

Interfacial Electric Field Construction of Hollow PdS QDs/Zn_{1-x}Cd_xS Solid Solution with Enhanced Photocatalytic Hydrogen Evolution

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1. Experimental Section

1.1 Chemicals

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$, AR, $\geq 99.0\%$), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, AR, $\geq 99.0\%$), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, AR, $\geq 98.0\%$), palladium chloride dihydrate ($\text{H}_2\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$, AR, $\geq 98.0\%$), cadmium (II) acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, AR, $\geq 98.0\%$), thiourea ($\text{CH}_4\text{N}_2\text{S}$, AR, $\geq 99.0\%$), anhydrous sodium sulfate (Na_2SO_4 , AR, $\geq 99.0\%$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, AR, $\geq 99.7\%$), lactic acid ($\text{C}_3\text{H}_6\text{O}_3$, AR, $\geq 85.0\%$) were purchased from Sinopharm Chemical Reagent. 5,5-Dimethyl-1-pyrrolene-N-oxide (DMPO, AR, $\geq 97\%$) was purchased from Aladdin. Nafion binder (5 wt.%, AR, DuPont520) was purchased from Sinero. All chemicals were used without further purification.

1.2 Synthesis of hexagonal ZnO.

Typically, $\text{Zn}(\text{Ac})_2$ (2 mmol) and hexamethylenetetramine (2 mmol) were added into 100 mL mixed ethanol aqueous solution (30%vol). The solution was then refluxed at 90 °C for 2 h. The white precipitates were collected by centrifugation and washed with water and ethanol for both 2 times. At last, the products were dried at 60 °C under vacuum overnight.

1.3 Synthesis of hollow ZnS.

The as-prepared 100 mg ZnO hexagonal particles were first dispersed in 40 mL of ethanol by sonication for 20 min. Then, 300 mg of thiourea was added into the 40 mL dispersion. The as-obtained solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C in an oven for 24 h. The precipitates were harvested by centrifugation and washed with water and ethanol for both 2 times. Then it's dried at 60 °C under vacuum overnight.

1.4 Synthesis of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solution.

A series of $Zn_{1-x}Cd_xS$ solid solution were synthesized, where x ($x=0.2, 0.4, 0.6, 0.8, 1.0$) represents the amount of substance ratio of Cd^{2+} to S^{2-} . Take the synthesis of $Zn_{0.6}Cd_{0.4}S$ solid solution as an example, first, 50 mg hollow ZnS were dispersed in 30 mL H_2O by sonication for 10 min. Then 4.10 mL $CdCl_2 \cdot 2H_2O$ aqueous solution (0.10 M) was added in the dispersion. Third, the as-obtained solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 160 °C in an oven for 24 h. Finally, the product was filtered, washed with water and ethanol for both 2 times, and dried at 60 °C under vacuum overnight. The synthesis process of other ratio of Cd^{2+} to S^{2-} is similar to the $Zn_{0.6}Cd_{0.4}S$, except for the usage amount of Cd^{2+} .

1.5 Synthesis of PdS QDs/ $Zn_{1-x}Cd_xS$ heterojunction.

A series of nwt% PdS QDs/ $Zn_{1-x}Cd_xS$ composites were constructed, where n ($n=0.1, 0.3, 0.5, 1, 3, 5$) represents the weight ratio of PdS QDs to $Zn_{1-x}Cd_xS$ which has the best HER performance. Take the synthesis of 0.5wt% PdS QDs/ $Zn_{1-x}Cd_xS$ composite as an example, typically, 50 mg of $Zn_{1-x}Cd_xS$ solid solution and 30 mL of ethanol were added into a 50 mL glass vial. Then, add 235 μ L $H_2PdCl_2 \cdot 2H_2O$ aqueous solution (0.01 M) and 235 μ L TAA aqueous solution (0.01 M) into the vial, maintained at 80 °C for 60 min. Finally, the product was filtered, washed with water and ethanol for both 2 times, and dried at 60 °C under vacuum overnight. The synthesis process of other nwt% PdS QDs/ $Zn_{1-x}Cd_xS$ composites is similar to the 0.5wt% PdS QDs/ $Zn_{1-x}Cd_xS$ composite, except for the usage amount of Pd^{2+} and TAA.

1.6 Characterization

The crystalline phases of samples were analyzed by X-ray diffractometer (XRD, SmartLab-SE, Rigaku) with Cu $K\alpha$ radiation (15 mA, 35 kV, and $k = 0.15406$ nm). The microstructures of samples were performed by field-emission scanning electron microscope (SEM, Hitachi S-4800) with an accelerating voltage of 15 kV and

transmission electron microscope (TEM, Tecnai F30) equipped with an energy dispersive X-ray spectroscopy (EDX) system. The microscope was operated at an acceleration voltage of 200 kV, which determines the energy of the transmitted electrons. X-ray photoelectron spectroscopy (XPS) was detected by Thermo Scientific ESCALAB Xi⁺ equipped with Al K_α radiation at 1486.6 eV. The ultraviolet visible (UV-vis) diffuse reflectance spectra (DRS) were acquired using a Varian-Cary 5000 spectrometer with BaSO₄ as a reference substance. Steady-state photoluminescence (PL) was recorded on a Hitachi F-7000 spectrophotometer with an excitation wavelength of 390 nm. Time-resolved photoluminescence (TRPL) spectra were obtained using an Edinburgh Instruments FLS980 fluorescence.

1.7 Electrochemical measurement

The photoelectrochemical experiments were conducted using an electrochemical workstation (CHI 760E, Shanghai Chenhua) in a standard three-electrode reaction cell. The counter electrode was a platinum plate, while the reference electrode was an Ag/AgCl electrode. The working electrode was prepared as follows: 10 mg of the sample was dispersed in 500 μL ethanol, 450 μL ultrapure water and 50 μL Nafion solution to form a suspension. Then, 50 μL of the suspension was coated onto a 1 cm × 1 cm FTO plate and dried at 60 °C. Photocurrent measurements were performed in a 0.1 M Na₂SO₄ solution under visible-light irradiation from a 300 W xenon light source. Electrochemical impedance spectra (EIS) and linear sweep voltammetry (LSV) were also carried out in a 0.1 M Na₂SO₄ aqueous solution.

1.8 Electron spin resonance radical trapping experiments

The electron spin resonance (ESR) spectra were acquired using a Bruker EMX-10/12 ESR spectrometer. The trapping experiments were performed as follows: 10 mg of synthetic samples were dispersed in 5 mL of ultrapure water 10 mM of DMPO,

using ultrasonication to form a mixed solution. Subsequently, the mixed suspension was injected into an ESR detector tube. It was then exposed to Xe lamp irradiation for 5 minutes. Afterward, ESR spectroscopy experiments were performed at room temperature. This solution was subjected to in situ ESR measurements to capture $\bullet\text{OH}$ species.

1.9 Computational methods

First-principle calculation of density of functional theory (DFT) was operated based on the Cambridge Sequential Total energy Package (CASTEP)¹. The exchange correlation interaction between electron and atomic nucleus was conducted by Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA) method. Grimme's DFT-D scheme was used to correct the van der Waals (vdW) dispersion. The calculation was operated on a $4\times 4\times 1$ supercell of $\text{Zn}_{0.6}\text{Cd}_{0.4}\text{S}$ and for 0.5wt% PdS QDs/ $\text{Zn}_{0.6}\text{Cd}_{0.4}\text{S}$ one of Zn atoms was displaced by a Pd atom. During the geometry optimization, $2\times 2\times 4$ Monkhorst-Pack k-point grid is employed. The energy cutoff was 560.50 eV. Moreover, the select convergence tolerance of 1.0×10^{-5} eV/atom for energy, 0.03 eV/Å for maximum force, 0.05 GPa for maximum stress, 0.001 Å for maximum displacement and 1.0×10^{-6} eV/atom for self-consistent field (SCF).

1.10 Photocatalytic performance evaluation

The photocatalytic H_2 evolution performance was tested in follows: 10 mg of the photocatalysts were introduced into a sealed tube reactor with a diameter of 16 mm and volume of 20 mL. The reactor contained 9 mL of ultrapure water and 1 mL of lactic acid, which were subjected to ultrasonication to ensure proper mixing and filled with argon for 5 min. Subsequently, visible-light irradiation was applied using a 300 W xenon lamp with a cut-off filter ($\lambda > 420$ nm) in 2 h irradiation. H_2 evolution

amount was analyzed by Agilent 7890 A gas chromatography with a thermal conductivity detector.

The testing of photocatalytic stability is mainly divided into the following steps. Firstly, perform photocatalytic activity testing according to the above steps; After completing the first test cycle, recorded H₂ amount and recycled all the catalysts by centrifugation, and label the test results as Cycle 1. Finally, repeat the above steps with the collected catalyst to obtain the following cyclic test data.

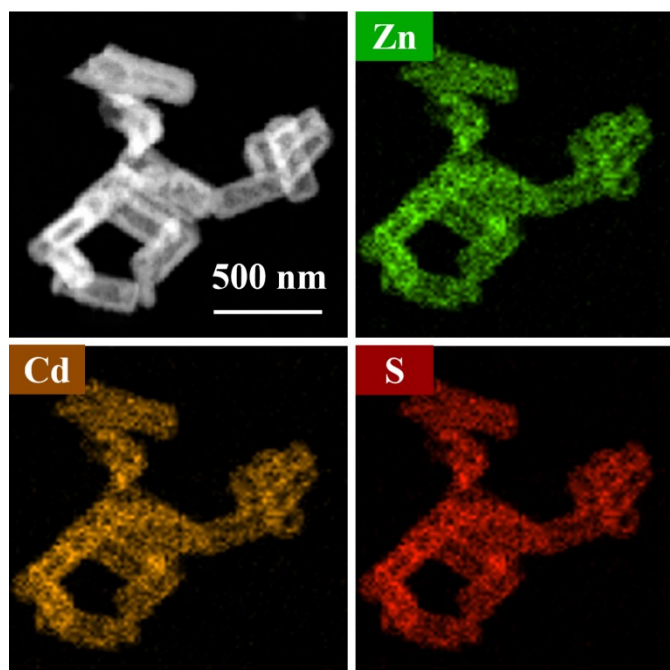


Fig. S1 Corresponding EDX elemental mapping images of the Zn_{0.6}Cd_{0.4}S sample.

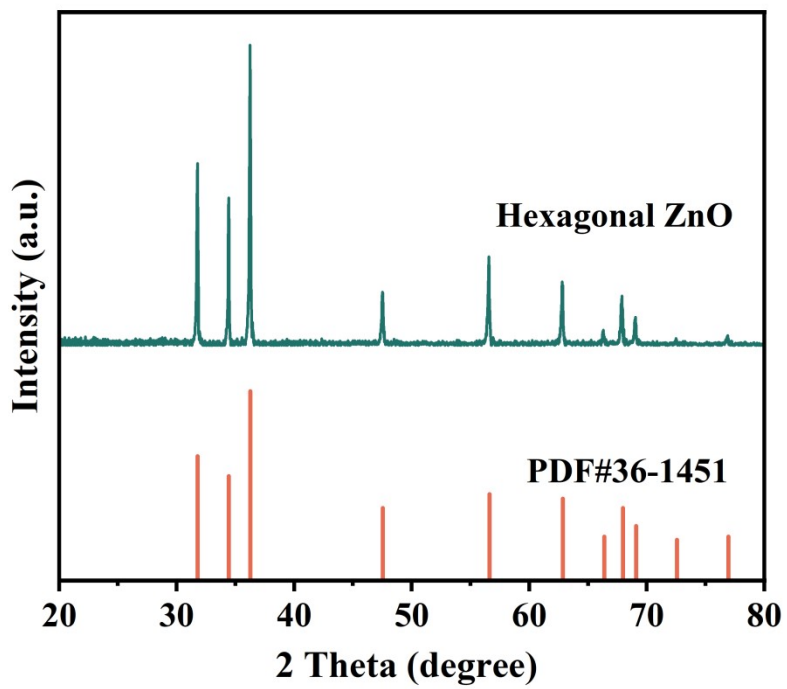


Fig. S2 XRD pattern of hexagonal ZnO.

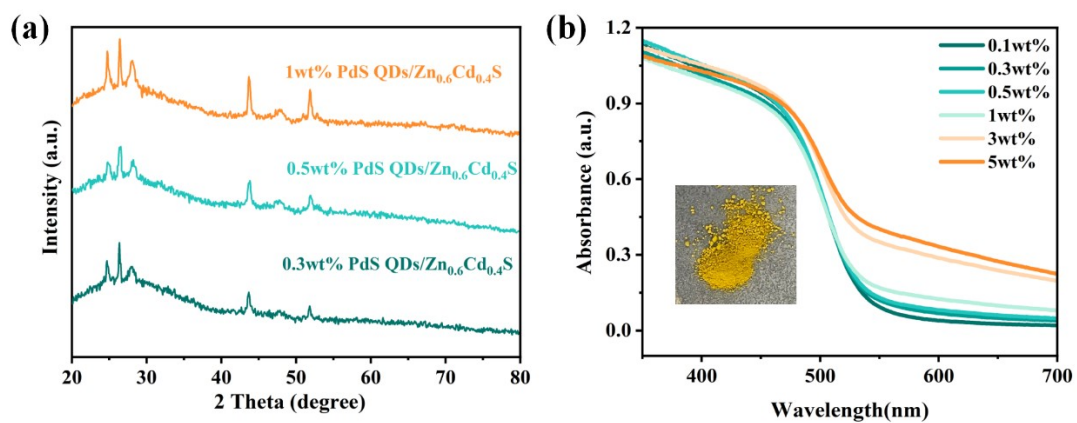


Fig. S3 (a) XRD patterns and (b) UV-vis DRS absorption plots of different loading amount of PdS QDs on Zn_{0.6}Cd_{0.4}S solid solution (the insert is the digital image of 0.5wt% PdS QDs/Zn_{0.6}Cd_{0.4}S sample).

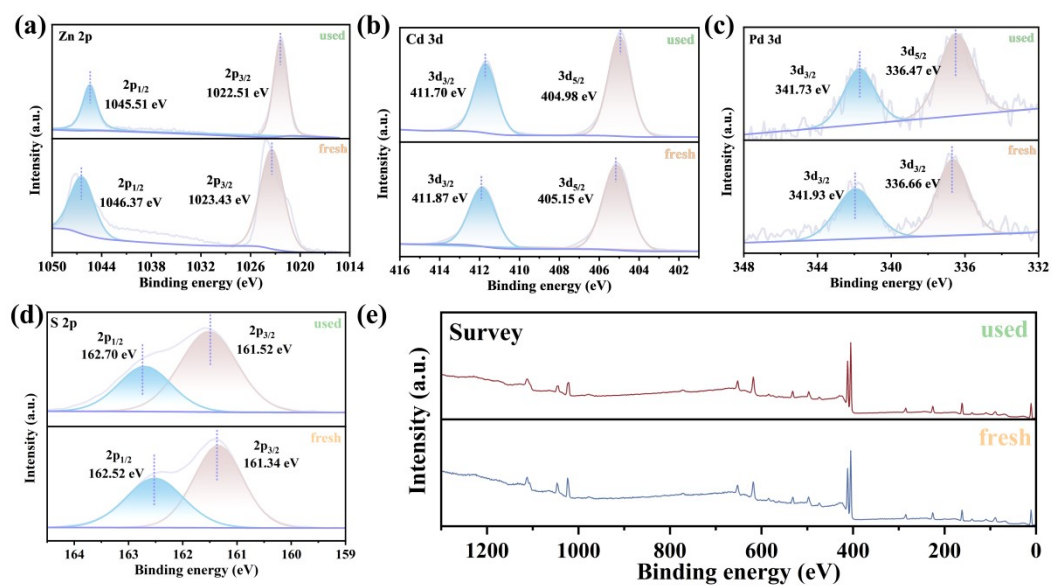


Fig. S4 (a) Zn 2p, (b) Cd 3d, (c) Pd 3d, and (d) S 2p of XPS pattern for 0.5wt% PdS QDs/Zn_{0.6}Cd_{0.4}S composite before and after photocatalytic reaction.

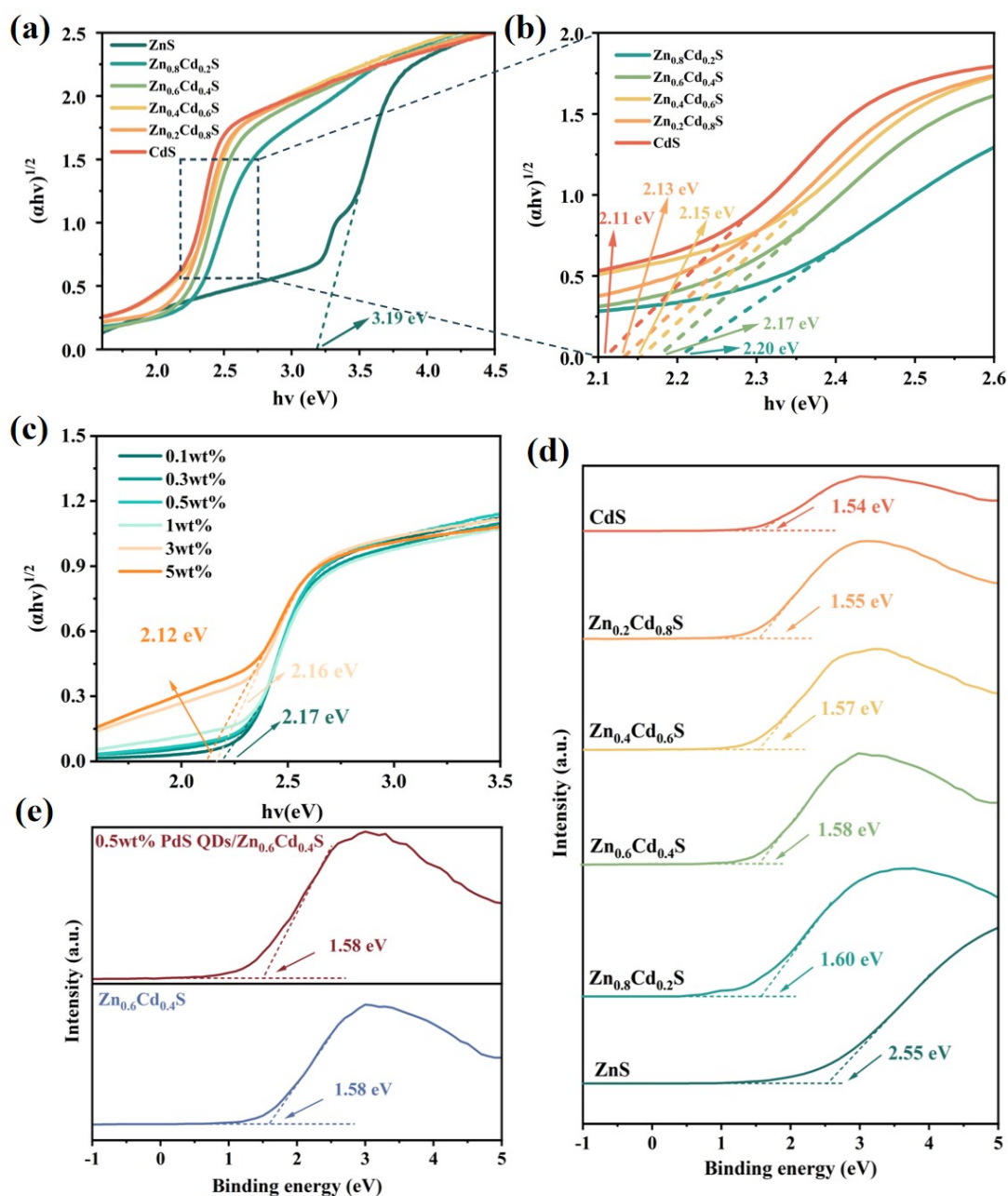


Fig. S5 $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots by Kubelka-Munk of (a, b) Zn_{1-x}Cd_xS solid solution and (c) nwt% PdS QDs/Zn_{0.6}Cd_{0.4}S. (c) Valence band XPS of (d) Zn_{1-x}Cd_xS solid solution and (e) 0.5wt% PdS QDs/Zn_{0.6}Cd_{0.4}S.

Table S1 EDS results of Cd: (Cd+Zn) ratio in $Zn_{1-x}Cd_xS$ samples.

Catalysts	Atoms ratio of Cd: (Zn+Cd)	
	Theoretical	Experimental
ZnS	0%	0%
$Zn_{0.8}Cd_{0.2}S$	20.00%	22.90%
$Zn_{0.6}Cd_{0.4}S$	40.00%	38.83%
$Zn_{0.4}Cd_{0.6}S$	60.00%	60.42%
$Zn_{0.2}Cd_{0.8}S$	80.00%	76.92%
CdS	100.00%	98.92%

Table S2. The corresponding binding energy positions of ZnS, CdS, Zn_{0.6}Cd_{0.4}S, 0.5wt% PdS QDs/Zn_{0.6}Cd_{0.4}S, used 0.5wt% PdS QDs/Zn_{0.6}Cd_{0.4}S.

Binding energy (eV)	Cd 3d _{3/2}	Cd 3d _{5/2}	S 2p _{1/2}	S 2p _{3/2}	Zn 2p _{1/2}	Zn 2p _{3/2}	Pd 3d _{1/2}	Pd 3d _{3/2}
ZnS	-	-	162.20	160.90	1044.40	1021.30	-	-
CdS	410.29	403.56	161.16	159.96	-	-	-	-
Zn _{0.6} Cd _{0.4} S	411.79	405.06	162.74	161.55	1045.08	1022.07	-	-
0.5wt% PdS QDs /Zn _{0.6} Cd _{0.4} S	411.87	405.15	162.70	161.52	1046.37	1023.43	341.93	336.66
used 0.5wt% PdS QDs/Zn _{0.6} Cd _{0.4} S	411.7	404.98	162.52	161.34	1045.51	1022.51	341.73	336.47

Table S3. Comparison of photocatalytic hydrogen evolution performance of different sulfide catalysts respectively.

Materials	H ₂ evolution		Sacrificial reagent	Ref.
	rate (mmol g ⁻¹ h ⁻¹)	Light source		
Ni/ZCS (6%)	31	300W Xe lamp UV irradiation(>420)	Na ₂ S/Na ₂ SO ₃	2
0.5wt% PdS QDs/Zn _{0.6} Cd _{0.4} S	27.6	300W Xe lamp UV irradiation(>420)	Lactic Acid	This Work
BP-Pt/CdS nanospheres	24.17	300W Xe lamp UV irradiation(>420)	Lactic Acid	3
<u>CdS@ZnNi-C</u>	15.7	300W Xe lamp (at 420)	Na ₂ S/Na ₂ SO ₃	4
CdS frame-in-cage	13.6	300W Xe lamp (>400)	Na ₂ S/Na ₂ SO ₃	5
Hollow Zn _{0.6} Cd _{0.4} S dodecahedral Cage	5.68	300W Xe lamp UV irradiation (>420)	Na ₂ S/Na ₂ SO ₃	6
Ag ₂ S@CdS/ZnS	3.76	300W Xe lamp (420~800)	Na ₂ S/Na ₂ SO ₃	7
ZnIn ₂ S ₄ /Mo ₂ TiC ₂	3.12	300W Xe lamp UV irradiation (>420)	TEOA	8
OFH-CZt	3.072	300W Xe lamp (320~780)	Na ₂ S/Na ₂ SO ₃	9
RGO-Zn _{0.8} Cd _{0.2} S	1.824	AM 1.5G	Na ₂ S/Na ₂ SO ₃	10
VZIS/NWO-5	1.781	300W Xe lamp UV irradiation (>420)	TEOA	11
CoS _x /g-C ₃ N ₄	0.629	350W Xe lamp (>400)	TEOA	12
CdS/Bi ₂ S ₃ -V _s	0.54	300W Xe lamp	Na ₂ S/Na ₂ SO ₃	13

Table S4. The values of R_{ct} from EIS spectra (Fig. 5b)

Samples	ZnS	CdS	$Zn_{0.6}Cd_{0.4}S$	0.5wt% PdS QDs/ $Zn_{0.6}Cd_{0.4}S$
R_{ct} (Ω)	3652	2451	1256	999

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