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### Supporting information

## Construction of heterojunctions between $\text{ReS}_2$ and twin crystal $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ for boosting solar hydrogen evolution

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## Experimental

### Preparation of twin crystal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (T-ZCS)

Firstly, twin crystal  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$  was prepared by a modified process according to previous reports.<sup>11, 13</sup> In detail, 5 mmol  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 5 mmol  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , and 12.5 mmol thioacetamide were added to 20 mL distilled water. After vigorous stirring for 1 h, 5 mL of 4 M NaOH aqueous solution was dissolved into the reaction mixture followed by constantly strong stirring for another 1 h. Then, the resulting mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated to 180 °C maintaining for 24 h. The products were collected by centrifuging and washing with distilled water and ethanol for many times in order to remove residual impurity. After dried under vacuum at 60 °C overnight, the final mixture was obtained, which is named as T-ZCS. For comparison, the traditional pure phase  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$  solid solution (P-ZCS) was prepared with the same procedure as described above except adding 4 M NaOH aqueous solution.

### Preparation of $\text{ReS}_2$ and $\text{ReS}_2/\text{T-ZCS}$ nanocomposites

$\text{ReS}_2/\text{T-ZCS}$  nanocomposites was prepared via a convenient one-step hydrothermal method. Firstly, 40.35 mg ammonium perrhenate ( $\text{NH}_4\text{ReO}_4$ ), 49.69 mg thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ) and 45.95 mg hydroxylamine hydrochloride ( $\text{HONH}_3\text{Cl}$ ) were dissolved in 25 mL deionized water under continuous stirring for 30 min. Then, 200 mg  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$  was added to the above solution followed by constantly strong stirring for another 30 min. The suspension was transferred into a 50 mL Teflon-lined autoclave, heated at 220 °C for 48 h, and followed to cool to room temperature. The final product was repeatedly washed with distilled water and ethanol for several time until the remaining impurities were completely removed. Then the mixture was dried in vacuum at 60 °C overnight and named as 10 wt% $\text{ReS}_2/\text{T-ZCS}$ . Similarly, x % ( $x = 2, 5, 12$  and  $15$ )  $\text{ReS}_2/\text{T-ZCS}$  were synthesized by changing the amount of  $\text{NH}_4\text{ReO}_4$ ,  $\text{CH}_4\text{N}_2\text{S}$  and  $\text{HONH}_3\text{Cl}$ .

By contrast, flower-like ReS<sub>2</sub> was synthesized by the same method but without adding twined Zn<sub>0.5</sub>Cd<sub>0.5</sub>S nanocomposites.

### **Characterization**

The X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV diffractometer using with Cu K $\alpha$  radiation ( $\lambda = 1.538 \text{ \AA}$ ). The scanning electron microscopy (SEM) images were examined by using a JSM 6700F microscope. The High-resolution transmission electron microscope (TEM and HRTEM) images were obtained on a JEM 2100 instrument operating at 200 kV. The X-ray photoelectron spectra (XPS) were collected on a Thermo Escalab 250 Xi with Mg K $\alpha$  (1253.6 eV). The UV-vis diffused reflectance spectra (DRS) were collected on a Hitachi UV-3900 spectrophotometer, and BaSO<sub>4</sub> was used as the reference sample. The Steady-state fluorescence spectra, time resolved fluorescence spectra, and fluorescence quantum yields were collected on a FLS 980 fluorescence spectrophotometer (Edinburgh instrument Ltd, England). The Brunauer–Emmett–Teller (BET) surface area and the pore size distributions were collected on a Micromeritics ASAP 2020 nitrogen adsorption apparatus under nitrogen adsorption.

### **Photoelectrochemical measurements**

The photoelectrochemical behaviors of the samples were taken by using a CHI760D electro-chemical work station (Chenhua Instrument, Shanghai, China) with a standard three-electrode system. The three-electrode electrochemical workstation: reference electrode: Hg/Hg<sup>2+</sup> (saturated KCl); working electrode: FTO electrode deposited with the nanocomposites; counter electrode: Pt sheet; 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The working electrode was prepared by drop-coating ethanol suspensions onto pre-cleaned FTO glass surface. Typically, 3 mg catalyst was dispersed in 5 mL ethanol by ultrasonic treatment for 1 h. Subsequently, the above solution was dropped onto a 1 cm x1 cm FTO glass electrode surface, and then dried at room

temperature. The working electrodes were dried at room temperature for overnight. The light source was A 300 W Xe lamp with a UV cut-off filter ( $\lambda > 420$  nm) during photocurrent measurements. The photo-responsive signals were analysed by i-t curves and the electrochemical impedance spectroscopy was tested at a frequency range from 0.01-105 Hz. The Impedance-Potential mode was used to record the Capacitance-voltage curve (Mott-Schottky plot) at a frequency of 600, 800 and 1000 Hz.

### **Photocatalytic H<sub>2</sub> evolution experiment**

Photocatalytic reactions of the samples were measured in a 250 mL closed quartz vial under the top irradiation. A 300 W xenon lamp (PLS-SXE 300D) equipped with a cut-off filter ( $\lambda > 420$  nm) was chosen as a visible light source and the area of surface irradiated was about 16.6 cm<sup>2</sup>. The cylinder reactor was kept at room temperature by a cooling water bath. In a typical photocatalytic experiment, 10 mg of the photo-catalysts was well dispersed in 100 mL aqueous solution of sacrificial reagent (0.35 M Na<sub>2</sub>S and 0.25 M Na<sub>2</sub>SO<sub>3</sub>) with a constant stirring. Before the irradiation, the system was bubbled with nitrogen for 30 min to remove the dissolved air completely. During experiment process, the produced gas was voluntarily analyzed by an on-line gas chromatograph to give the H<sub>2</sub> production rate with (GC 7900, high-purity N<sub>2</sub> as carrier gas).

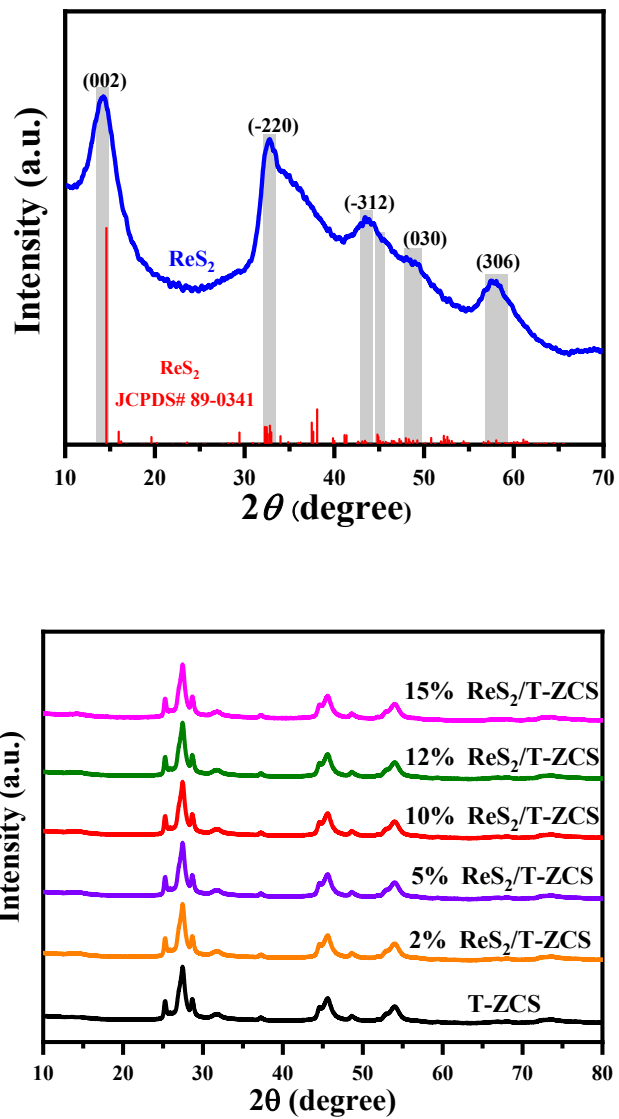
The apparent quantum efficiency (AQY) was measured under similar photocatalytic reaction conditions by using a 420 nm band pass filter and an irradiatometer. The AQY was measured by the following equation (1):

$$AQY = \frac{N_{H_2}}{N_p} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$

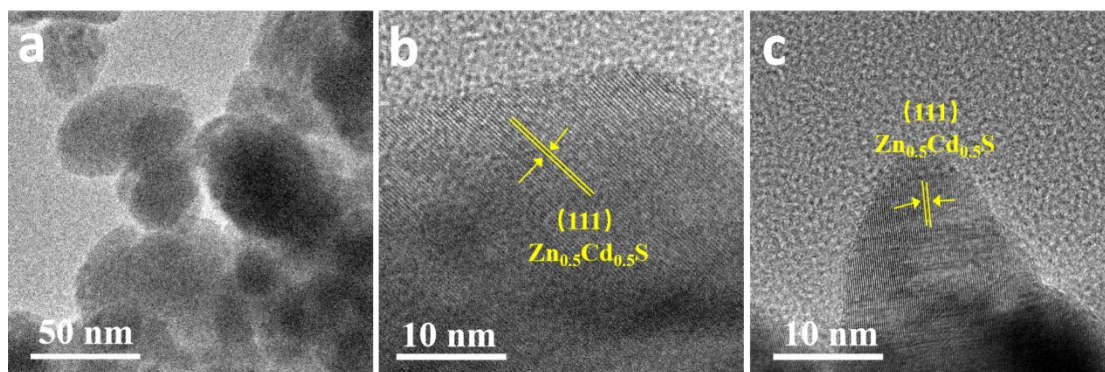
$$= \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{number of incident photons}} \times 100\%$$

The power of incident light (P) was 0.162 J<sup>-1</sup>, corresponding to the number of incident photons ( $3.42 \times 10^{17}$  photons per second), which was measured by using an optical power meter (Beijing Normal University Optical Instrument, FZ-

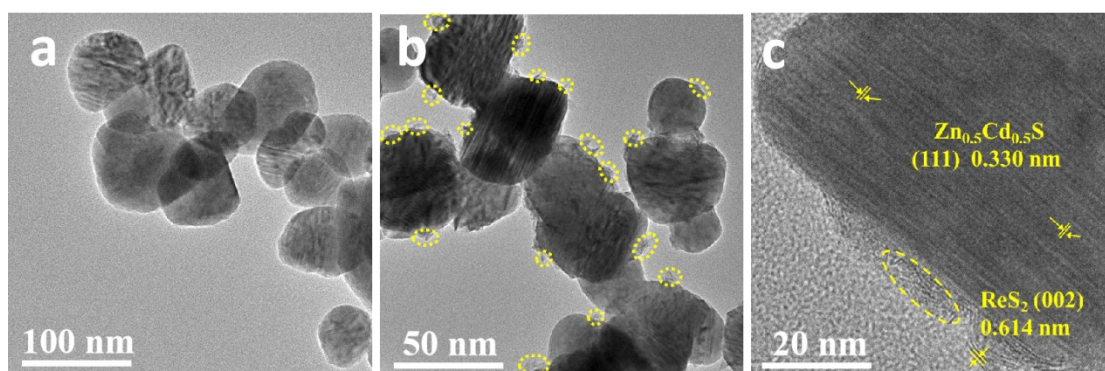
A).



**Fig. S1** XRD patterns of as-prepared ReS<sub>2</sub> sample and standard XRD card of triclinic phase ReS<sub>2</sub>, T-ZCS and ReS<sub>2</sub>/T-ZCS samples with different amount of ReS<sub>2</sub>.

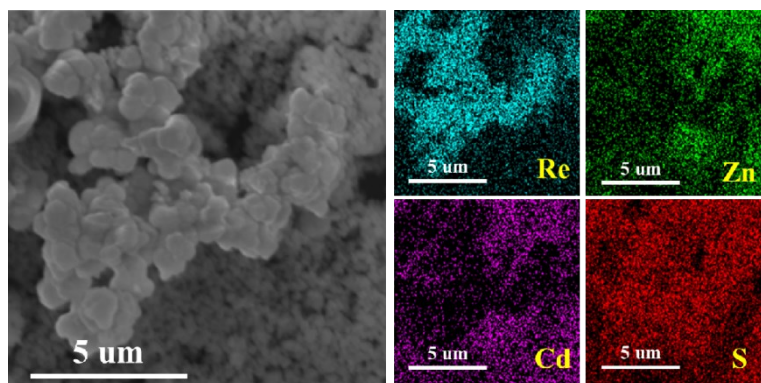


**Fig. S2** TEM and HRTEM images of pure phase P-ZCS.

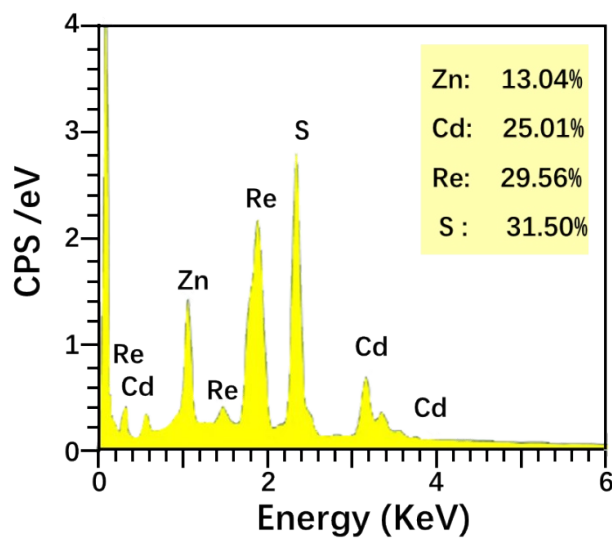


**Fig. S3** TEM images of (a) twin crystal T-ZCS, (b) 10%  $\text{ReS}_2$ /T-ZCS. HRTEM images of (c) 10%  $\text{ReS}_2$ /T-ZCS.

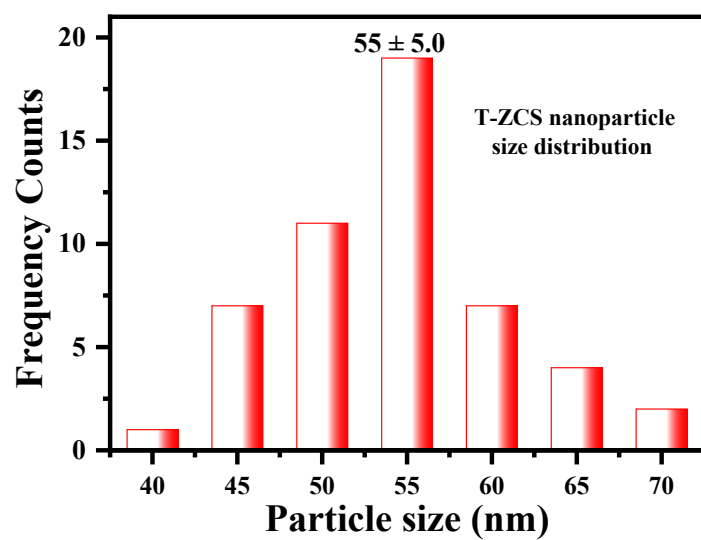




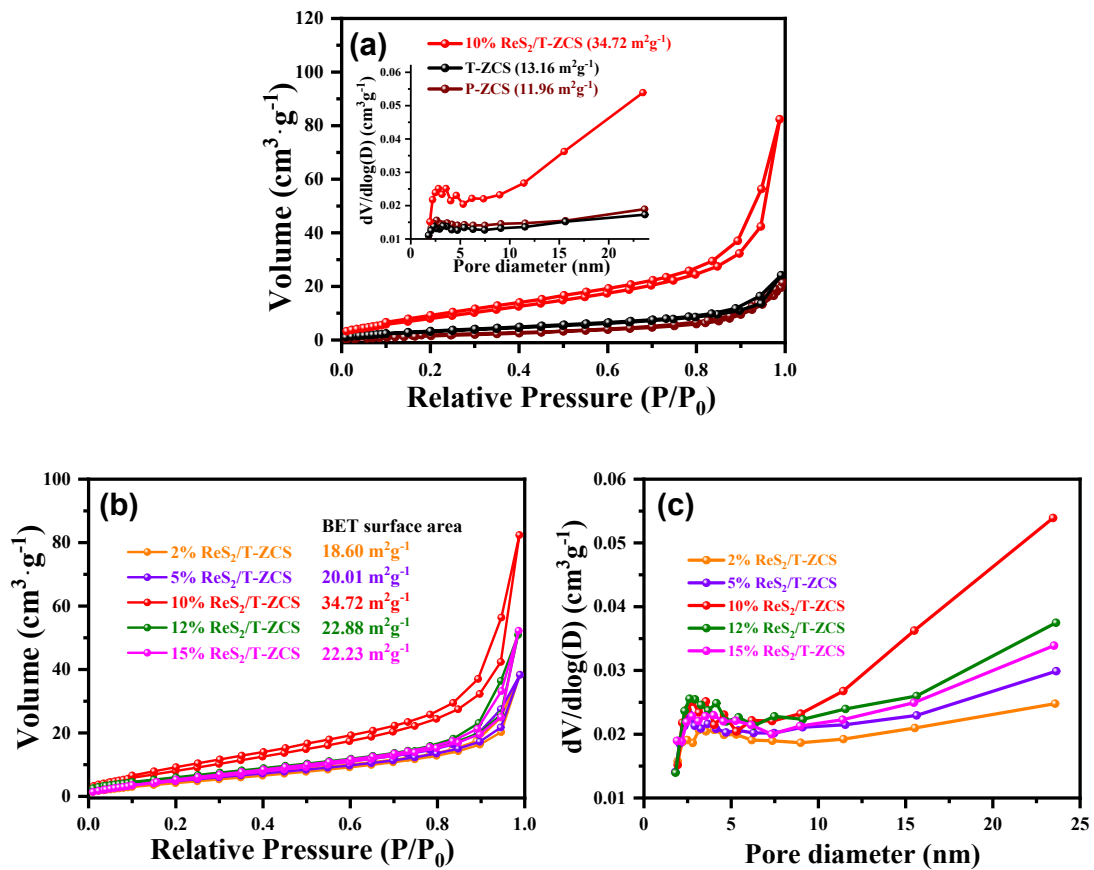
**Fig. S4** Element mapping images of 10% ReS<sub>2</sub>/T-ZCS.



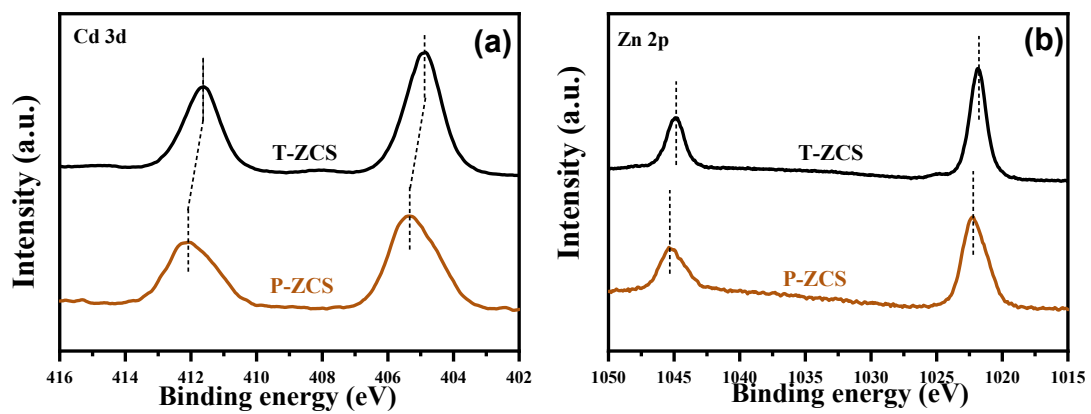
**Fig. S5** EDS spectrum of 10% ReS<sub>2</sub>/T-ZCS.



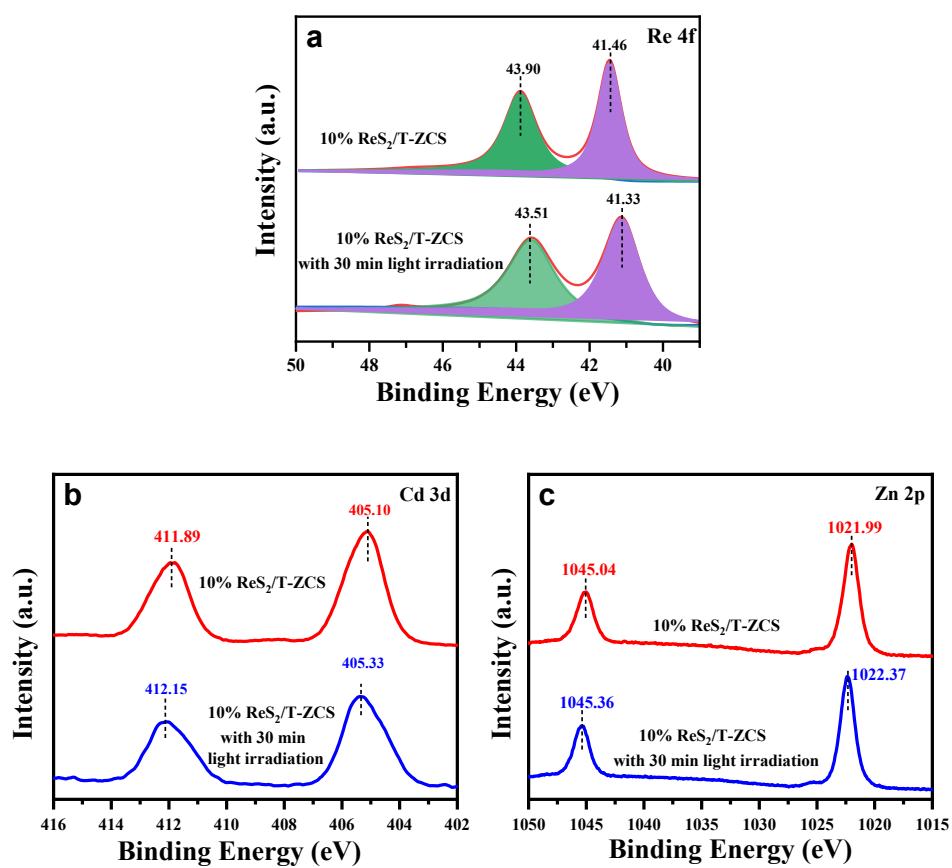
**Fig. S6** Average diameter distribution of T-ZCS nanoparticles.



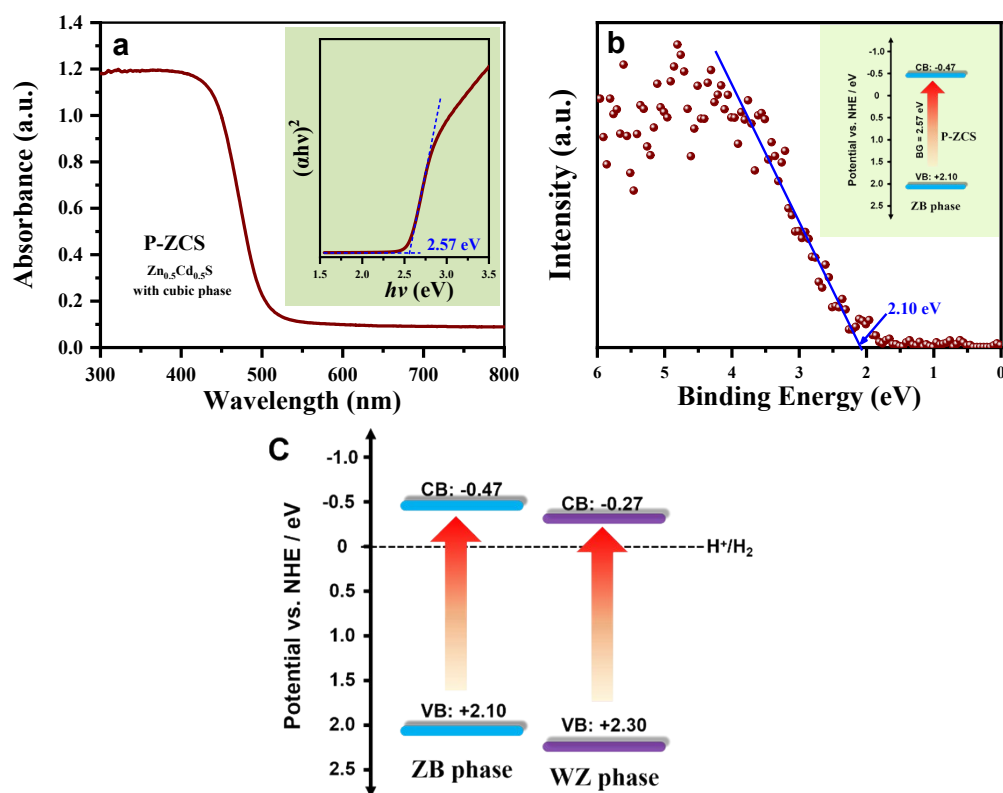
**Fig. S7** (a) Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of T-ZCS, P-ZCS and 10% ReS<sub>2</sub>/T-ZCS samples. (b) Nitrogen adsorption-desorption isotherms and pore size distribution curves of (c) ReS<sub>2</sub>/T-ZCS samples with different ReS<sub>2</sub> contents.



**Fig. S8** High-resolution XPS spectra of (a) Cd 3d and (b) Zn 2p of P-ZCS and T-ZCS samples.

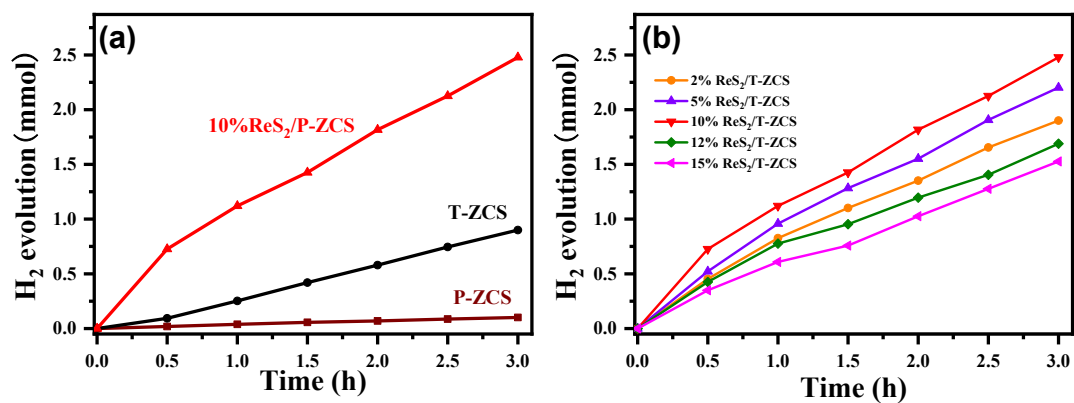


**Fig. S9** (a) Re 4f, (b) Cd 3d and (c) Zn 2p XPS spectra of ReS<sub>2</sub>/T-ZCS before and after 30 min light irradiation.

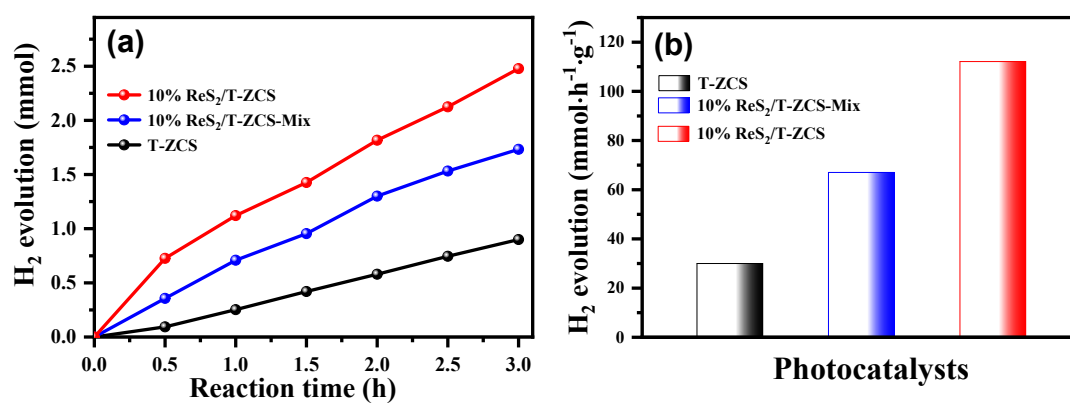


**Fig. S10** (a) UV-vis diffuse reflection spectra and corresponding Tauc plots of P-ZCS. (b) VB-XPS spectrum of P-ZCS. (c) band structure diagrams of twin ZCS with ZB and WZ phases.

We combined theoretical calculation and experiment method to determine the band energy position of T-ZCS. By means of theoretical calculation method, Haoming Cheng's group reported that the conduction and valence band position of ZB phase are slightly higher with the value of 0.2~0.3 eV than that of WZ phase (*ACS Appl. Mater. Interfaces*, **2015**, 7, 22558) At the same time, we prepared pure  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$  solid solution (P-ZCS) with ZB phase and determined its bandgap structure via Tauc plot of UV-vis spectra (Fig. S10a) and VB-XPS spectra (Fig. S10b), which exhibits the CB and VB about -0.47 eV and +2.10 eV, respectively. Therefore, the band level of CB and VB in WZ phase is calculated to be -0.27 eV (-0.47+0.2) and +2.3 eV (2.1+0.2), respectively. The band structure alignment of twin T-ZCS is illustrated in Fig. S10c. It can be seen that the CB level of both ZB and WZ phase satisfies the requirement of reducing  $\text{H}_2$  evolution. The electron transferring from CB of ZB to WZ can still reduce  $\text{H}^+$  to  $\text{H}_2$ .



**Fig. S11** Photocatalytic hydrogen evolution under visible light irradiation for 3 h over (a) pure phase P-ZCS, twin crystal T-ZCS and 10% ReS<sub>2</sub>/T-ZCS catalysts and (b) ReS<sub>2</sub>/T-ZCS with different ReS<sub>2</sub> contents.



**Fig. S12** (a) Photocatalytic hydrogen evolution and (b) H<sub>2</sub> evolution rate under visible light irradiation for 3 h over twin crystal T-ZCS and 10% ReS<sub>2</sub>/T-ZCS-Mix and 10% ReS<sub>2</sub>/T-ZCS samples.



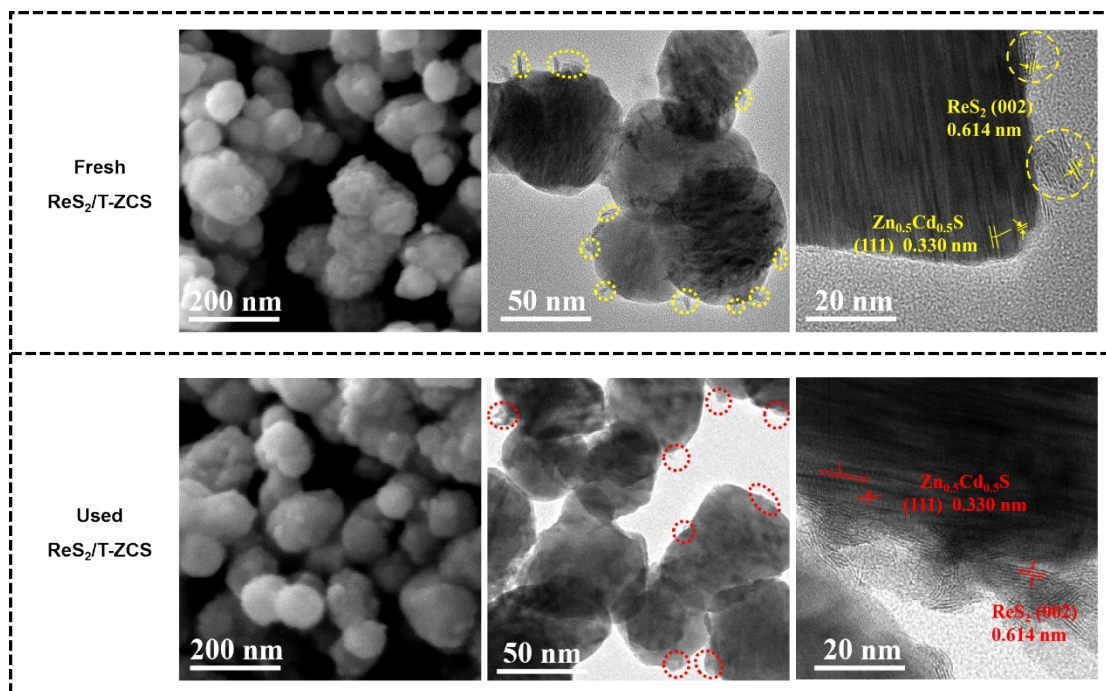
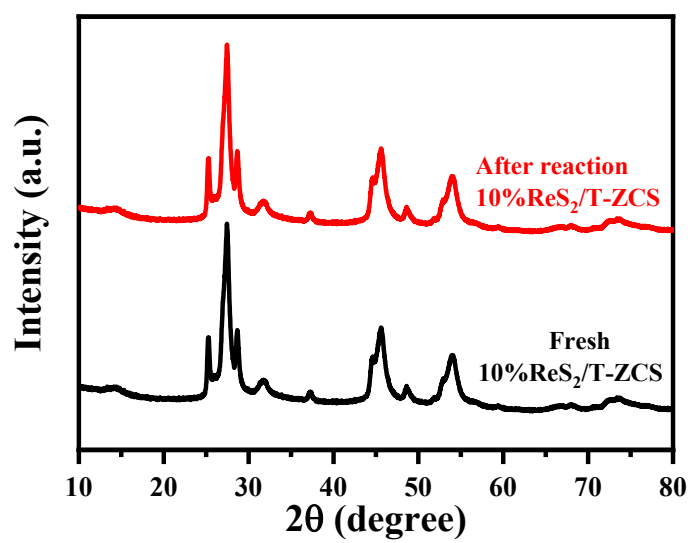
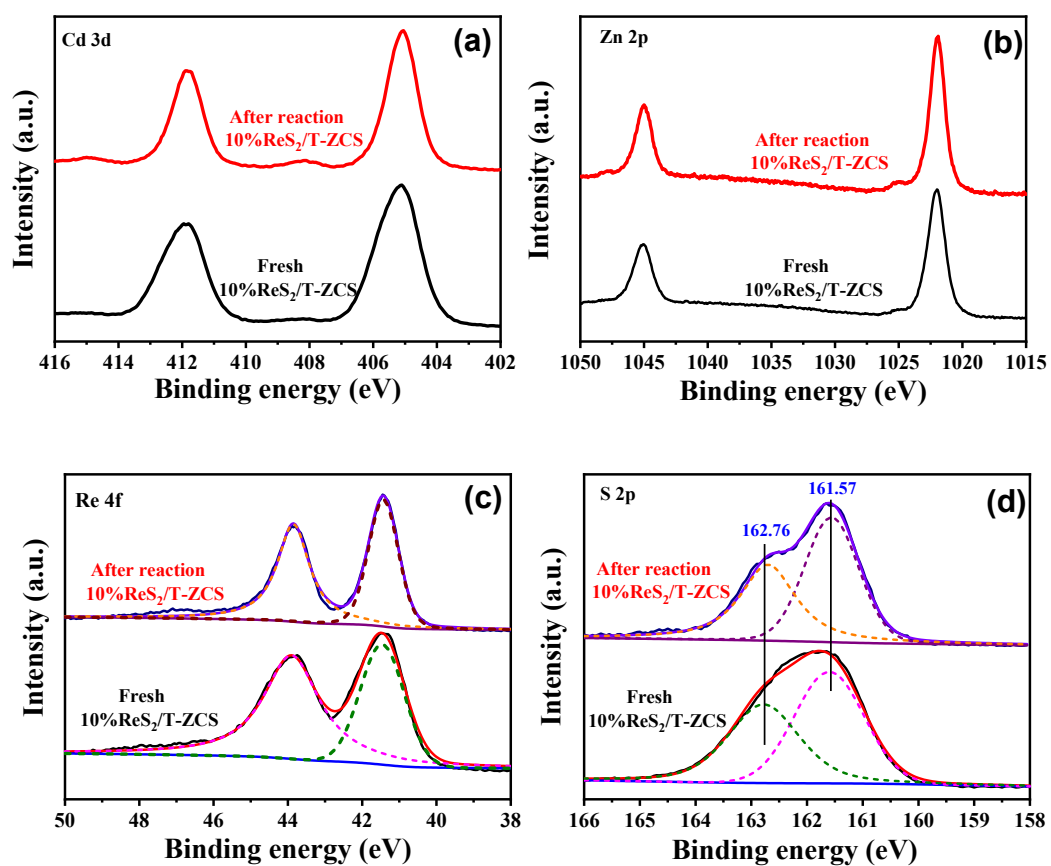


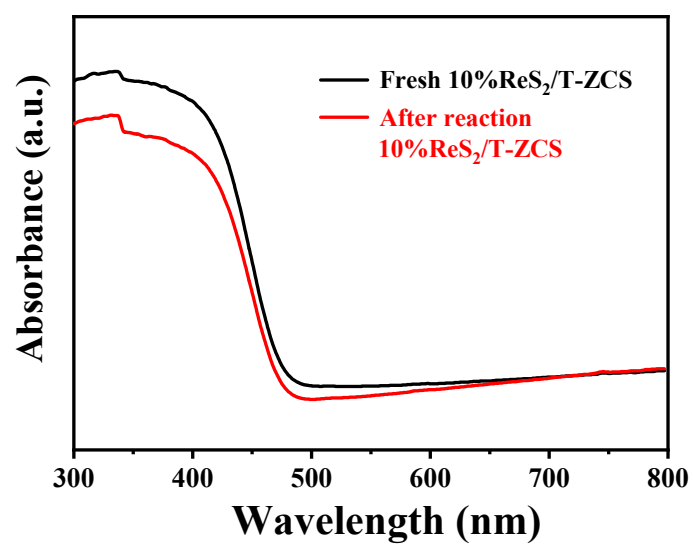
Fig. S13 SEM and TEM of used 10%  $\text{ReS}_2/\text{T-ZCS}$  samples.



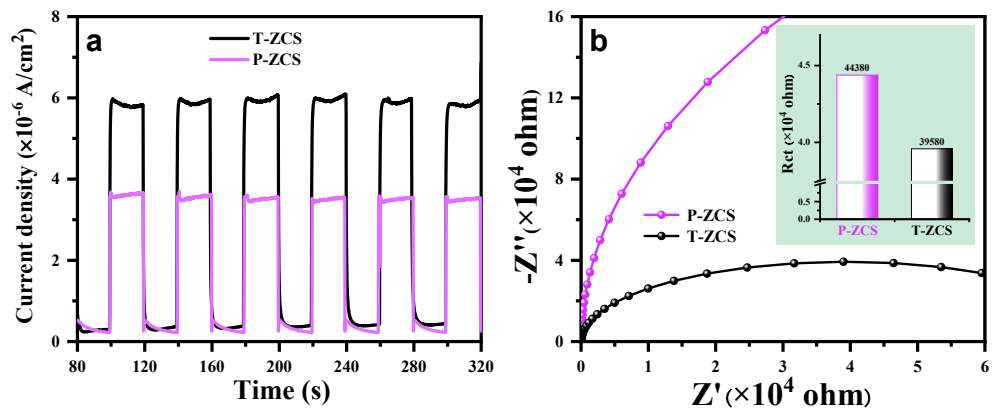
**Fig. S14** XRD pattern of fresh 10% ReS<sub>2</sub>/T-ZCS and used 10% ReS<sub>2</sub>/T-ZCS samples.



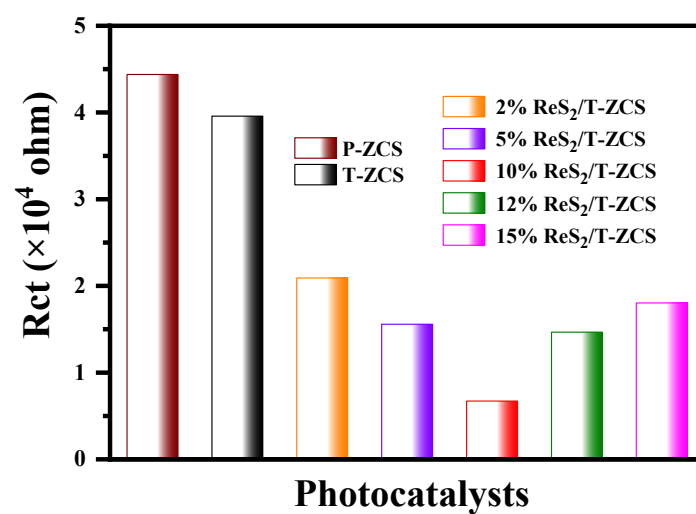
**Fig. S15** (a) Cd 3d, (b) Zn 2p, (c) Re 4f, (d) S 2p high resolution XPS spectra of fresh 10%  $\text{ReS}_2/\text{T-ZCS}$  and used 10%  $\text{ReS}_2/\text{T-ZCS}$  samples.



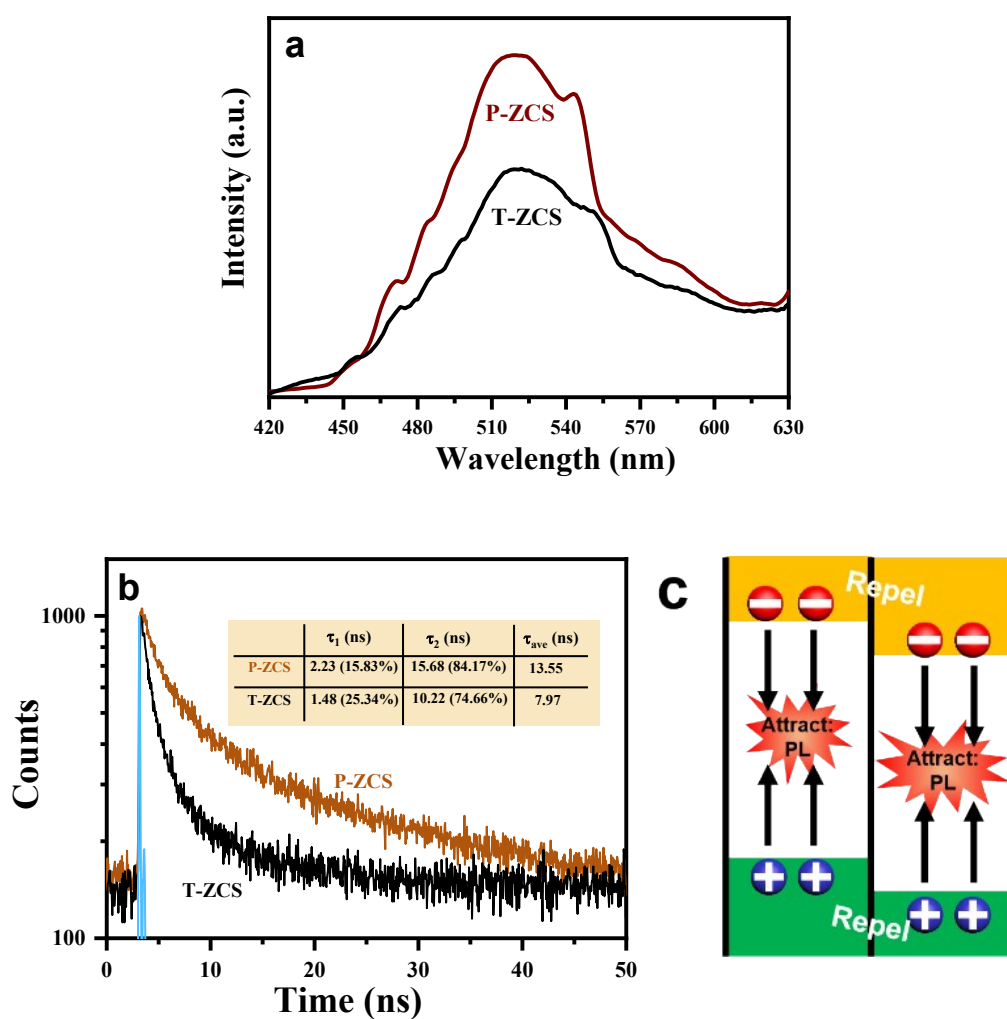
**Fig. S16** UV-vis spectra of fresh 10% ReS<sub>2</sub>/T-ZCS and used 10% ReS<sub>2</sub>/T-ZCS samples.



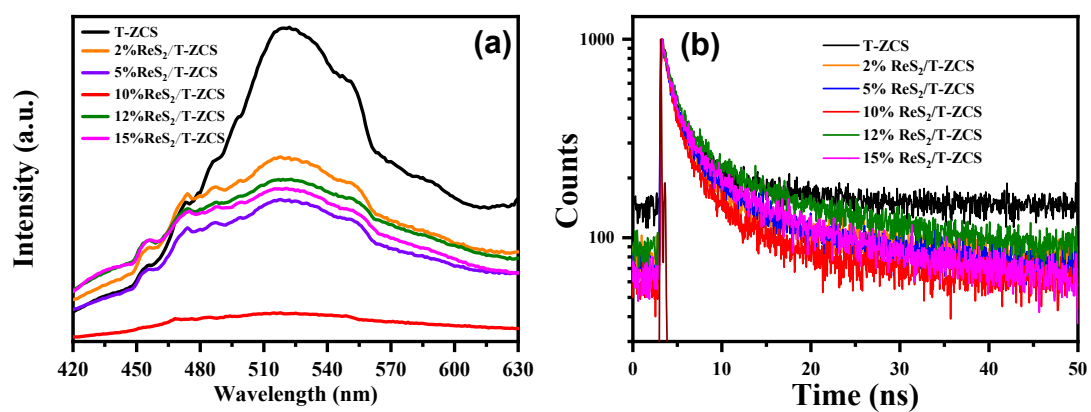
**Fig. S17** (a) Transient photocurrent response curves and (b) EIS Nyquist plots of P-ZCS, T-ZCS.



**Fig. S18** Charge transfer resistance of P-ZCS, T-ZCS and ReS<sub>2</sub>/T-ZCS samples.

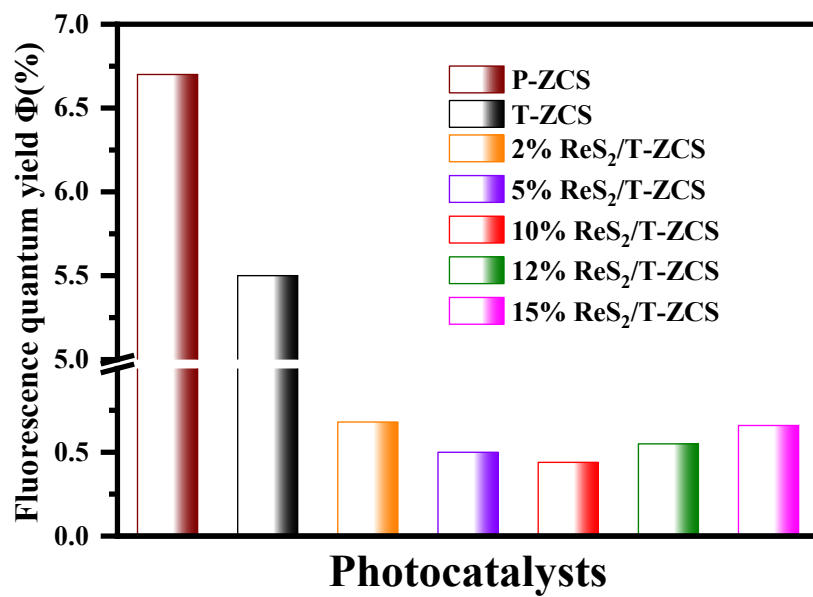


**Fig. S19** (a) PL spectra and (b) decay curves of P-ZCS and T-ZCS samples. (c) Illustration of charge repel and opposite charge attract.



**Fig. S20** (a) Photoluminescence spectra (PL), (b) decay curves of T-ZCS and ReS<sub>2</sub>/T-ZCS samples with different amount of ReS<sub>2</sub> excited at 375 nm.





**Fig. S21** Absolute fluorescence quantum yield of P-ZCS, T-ZCS and ReS<sub>2</sub>/T-ZCS samples.

**Table S1** The experimental data of Brunauer-Emmett-Teller (BET) and Pore diameter of P-ZCS, T-ZCS and ReS<sub>2</sub>/T-ZCS samples with different ReS<sub>2</sub> contents.

Sample	Surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore Volume [cm <sup>3</sup> /g]	Pore Size <sup>a</sup> [nm]
P-ZCS	11.96	0.0312	10.53
T-ZCS	13.16	0.0357	10.84
2% ReS <sub>2</sub> /T-ZCS	18.60	0.0577	12.40
5% ReS <sub>2</sub> /T-ZCS	20.01	0.0576	11.51
10% ReS <sub>2</sub> /T-ZCS	34.72	0.1253	14.43
12% ReS <sub>2</sub> /T-ZCS	22.88	0.0739	12.92
15% ReS <sub>2</sub> /T-ZCS	22.23	0.0745	13.40

<sup>a</sup> Average pore diameters were calculated from adsorption branches using BJH model.

**Table S2** Time constant  $\tau$  and the fluorescence quantum yield of photocatalysts

Sample	Absolute fluorescence quantum yield	$\tau_1$		$\tau_2$		$\tau_{ave}$
		[ns]	%	[ns]	%	[ns]
P-ZCS	6.70%	2.23	15.83	15.68	84.17	13.55
T-ZCS	5.50%	1.48	25.34	10.22	74.66	7.97
2% ReS <sub>2</sub> /T-ZCS	0.68%	1.47	33.17	9.85	66.83	7.07
5% ReS <sub>2</sub> /T-ZCS	0.50%	1.34	25.34	8.11	62.62	5.58
10% ReS <sub>2</sub> /T-ZCS	0.44%	1.29	37.16	7.20	62.84	5.00
12% ReS <sub>2</sub> /T-ZCS	0.55%	1.42	39.65	11.11	60.35	8.54
15% ReS <sub>2</sub> /T-ZCS	0.66%	1.58	26.46	12.34	73.54	9.49