

# Supporting Information

## **Self-Supported CdSe Nanowire/Nanosheet Photoanodes on Cadmium Foil via *In-Situ* Hydrothermal Transformation of CdSe(en)<sub>0.5</sub> Complex Nanostructures**

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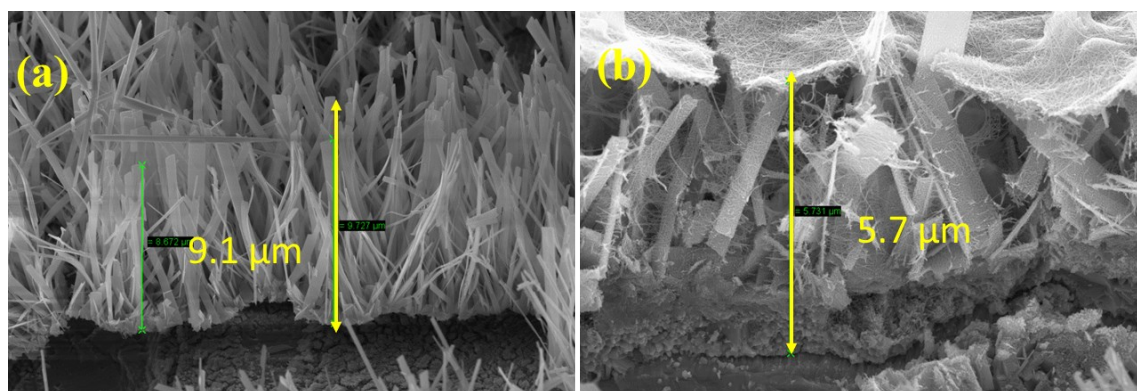
**Table S1.** PL lifetime parameters of the photoelectrode materials.

Sample	A <sub>1</sub> (%)	τ <sub>1</sub> (ns)	A <sub>2</sub> (%)	τ <sub>2</sub> (ns)	A <sub>3</sub> (%)	τ <sub>3</sub> (ns)	A <sub>4</sub> (%)	τ <sub>4</sub> (ns)	$\langle \tau \rangle$ a) (ns)
CdSe(en) <sub>0.5</sub>	57	1.1	35	4.8	7	25	1	124	47
Cd(OH) <sub>2</sub> - CdSe NW/NS hetero- structure	63	0.04	36	0.28	1	2.1	-	-	0.4

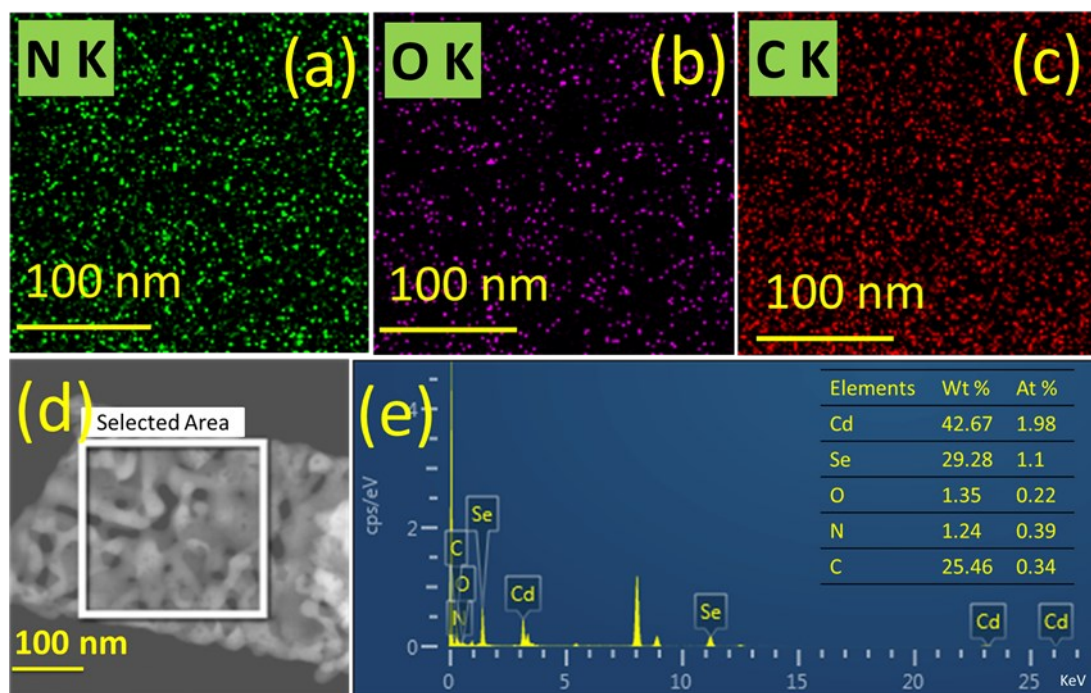
The time-resolved PL intensity is defined by  $I(t) = \sum A_i e^{-t/\tau_i}$ , where  $I(t)$  is the PL intensity as a function of time,  $A$  is the amplitude,  $\tau$  is the PL lifetime, and  $i$  is 3 or 4. <sup>a)</sup> The intensity-weighted average lifetime is calculated by  $\langle \tau \rangle = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$ .

**Table S2.** Comparison table for photoelectrochemical performances of CdSe based photoanodes synthesis via various techniques.

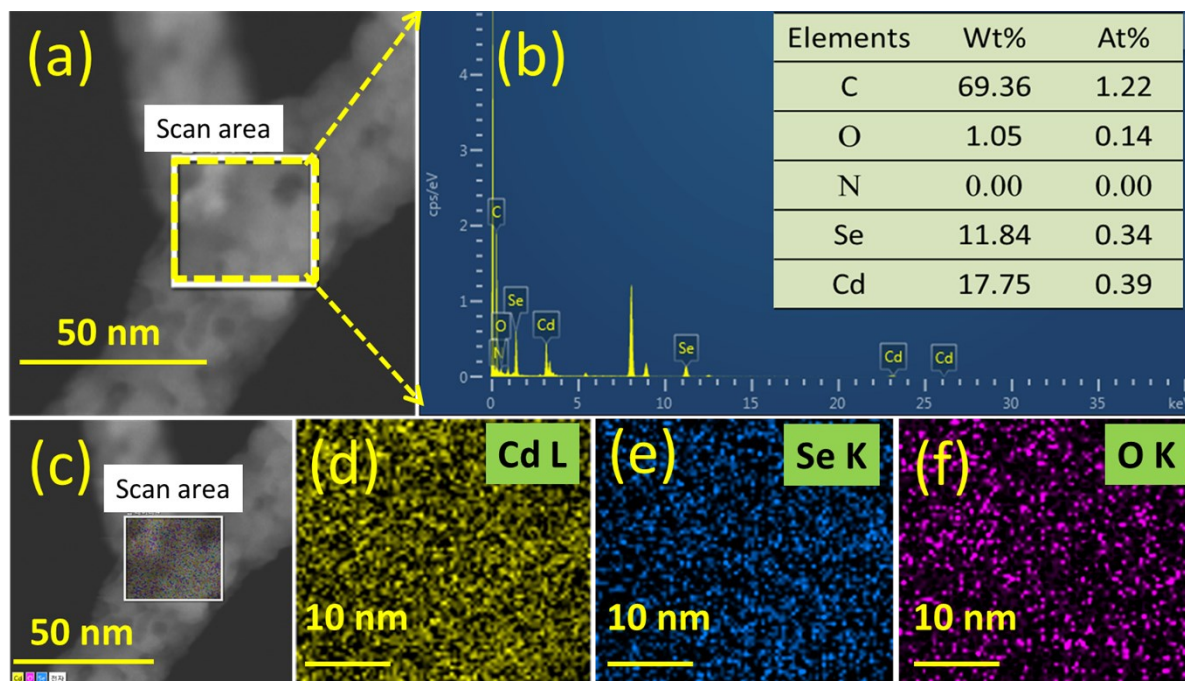
Photoelectrode	Synthesis Technique	Experimental conditions (Electrolyte, light source)	Photocurrent
CdSe sol-gel films <sup>[1]</sup>	sol-gel films	0.1 M polysulfide aqueous solution (Na <sub>2</sub> S + NaOH + S) White light irradiation (100 mW/cm <sup>2</sup> )	~75 μA cm <sup>-2</sup> at -0.57 V vs Ag/AgCl
CdSe-nC60 Electrodes <sup>[2]</sup>	Electrophoretic deposition	0.1 M Na <sub>2</sub> S white light illumination (λ > 300 nm)	0.25 mA.cm <sup>-2</sup> , respectively
CdSe QDs electrode <sup>[3]</sup>	Dispersion of PTZ modified CdSe QDs in thioglycolic acid and adsorption on NiO/FTO	0.1 M Na <sub>2</sub> SO <sub>4</sub> 300 W Xe-lamp with a UV cut-off filter (λ > 400 nm)	-180 μA.cm <sup>-2</sup> at -0.1 V versus NHE
CdSe NWs <sup>[4]</sup>	Electrophoretic deposition (EPD)	M Na <sub>2</sub> S and 0.1 M S AM 1.5 illumination	0.18 mA.cm <sup>-2</sup>
CdSe porous NW/NS on Cd Foil (In this work)	Hydrothermal transformation of CdSe(en) <sub>0.5</sub> directly on the Cd foil	0.1 M Na <sub>2</sub> S/0.02M Na <sub>2</sub> SO <sub>3</sub> Light source: 300 W Xe lamp (λ > 420 nm).	6.1 mA/cm <sup>2</sup> at -0.3 V versus Ag/AgCl



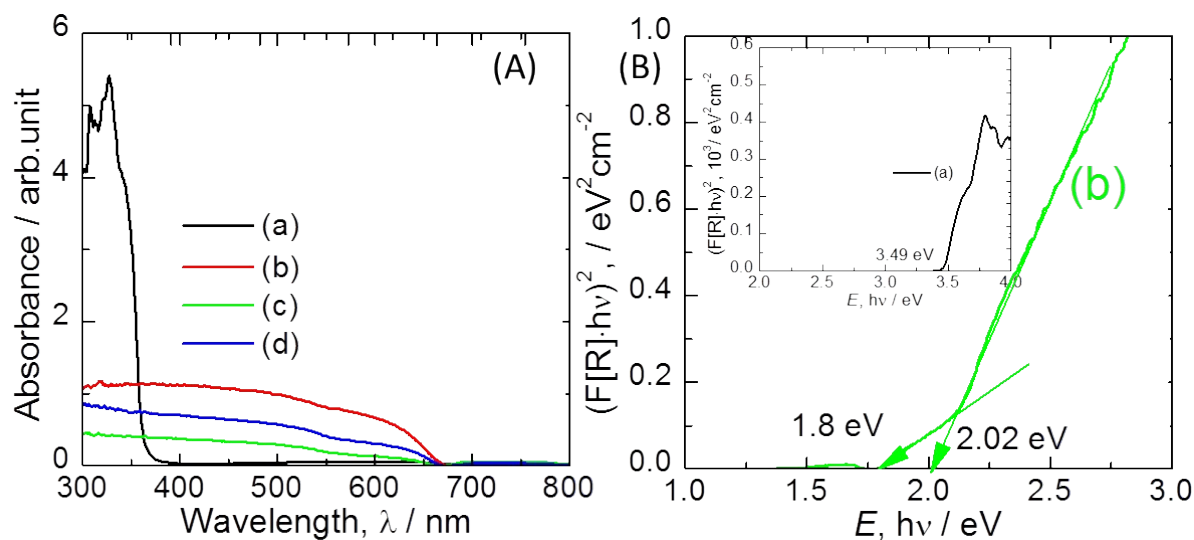
**Figure S1** Field emission scanning electron microscopy images of cross-sections of (a) CdSe(en)<sub>0.5</sub> nanosheets and (b) CdSe nanowires/nanosheets grown on Cd substrate at 160 °C for 6h.



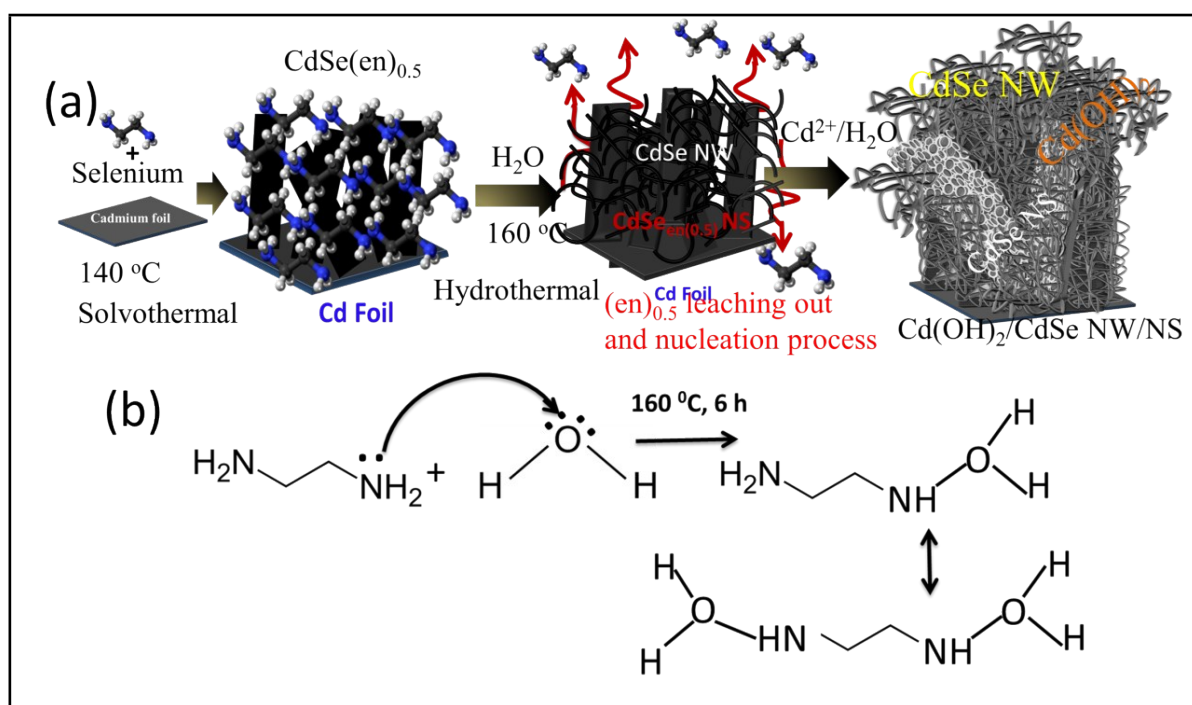
**Figure S2** (a-c) EDS elemental mapping of selected area in Figure 2(G), (d, e) corresponding TEM-EDS spectrum of the porous CdSe NW/NS. Inset of Figure S2e shows the shows elemental composition (wt% and at%) Cd, Se, N, C and O elements.



**Figure S3** (a) TEM (b) EDS spectrum and (c-f) elemental mapping images of nanowires obtained after second hydrothermal treatment (160 °C for 6 h) of the CdSe(en)<sub>0.5</sub> nanosheets. Inset of Fig S3b shows elemental compositions (wt% and at%) of Cd, Se, and O elements.



**Figure S4** (A) Kubelka–Munk absorption of (a) CdSe(en)<sub>0.5</sub> nanosheets and Cd(OH)<sub>2</sub>/CdSe NW/NS's heterostructure grown on Cd substrate at 160 °C for (b) 3h, (c) 6 h and (d) 12h, respectively. (B) Plots of  $(\alpha hv)^2$  vs.  $hv$  for optimum (a) CdSe(en)<sub>0.5</sub> nanosheets and Cd(OH)<sub>2</sub>/CdSe NW/NS's heterostructure grown on Cd substrate at 160 °C for 6 h.



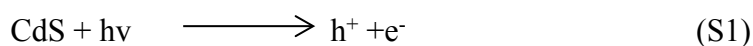
**Figure S5** Transformation mechanism of  $\text{CdSe}(\text{en})_{0.5}$  into  $\text{Cd}(\text{OH})_2/\text{CdSe}$  nanowire/nanosheet heterostructure on Cd foil.

### ***Ion exchange process during the Photoelectrochemical analysis***

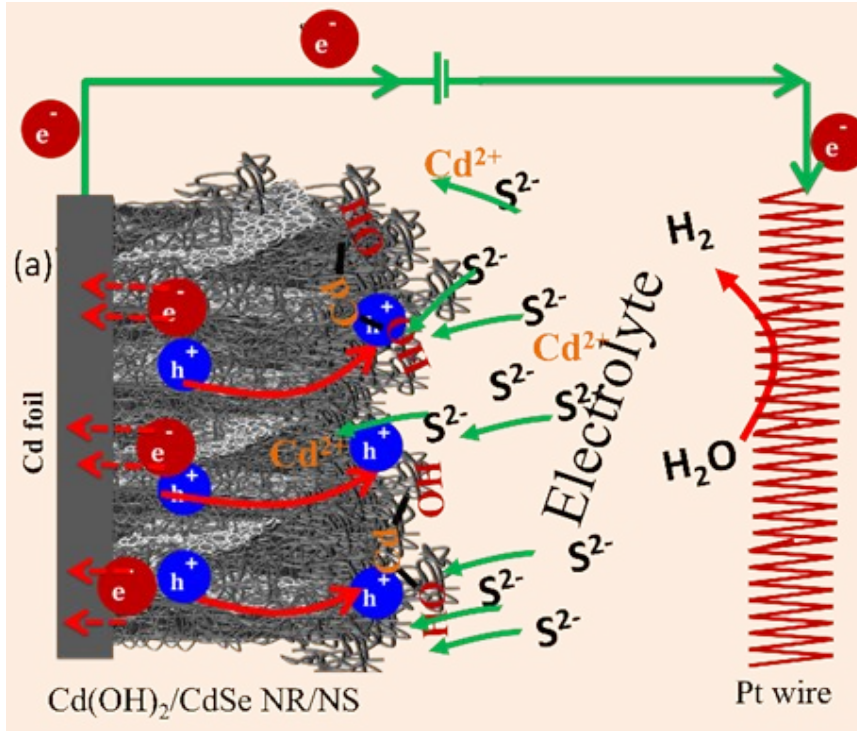
During the PEC measurement the  $\text{Cd}(\text{OH})_2$  on surface of CdSe NW/NS are converted in to CdS *via* reactions with the source of sulfide (i.e.  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$ ). A possible ion exchange process on the CdS/CdSe NW/NS is suggested as following Figure S6:

Once the CdS is formed on the surface of  $\text{Cd}(\text{OH})_2$  passivated CdSe porous nanowires/nanosheets grown on Cd substrate. The reaction mechanism for the photocatalytic hydrogen production over CdS/CdSe NW/NS in the presence of  $\text{S}^{2-}$  and  $\text{SO}_3^{2-}$  are given below [5, 6]

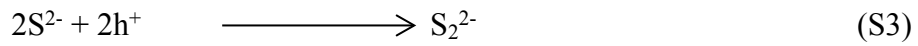
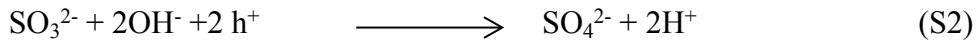
Under visible light illumination reactions at the CdS/CdSe NW/NS working electrode:



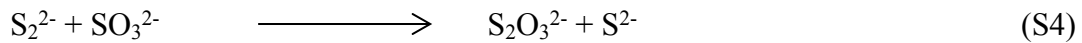
Further, the photogenerated holes in the CdS/CdSe NW/NS oxidize  $\text{SO}_3^{2-}$  and  $\text{S}^{2-}$  to  $\text{SO}_4^{2-}$  and  $\text{S}_2^{2-}$ .



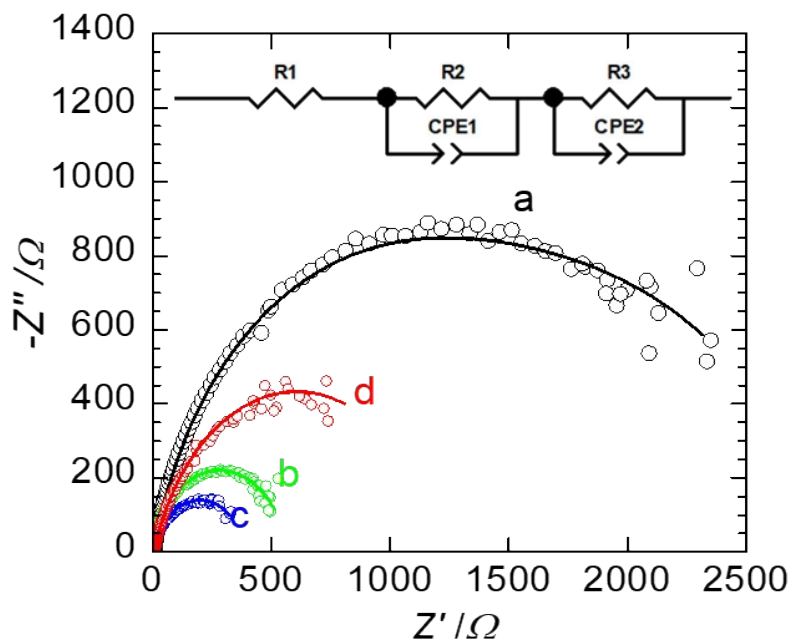
**Figure S6.** The schematics of the probable ion-by-ion mechanism during PEC measurement in the Cd(OH)<sub>2</sub> passivated CdSe porous nanowires/nanosheets grown on Cd substrate.



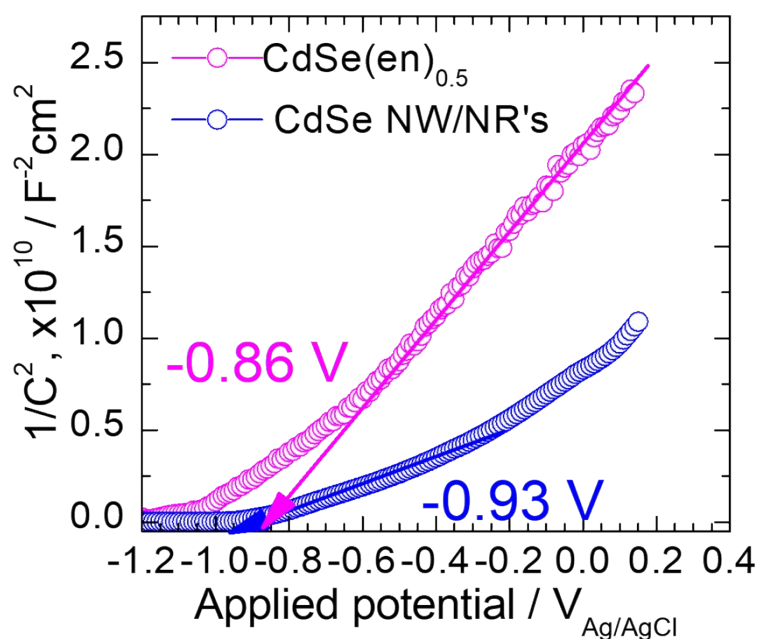
The production of S<sub>2</sub><sup>2-</sup> ions compete with the reduction of protons and suppressed by mixing with SO<sub>3</sub><sup>2-</sup> ions as below



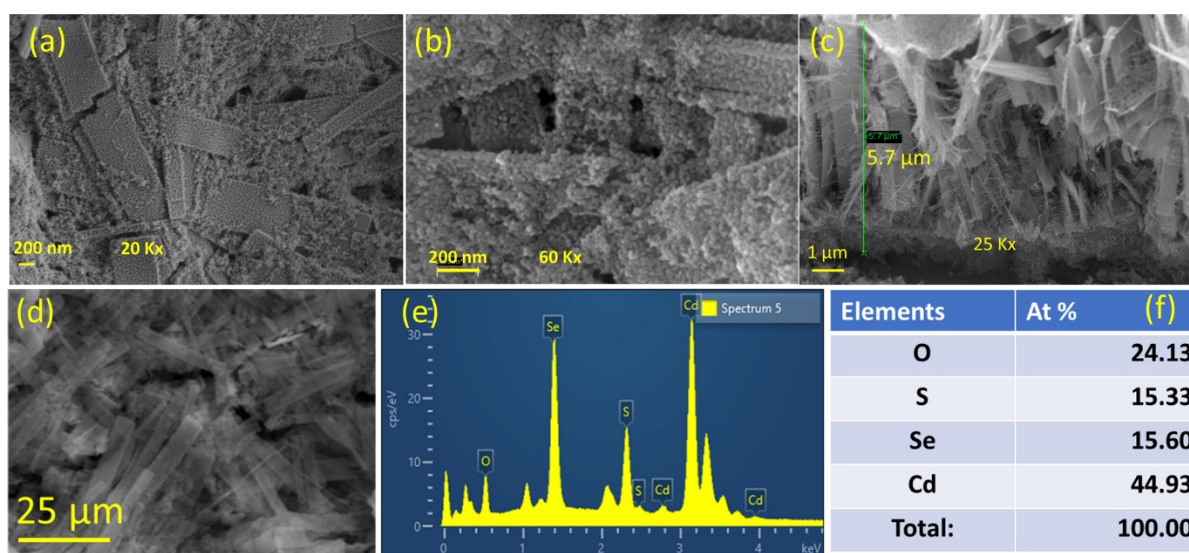
The presence of excess S<sup>2-</sup> ions in the electrolyte also stabilizes the photoelectrode surface during the photoelectrochemical measurements because the formation of sulfur defects could be suppressed.



**Figure S7.** EIS of (a) CdSe(en)<sub>0.5</sub> nanosheets grown on Cd substrate at 140 °C for 12 h and Cd(OH)<sub>2</sub>/CdSe NW/NS heterostructures grown on Cd substrate at 160 °C for (b) 3 h, (c) 6 h, (d) 12 h, respectively. Inset shows the equivalent circuit model was used to fit the EIS results.

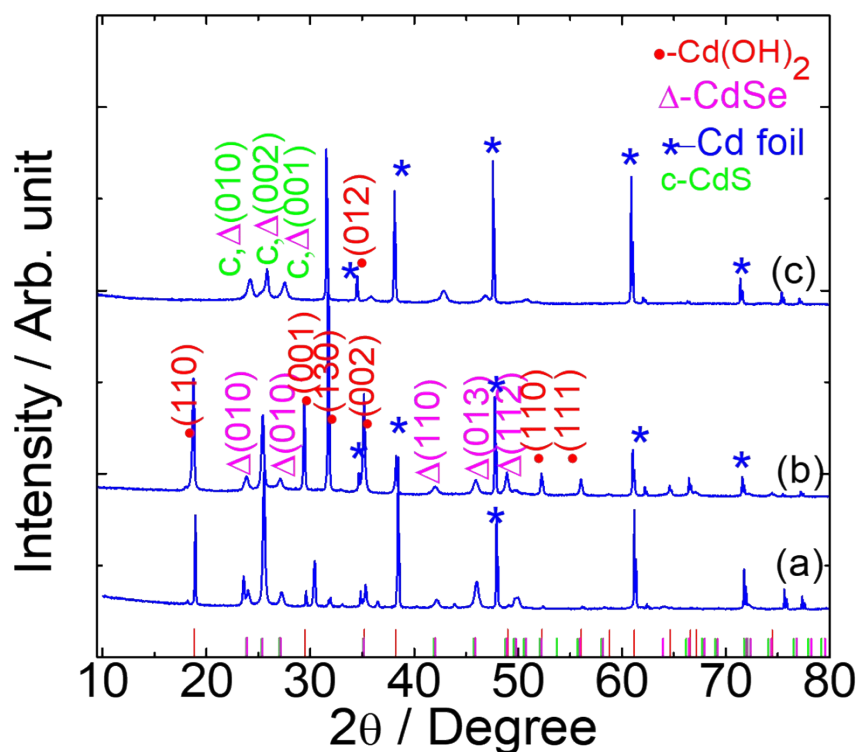


**Figure S8** (a, b) Mott–Schottky plots of the  $\text{CdSe(en)}_{0.5}$  and optimum  $\text{Cd(OH)}_2/\text{CdSe}$  NW/NR's heterojunction photoelectrodes (prepared at 160 °C, 6h) in 0.1  $\text{Na}_2\text{S}$ +0.01 M  $\text{Na}_2\text{SO}_3$  solution (pH = 12.8) at 1000 Hz under the dark conditions.



**Figure S9.** (a, b) Typical low and high magnified FESEM images (c) cross-section vies and (d, f) is the corresponding EDS result for  $\text{Cd(OH)}_2$  passivated  $\text{CdSe}$  porous nanowires/nanosheets after 3 h PEC measurements.

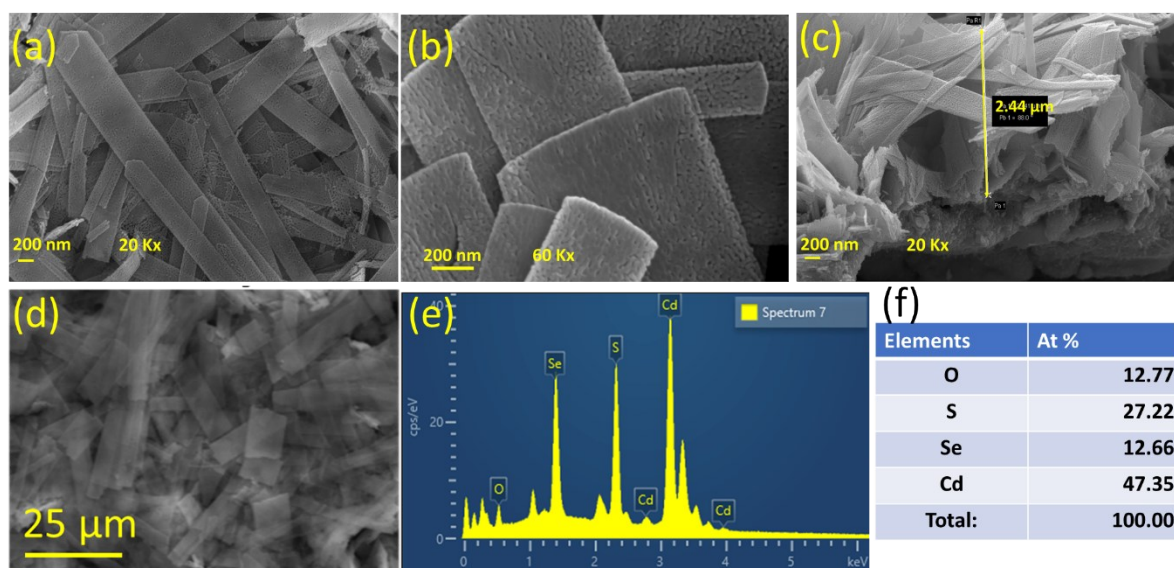




**Figure S10.** (a, b) XRD for Cd(OH)<sub>2</sub>/CdSe NW/NS's after 3 h PEC measurements in 0.1 M Na<sub>2</sub>S/0.02 M Na<sub>2</sub>SO<sub>3</sub> electrolyte, and (c) XRD pattern of the CdS<sub>x</sub>Se<sub>1-x</sub> photoelectrode prepared via addition of 0.1 M Na<sub>2</sub>S during the second hydrothermal solution.

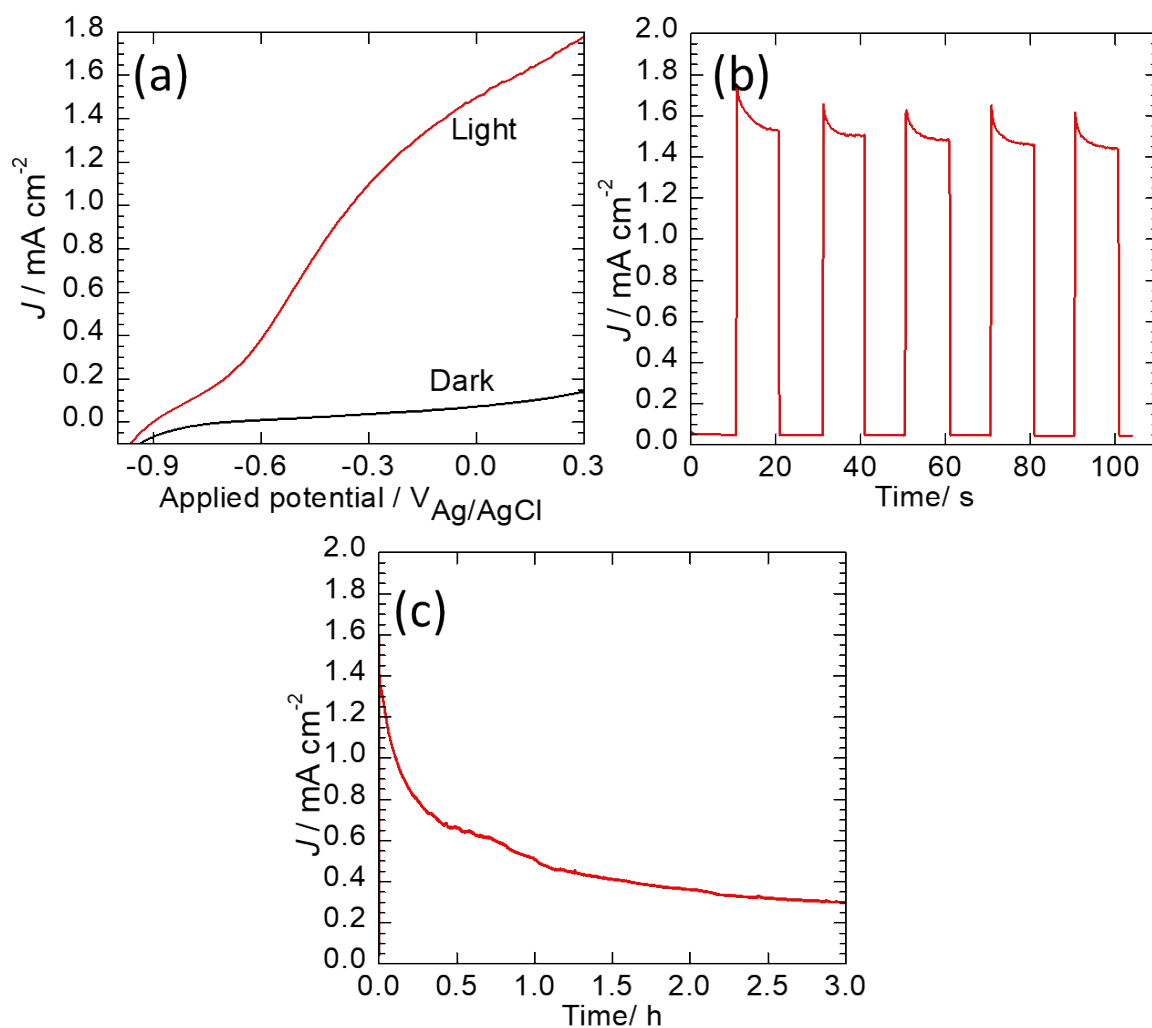
#### Additional Discussion

Figure S10 (a, b) shows the XRD for Cd(OH)<sub>2</sub>/CdSe porous NW/NS before and after 3 h PEC measurements. It is found that after the PEC measurement the crystal structure of Cd(OH)<sub>2</sub>/CdSe NW/NS is slightly disturbed and in addition to the hexagonal Cd(OH)<sub>2</sub> (JCPDS no. 98-002-3415), the presence of cubic CdS (JCPDS no. 98-002-9278) are overlapped with the cubic phase of CdSe (JCPDS no. 98-062-0436). This suggest that, after the PEC measurements in the Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> aqueous solution the pristine Cd(OH)<sub>2</sub>/CdSe NW/NS underwent partial sulfurization. However, we cannot exactly calculated the ratio of Cd(OH)<sub>2</sub> to CdS, because both phases have a disordered structure. On the other handed Figure S10 (c) shows the XRD pattern of the CdS<sub>x</sub>Se<sub>1-x</sub> photoelectrode prepared via addition of 0.1 M Na<sub>2</sub>S during the second hydrothermal solution. It confirms that the formation of CdS/CdSe heterojunction during *in situ* hydrothermal process.

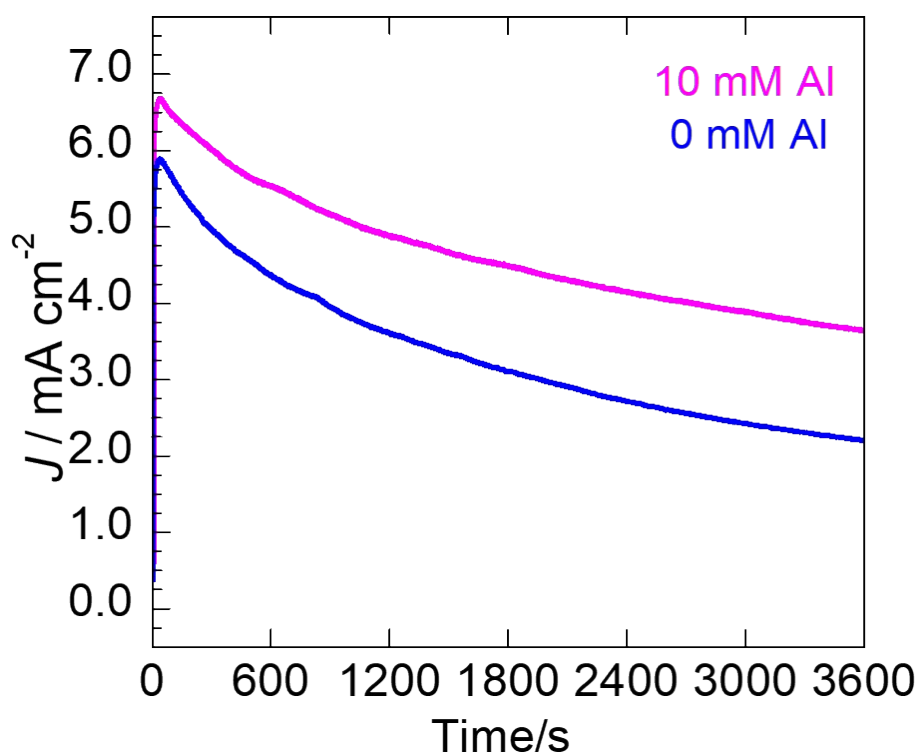


**Figure S11.** (a, b) Low and high magnified FESEM images (c) cross-section views and (d, f) is the corresponding EDS result for  $\text{CdS}_x\text{Se}_{1-x}$  photoelectrode prepared via addition of 0.1 M  $\text{Na}_2\text{S}$  during the second hydrothermal solution.

Figure S11 (a, b) shows the rough and porous surface of  $\text{CdS}_x\text{Se}_{1-x}$  photoelectrode. The lengths of the nanobelts range from 2.2 to 2.44 micrometers, and the width from 160 to 660 nm as shown in the cross-section (Figure S11(c)). The EDS results (Figure S11(d-f)), show a more atomic ratio of sulfur in the  $\text{CdS}_x\text{Se}_{1-x}$  photoelectrode than the porous  $\text{Cd}(\text{OH})_2/\text{CdSe}$  NW/NS's after 3 h PEC measurements in 0.1 M  $\text{Na}_2\text{S}/0.02$  M  $\text{Na}_2\text{SO}_3$  electrolyte.



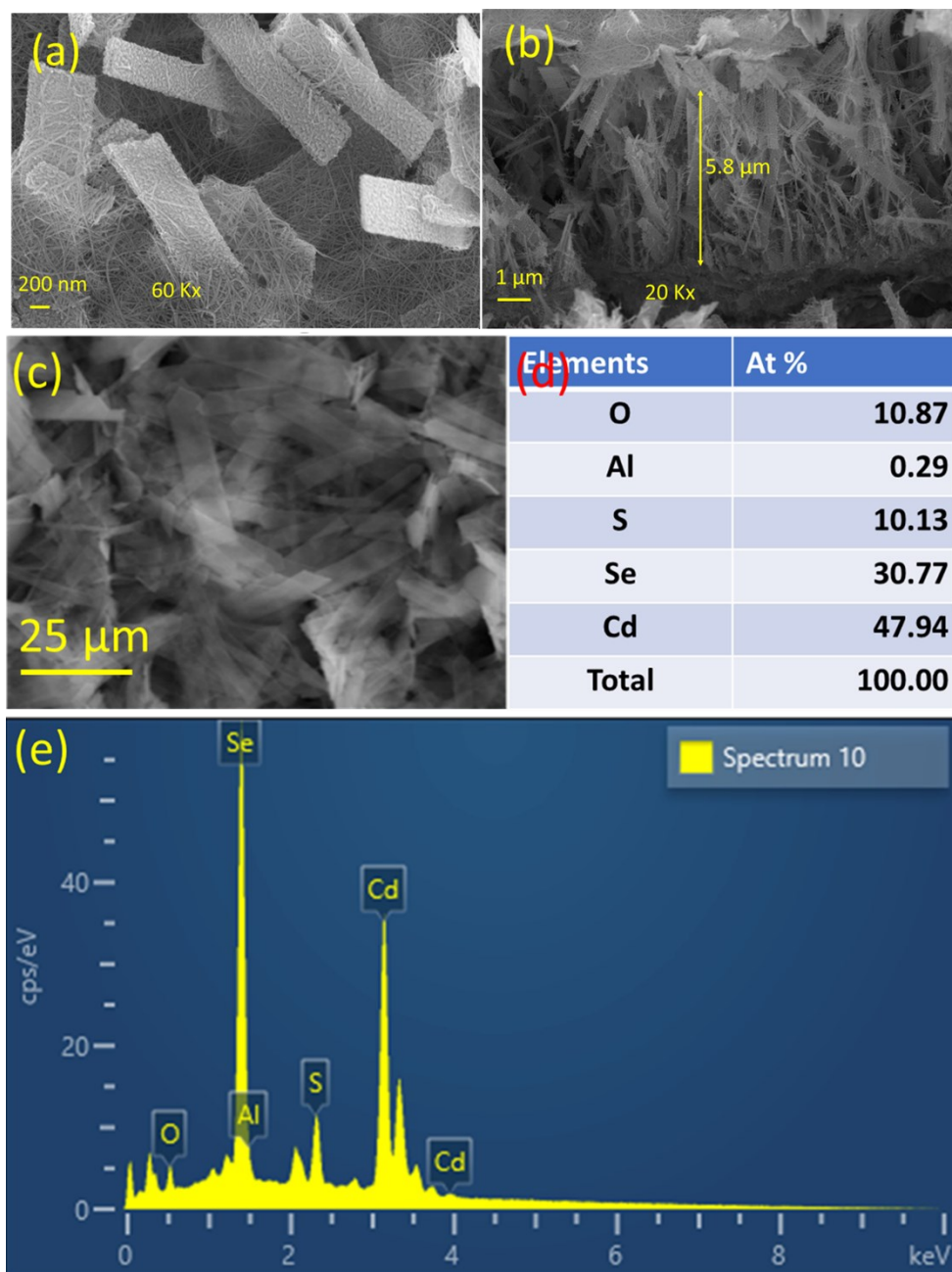
**Figure S12.** (a) Photocurrent density vs. applied potential curves, (b) photocurrent density vs. time at 0.0 V vs.  $\text{Ag/AgCl}$  and (c) stability test at 0 V versus  $\text{Ag/AgCl}$  under visible light (>420 nm) illumination ( $100 \text{ mW cm}^{-2}$ ) of  $\text{CdS}_x\text{Se}_{1-x}$  photoelectrode prepared via addition of 0.1 M  $\text{Na}_2\text{S}$  during the second hydrothermal synthesis. 0.1 M  $\text{Na}_2\text{S}/0.02 \text{ M Na}_2\text{SO}_3$  was used as electrolyte.



**Figure S13.** Amperometric  $J-t$  curves of the of 0 mM Al and 10 mM Al modified Cd(OH)<sub>2</sub>/CdSe NW/NS photoanodes at -0.3 V versus Ag/AgCl in 0.1 M Na<sub>2</sub>S /0.02M Na<sub>2</sub>SO<sub>3</sub> (pH 12.8). Light source: 300 W Xe lamp ( $\lambda > 420$  nm).

#### Additional discussion

Thus, modification with the Al<sub>2</sub>O<sub>3</sub> overlayer can facilitates the photogenerated hole transfer accumulated on the surface of the Cd(OH)<sub>2</sub>/CdSe NW/NS photoelectrode to the Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> electrolyte, which further improves the photocurrent density and the stability of the electrode. Figure S13 illustrates the amperometry,  $J-t$  curves of 0 mM Al and 10 mM Al modified Cd(OH)<sub>2</sub>/ CdSe NW/NS photoanodes under continuous illumination at -0.3 V versus Ag/AgCl. The photocurrent of bare Cd(OH)<sub>2</sub>/ CdSe NW/NS photoanodes is slightly improved after the Al<sub>2</sub>O<sub>3</sub> modifications. Thus, recombination at the surface as well as in the bulk are contributing the decrease in photocurrent and therefore attempt to improve the performance further should be focused on the bulk modification like doping or heterostructure and cocatalyst.



**Figure S14** (a, b) FESEM top and cross section images, (c-e) selected FESEM, elemental composition table (wt% and at%) and corresponding EDS pattern of optimum 10 mM Al modified Cd(OH)<sub>2</sub>/CdSe (NW/NS) photoanodes.

## References

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