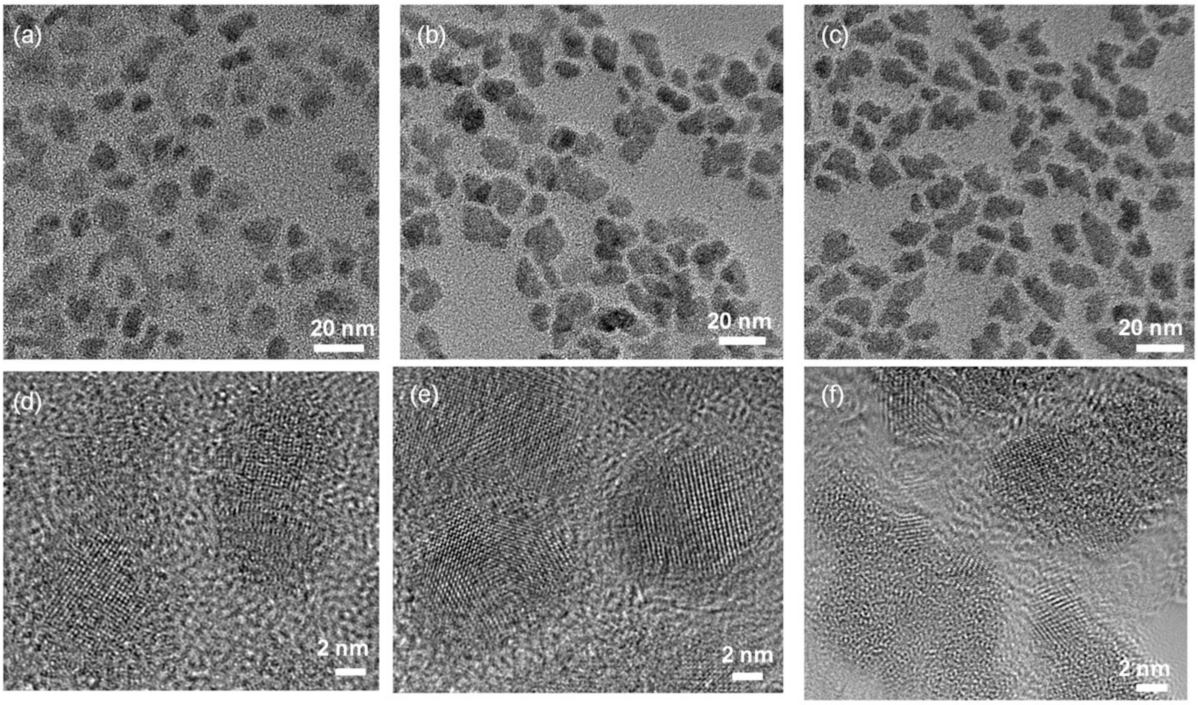

Fig. S7 TEM and HR-TEM of as-synthesized SnSe nanocrystals using the concentration of $SnCl_2$ of 0.2 M at different temperatures: (a, d) 100 °C; (b, e) 90 °C and (c, f) 80 °C.

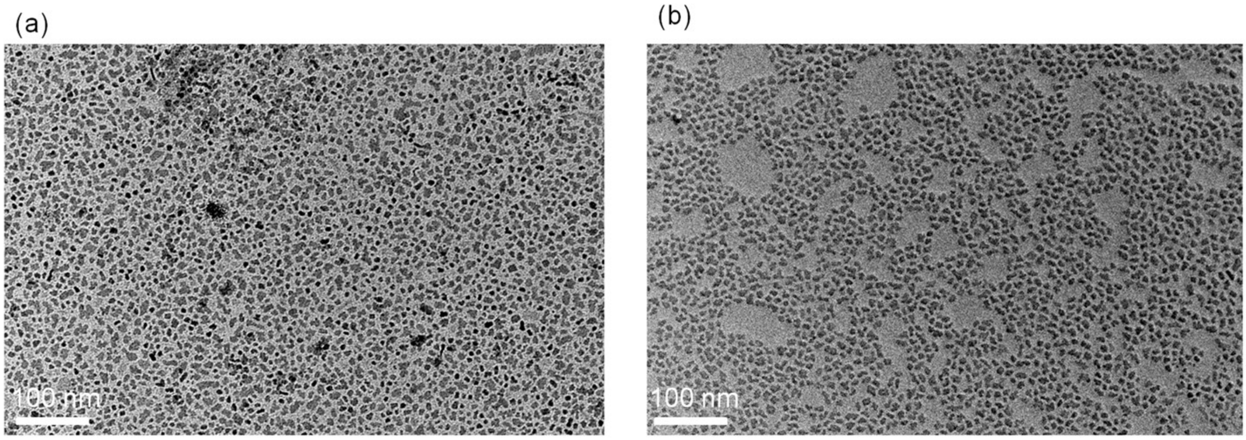

Fig. S8 TEM images of (a) SnSe-ZnOA, and (b) SnSe/ZnSe QDs. The SnSe QDs seed were syntheszied with Sn/Se ratio of 4 and concentration of $SnCl_2$ of 0.4 M at 100 °C.

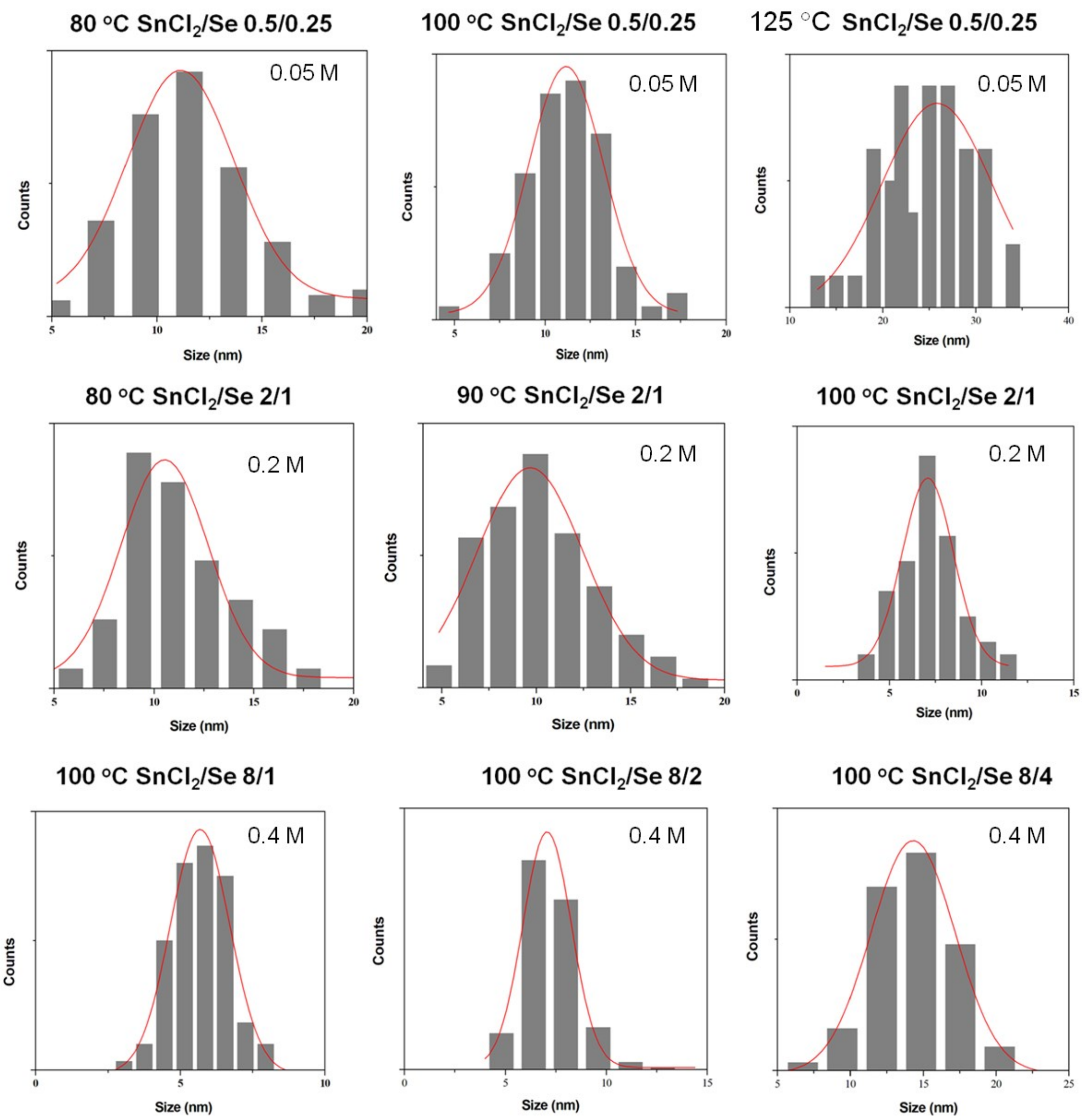

Fig. S9 Size distribution of SnSe-ZnOA QDs synthesized under different reaction conditions. The concentrations of the $SnCl_2$ were included in the figures.

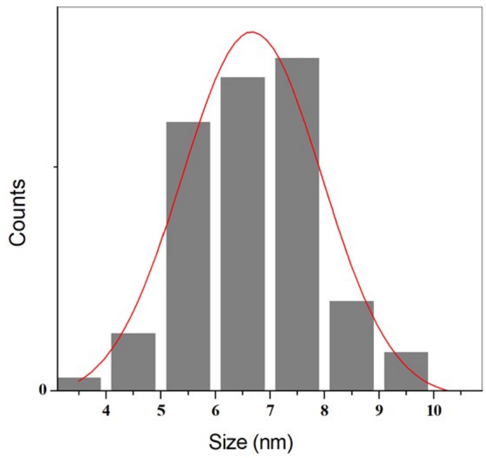

Fig. S10 Size distribution of SnSe/ZnSe QDs. The SnSe QDs seed were syntheszied with Sn/Se ratio of 4 and concentration of $SnCl_2$ of 0.4 M at 100 °C.

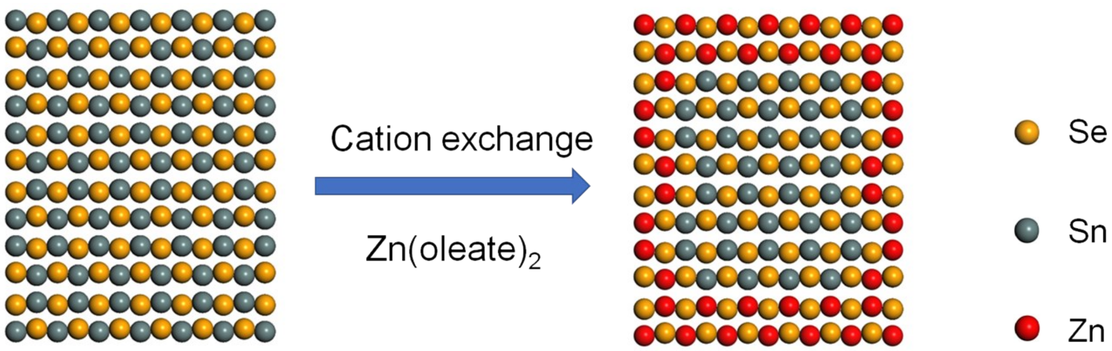

Fig. S11 Scheme for the preparation of Zn stabilized SnSe QDs.

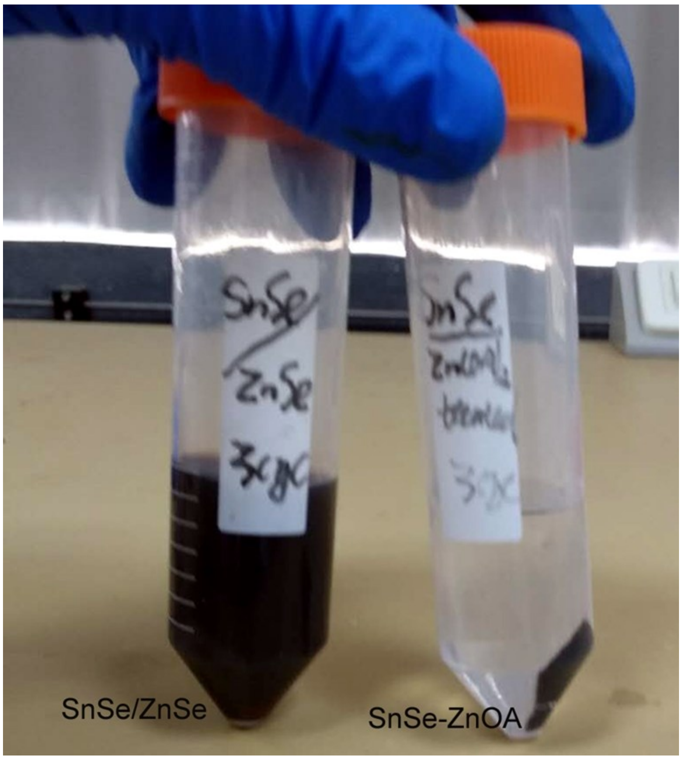

Fig. S12 Photographs of the SnSe/ZnSe (left) and SnSe-ZnOA (right) QDs synthesized at 100 °C with Sn/Se ratio of 4:1. The as-prepared QDs were purified three cycles, then the mixture was centrifuged at 6000 g for 10 min. The precipitation of QDs in the bottom of the tube indicates that the colloidal stability of the SnSe-ZnOA is not good. To fairly compare the colloidal stability of the samples, all the parameters (amount of QDs, volume of ethanol and toluene, centrifugation rate and time) are identical during the purification process.

Fig. S13 The photograph of the photoanode after SnSe/ZnSe QDs deposition. A brown color indicates the successful deposition of SnSe/ZnSe QDs into the TiO_2 film. The anode was further sealed by the epoxy glue.

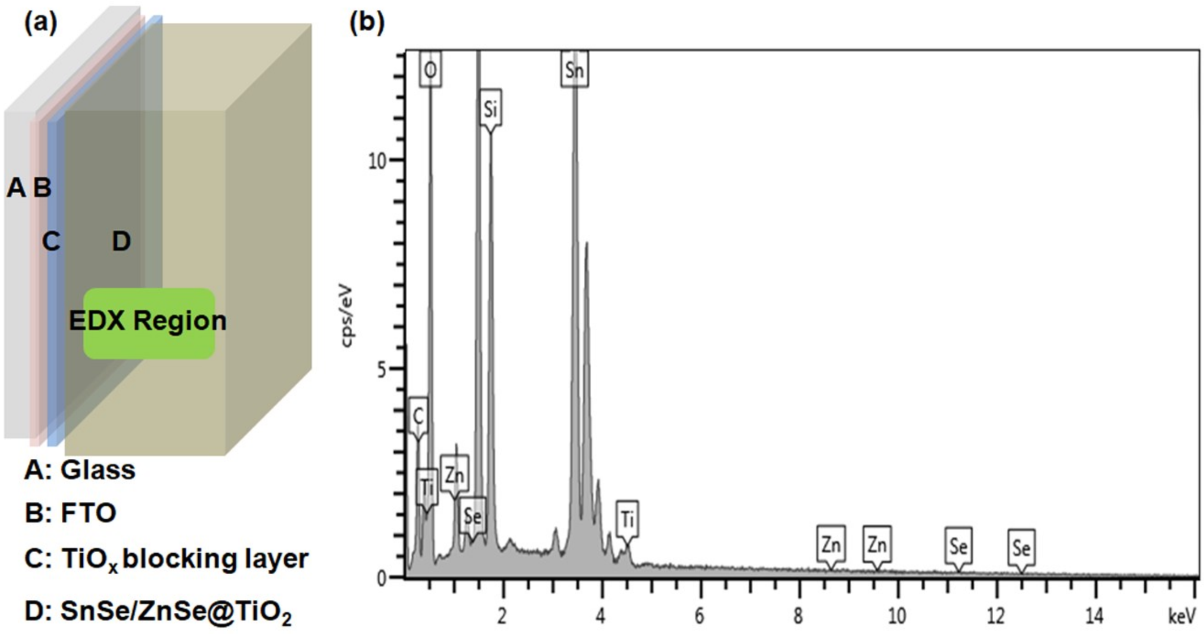

Fig. S14 (a) Scheme of the configuration of the photoanode after SnSe/ZnSe QDs deposition. (b) EDS of the anode with the fixed region (green). Due to the cross-section of the film is not flat, we cannot precisely do the EDS mapping for the cross-section.

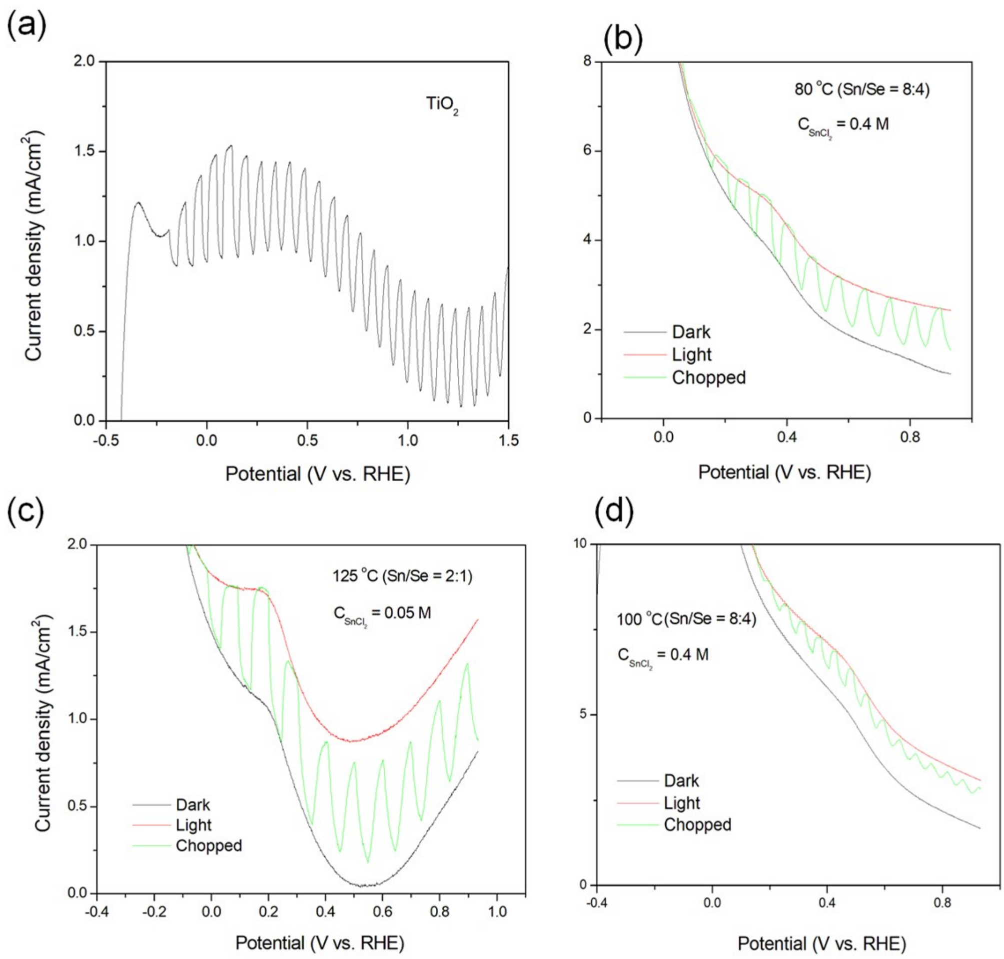

Fig. S15 *J-V* (versus RHE) of photoelectrodes in the dark (black curve), under continuous (red curve) and chopped (green curve) illumination (AM 1.5G, 100 mW/cm^2): (a) TiO_2; (b) SnSe QDs synthesized at 80 °C; (c) SnSe/ZnSe QDs using SnSe seed synthesized at 125 °C; (d) SnSe QDs synthesized at 100 °C

Table S1 Cost of chemicals for SnSe/ZnSe quantum dots in an industrial scale production.

Chemical	Batch size Kg	Price per batch ($)	Price per $/g	Source link
$SnCl_2$	1000	2000	2	https://www.alibaba.com/product-detail/high-purity-tin-chloride-SnCl2-for_60685592707.html?spm=a2700.galleryofferlist.0.0.1b9462728nn9Ps

Selenourea	1000	1000	1	https://www.alibaba.com/product-detail/SELENOUREA-CAS-630-10-4-_741095164.html?spm=a2700.galleryofferlist.0.0.4b1c5178JuzKPK
Oleylamine	1000	4500	4.4	https://www.alibaba.com/product-detail/Oleylamine-CAS-112-90-3_1600084783607.html?spm=a2700.galleryofferlist.0.0.2bdc3356eUnpcE&s=p
Oleic acid	1000	1300	1.3	https://www.alibaba.com/product-detail/zhonglan-Oleic-acid-CAS-112-80_62505264286.html?spm=a2700.galleryofferlist.0.0.4fb31517U7XJtW&s=p
Zinc acetate dihydrate	1000	2180	2.18	https://www.alibaba.com/product-detail/zinc-acetate-dihydrate-manufacturer_60618403238.html?spm=a2700.galleryofferlist.0.0.6e5f38b049LQ99&s=p
Octadecene	1000	3	0.003	https://www.alibaba.com/product-detail/Chinese-professional-manufactuer-of-Octadecene-CAS_62514487508.html?spm=a2700.galleryofferlist.0.0.6a4272d4hJtX7J
Ethanol	1000	1000	1	https://www.alibaba.com/product-detail/99-9-absolute-ethanol-Colorless-clear_1600085414077.html?spm=a2700.galleryofferlist.0.0.6b3923862flMDK&s=p
Toluene	4	20	5	https://www.reagent.com.cn/goodsDetail/69e5ab91b6534aa3bae60b8e860ac32f

Table S2. Estimated prices for SnSe/ZnSe quantum dots in the lab scale. The calculation considers the cost of chemicals used for one batch reaction (0.76 g $SnCl_2$, 0.125 g Selenourea, 9 mL oleylamine, 3 mL oleic acid, 0.5 g Zinc acetate dihydrate, 10 mL Octadecene, 50 mL ethanol and 30 mL toluene with the production of 0.1 g SnSe/ZnSe for one batch).
Based on ref. 1, we also estimate non-material-related cost as 0.016 $/g for quantum dots in our price estimations as an additional expense in the QD production.

Product	Cost per Gram ($/g)
SnSe/ZnSe QDs	0.27
$CuInSe_2$/ZnS QDs[1]	0.59

1. Wu, K.F., Li H.B., and Klimov, V.I. Tandem luminescent solar concentrators based on engineered quantum dots, *Nature Photonics*, 2018, 12, 105-110.

Table S3 Atomic ratio of the metallic Sn/Sn-Se based on the high resolution XPS data as shown in Figure 3a.

QDs	Peak position (metallic Sn) (eV)		Peak position (Sn-Se) (eV)		Atomic ratio of metallic Sn/Sn-Se
SnSe	493.71	485.35	494.75	486.35	42:100
SnSe-ZnOA	493.77	485.19	495.01	486.56	28: 100
SnSe/ZnSe			495.35	486.69	0

Table S4 Molar ratio of the Sn/Se/Zn based on the high resolution XPS data. SnSe QDs were synthesized at 100 °C with Sn/Se ratio of 4:1 and concentration of $SnCl_2$ of 0.4 M. The calculated ZnSe thickness in SnSe-ZnOA is 0.05 nm and the thickness of the SnSe/ZnSe is 0.3 nm based on EDS data.

QDs	Molar ratio of Sn/Se/Zn (XPS)	Molar ratio of Sn/Se/Zn (EDS)	Thickness (nm)
SnSe	10: 7	10:7.5	----
SnSe-ZnOA	10: 6:0.6	10: 7:0.5	0.05
SnSe/ZnSe	10: 4:20	10:5:3.8	0.3

Hydrogen generation calculation

Based on the methodology discribed in Ref. 1, we can calculate the hydrogen generation rate.

The theoretical number of moles of hydrogen was obtained according to Faraday's law:

$$q = nF$$

With the definitions of electrolysis based on the following equations:

$$n = \frac{m}{m_e} \quad and \quad q = \int_{t_1}^{t_2} I dt$$

Where n is the number of equivalents, m is the mass of the substance liberated at an electrode in grams (g), $m_e$is the molar mass of the substance in grams per mol (g/mol), i.e. n equals to the number of moles. A common assumption on the current being constant over time, allow us to us the mathematical equivalent that can be simplified as [2]:

$$n = \frac{1q}{zF} = \frac{1I \times t}{z \ F}$$

Where z is the numberoftransferred electrons per mole of water (i.e. z=2), q is the electric charge in coulombs (C), F is the Faraday constant (i.e. 96484.34 C/mole), I is the photocurrent in amperes (A) and t is time in seconds (s).

We used the CdSe/CdS QDs sensitized anode and Pt counter electrode as a reference to monitor the H_2 evolution as a function of time as this type QD is more stable compared to SnSe/ZnSe QDs and present very accurate trend between the current density and time (Ref. 3). Based on the calibration curve in Ref. 3, we calculated the hydrogen generation rate in the similar PEC by using the above-mentioned equation.

References:

[1] F.C.J. Strong, Faraday's laws in one equation, J. Chem. Educ. *38* (1961) 98.

[2] W.B. Jensen, Faraday's Laws or Faraday's Law?, J. Chem. Educ. *89* (2012) 1208-1209.

[3] R. Adhikari, L. Jin, F. Navarro-Pardo, D. Benetti, B. AlOtaibi, S. Vanka, H. G. Zhao, Z. T. Mi, A. Vomiero, F. Rosei, High efficiency, Pt-free photoelectrochemical cells for solar hydrogen generation based on "giant" quantum dots, Nano Energy 27 (2016) 265–274.