Supplementary Information (SI) for New Journal of Chemistry.

Supplementary Material

Bifunctional CdS QDs@ZnS/ZnO Composites with Double S-Scheme Heterojunctions and Oxygen-Rich Vacancies for Enhanced Photocatalysis

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Experimental parts

Materials and reagents

Zinc acetate anhydrous ($C_4H_6O_4Zn$, purity ≥98.0%) was purchased from Sinopharm Chemical Reagent Company Limited; thioacetamide (TAA, C_2H_5NS, purity ≥99.0%), anhydrous sodium sulfate (Na_2SO_4, purity ≥99.0%), anhydrous sodium sulfite (Na_2SO_3, purity ≥97.0%) and cadmium nitrate tetrahydrate ($CdN_2O_6{\cdot}4H_2O$, purity ≥99.0%) were purchased from Tianjin City Komeo Chemical Reagent Co. Sodium hydroxide (NaOH, purity ≥99.0%), p-benzoquinone ($C_6H_4O_2$, BQ, purity ≥99.0%), isopropanol (C_3H_8O, IPA, purity ≥99.7%), disodium ethylenediaminetetraacetic acid ($C_{10}H_{14}N_2Na_2O_8$, EDTA-2Na, purity ≥99.0%) were purchased from Tianjin Kaitong Chemical Reagent Co. Thioglycolic acid (TGA, $C_2H_4O_2S$, purity ≥99.0%) was purchased from Sigma Aldrich (Shanghai) Trading Co. Sodium sulfide hydrate (Na_2S-$9H_2O$, purity ≥99.0%) was purchased from Tianjin Damao Chemical Reagent Factory; Rhodamine B ($C_{28}H_{31}ClN_2O_3$, purity ≥99.0%) and methylene blue ($C_{25}H_{30}ClN_3$, purity ≥99.0%) were purchased from Tianjin Guangfu Fine Chemical Research Institute; Methyl orange ($C_{14}H_{14}N_3NaO_3S$, purity ≥99.0%) was purchased from Tianjin Guangfu Science and Technology Development Company Limited; Ciprofloxacin hydrochloride (CIP, $C_{18}H_{18}FN_3O_3$, purity ≥98.0%) was purchased from Shanghai Ron Chemical Technology Co. Tetracycline hydrochloride (CTC, $C_{22}H_{22}Cl_2N_2O_7$, purity ≥80.0%) was purchased from Shanghai Aladdin Biochemical Technology Co.

Preparation of ZnS/ZnO

ZnS/ZnO composites were prepared by microwave-assisted synthesis strategy. First, 0.20 mmol, 0.50 mmol, and 0.80 mmol of C_2H_5NS and different amounts of $Zn(CH_3COO)_2$ were dissolved in 25 mL of deionized water and ultrasonicated for 30 min and stirred for 1 h to disperse homogeneously to form the precursor solution. Next, 1 mmol of pre-prepared ZnO powder was added to the precursor solution and continued to stir for 1 h. Finally, the mixed solution was transferred to a PTFE standard kettle and put into a microwave reactor at 160 ℃ for 45 min (power 300 W), cooled to room temperature, washed and vacuum-dried for 24 h. The ZnS/ZnO composites prepared as described above were labeled as ZnS/ZnO-0.20, ZnS/ZnO-0.50, and ZnS/ZnO-0.80, respectively.

Characterization

The XRD spectra of the samples were analyzed by a Bruker-AXS (D8) X-ray diffractometer (XRD) with Cu target, Kα rays (λ=0.15406 nm), scanning range of 5°~90°, scanning speed of 1°/min, operating voltage of 40 kV, and operating current of 180 mA The surface valence of the samples was determined by a VG ADES400 X-ray photoelectron spectrometer (XPS) to determine the surface valence of the samples, using Mg Kα rays (hv = 1486.4 eV) as the excitation source, with a vacuum of 10^{-8} Pa and and a C 1s peak (binding energy 284.8 eV) as the calibration reference to complete the linearity correction. In-situ XPS measurements were performed using the PHI5000 VersaProbe IV in-situ X-ray photoelectron spectrometer. A scanning electron microscope (SEM) S 4700 from Hitachi, Japan was used to analyze the morphology of the samples with an operating voltage of 5 kV. The photoluminescence (PL) spectra of the samples were tested using an F 7000 fluorescence spectrophotometer from Hitachi, Japan. The electrochemical impedance (EIS) of the samples was tested using a PEC 1000 photoelectrochemical test system from Porphyrite. Specific surface area and pore size of the samples were determined by a 3H-2000 specific surface area and pore size analyzer from Beijing Best Company at 77 K temperature. The TU-1901 UV-vis double-beam spectrophotometer produced by Beijing Pudian General Instrument Co., Ltd. was used to obtain the UV-vis diffuse reflectance spectra of the samples to be measured with $BaSO_4$ as the reference standard. The absorbance properties of the solution samples were also determined with the help of this equipment. The EPR parameters of the target samples were tested and characterized using a Bruker-A300/E500 Electron Paramagnetic Resonance Spectrometer provided by Bruker (Beijing) Technology Co. Inductively coupled plasma optical emission spectroscopy (ICP-OES) testing was performed on solutions post-photocatalytic cyclic reactions using United States-Agilent-5110 instrument (The instrument parameters were RF power, 1250 W, Plsama flow, 12.0 $L\cdot min^{-1}$, Auxiliary flow: 1.0 $L\cdot min^{-1}$, Nebulizer flow: 0.7 $L\cdot min^{-1}$).

Electrochemical experiments

The transient photocurrent response of the sample was measured in the PEC 1000 photochemical test system (PEC-1000, Bofill). The light source was a 300 W Xe lamp. The electrodes were the working electrode (titanium sheet coated with 1.0 cm × 1.0 cm photocatalyst), the reference electrode (Ag/AgCl, saturated KCl), and the counter electrode (Pt sheet). The open circuit voltage is about 0.2 V, and the electrolyte is Na_2SO_4 (0.1 $mol\cdot L^{-1}$) solution. The working electrode was made as follows: 0.1 g of catalyst was first put into 5 mL of ethanol, sonicated for 10 min, and then agitated to form a suspension. After that, the suspension was coated onto a 2.0 cm x 1.0 cm titanium sheet. Finally, the prepared titanium sheet was desiccated in a drying chest at 50 °C for 30 min.

Electrochemical impedance testing of the samples was performed on a PEC1000 photoelectrochemical test system. The electrodes were working electrode (nickel foam coated with 1.0 cm × 1.0 cm photocatalyst), reference electrode (Ag/AgCl, saturated KCl), and counter electrode (Pt wire). The open-circuit voltage was about 0.2 V, and the electrolyte was Na_2SO_4 (0.75 $mol\cdot L^{-1}$) solution. The working electrode was fabricated as follows: first, 0.1 g of catalyst was dispersed in 5 mL of ethanol and 1 mL of polytetrafluoroethylene dispersion, and ultrasonic action was performed for 10 min, and the suspension was stirred to form. Then the suspension was coated on a 2.0 cm × 1.0 cm nickel foam, and finally the prepared nickel foam was put into a drying oven and dried at 50 °C for 30 min.

The electrochemical Mott-Schottky measurements were carried out on the same electrochemical system with FTO plate coated with 1.0 cm × 1.0 cm photocatalyst, Ag/AgCl electrode as reference electrode, Pt plate as counter electrode, respectively. And electrolyte is Na_2SO_4 (0.2 $mol\cdot L^{-1}$) solution. The specific production method of the working electrode is as follows: first, 0.003 g catalyst was added to 0.5 mL DMF to form the suspension with ultrasound for 30 min, and then the suspension was coated on 1.0 cm × 1.0 cm FTO sheet. Finally, the prepared FTO sheet was put into a drying oven and dried at 100 °C for 1 h.

All the electrochemical experiments were carried out at room temperature.

Photocatalytic degradation experiments

Multi-mode photocatalytic performance experiments include simulated sunlight photocatalysis, visible light photocatalysis, and UV light. The photocatalytic degradation performance of the prepared samples was evaluated using the decolourisation results of RhB solution. Firstly, 150 mg of the photocatalyst was completely dispersed in 90 mL (50 $mg\cdot L^{-1}$) of RhB solution, and the suspension was placed in dark conditions for 30 min to achieve adsorption-desorption equilibrium. The simulated sunlight photocatalysis experiments were performed by exposing the samples to an Xe lamp (MC-PF300, 300 W, Beijing Merry Change Technology Co, Ltd) for a certain time. The solutions were extracted at certain intervals and then centrifuged. The corresponding absorbance values were measured by UV–Vis spectrophotometer (TU-1901 type), and the degradation rate was calculated according to the formula $C_t/C_0=A_t/A_0$, where C_0 and A_0 are the concentration and absorbance value of the simulated pollutant before light exposure, respectively, and C_t and A_t are the concentration and absorbance value of RhB at the photocatalytic time of t min. The reaction device for the UV light photocatalysis experiment was homemade with a built-in light source of 125 W high-pressure mercury lamp at an emission wavelength of 313.2 nm, and the photocatalytic reaction was cooled by circulating water to the reaction device. The light source of the visible light photocatalytic experimental setup was regulated by a 420 nm cutoff filter on the Xe lamp. The different contaminant experiments were realized by replacing RhB solutions with methyl orange (MO), methylene blue (MB), tetracycline hydrochloride (TC) and ciprofloxacin (CIP).

The reaction solution models for the photocatalytic degradation experiments in different aqueous environments were river water (from Yalu River in Qiqihar City, Heilongjiang Province, China), lake water (from the water of Labor Lake in Qiqihar City, Heilongjiang Province, China) and tap water (from the domestic water of the Middle Campus of Qiqihar University, Heilongjiang Province, China). The light source for photocatalytic degradation performance testing in different water environments was a 300 W Xe lamp (MC-PF300, 300 W, Beijing Merry Change Technology Co, Ltd), and the reaction time was 120 min.

Photocatalytic hydrogen production experiment

The photocatalytic hydrogen production experiments were carried out in a vacuum reactor connected to a closed loop system (labsolar-III AG system). 0.1 g of the photocatalyst was dispersed in 40 mL of distilled water, and 10 mL of methanol was added as a sacrificial agent. Under the condition of vacuum degassing and constant stirring, the experiment of hydrogen production by photolysis of water started. A 300 W Xe lamp was used as the light source and fixed at 10 cm from the reaction solution; high-purity nitrogen was used as the carrier gas with a flow rate of 0.5 $mL \cdot s^{-1}$; the output pressure was 0.4~0.5 MPa, and the working voltage and current were about 20 mV and 50 mA, respectively. During the reaction, circulating cooling water kept the reactor's temperature at about 5 °C. Hydrogen production was analyzed by online gas chromatography, and the gas was collected for a certain irradiation time; the reaction was carried out for 8 h. The column was a 0.5 nm molecular sieve column, and the detector was a thermal conductivity detector (TCD). Based on the peak areas at different reaction times, the hydrogen production was calculated from the formula x $mmol \cdot g^{-1}$ = peak area/ (22.4*hydrogen standard curve*y) (where 22.4 $L \cdot mol^{-1}$ is the molar volume constant for the gas standard and y is the catalyst mass of 0.1 g) and the activity of the photocatalyst was measured by the total hydrogen production for 8 h.

Results and discussions

Formula part

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \text{(Formula S1)}$$

Where K is Scherrer's constant (approximately 0.89), λ is the X-ray wavelength (Cu-Kα radiation = 1.540 Å), D is the grain size, β is the diffraction peak half-height width in radians (FWHM), and θ is the Bragg diffraction angle.

$$\alpha hv = A(hv-Eg)^n \qquad \text{（Formula S2）}$$

Where α is the absorption coefficient, h_v is the discrete photon energy, A is the proportionality constant, n is the optical frequency, and E_g is the bandgap energy.

$$E_{CB}\ (vs\ NHE) = E_{FB}\ (vs\ Ag/AgCl)\ +0.2\ eV \qquad \text{（Formula S3）}$$

$$C_x = C_0 \times f \times V_0 \times 10^{-3}/V \times 10^{-3} = C_1 \times V_0/V \qquad \text{(Formula S4)}$$

Where V is the volume of sample taken for analysis, measured in mL and recorded using a pipette or pipette tube; V_0 is the volume of the sample after digestion and dilution to a fixed volume, measured in mL; f is the dilution factor; C_0 is the concentration of the element in the test solution, in mg·L^{-1}, obtained from instrumental analysis; C_1 is the element concentration in the undiluted sample digest solution, in mg·L^{-1}, where C_1(mg·L^{-1}) = C_0(mg·L^{-1}) × f; C_x is the final test result for the measured element, in mg·L^{-1}.

$$-lnC_t/C_0=kt \qquad \text{（Formula S5）}$$

Where t is the reaction time, C_0 and C_t are the pollutant concentrations at the initial and t moments, respectively, and k is the pseudo-primary rate constant.

$$AQY = \frac{1.2 \times 10^8(\nu \times K)}{(I \times A \times \lambda)} \times 100\% \qquad \text{(Formula S6)}$$

Where v is the reaction rate, with the unit of mol·s^{-1}. λ is the incident wavelength, with the unit of nm. K is the number of electrons transferred in the reaction. In the measurement of the quantum yield of water splitting for hydrogen production, K=2. I is the optical power density, with the unit W·m^{-2}. A is the incident illumination area, with the unit of m^2.

Theoretical calculation methods

The structural optimization and the energy band calculations are conducted using VASP package, based on projector augmented wave (PAW) method.[1, 2] The PBE exchange-correlation functional within the generalized gradient approximation (GGA) is employed.[3] The cutoff energy of the kinetic energy is 400 eV. The slabs containing 64 atoms for ZnO (101), ZnS (111) and CdS

(111) are built with a vacuum of 15 Å. The k-mash in the Brillouin zone via Monkhorst-Pack method is 2×2×1 for all calculations.[4] The energy convergence is 1.0×10^{-5} eV. All atoms are allowed to fully relax until the force exerted on each atom was less than 0.02 eV $Å^{-1}$ during structural optimization. The van der Waals (vdW) interaction is involved via the DFT-D3 method.[5] And the corrections to the potential and forces have been considered along the z-axis. Work function (*Wf*) is defined as the minimum energy required to remove an electron from the bulk of a material through a surface to a point in vacuum immediately outside the surface. At 0 Kelvin and a perfect vacuum, the work function is described by formula:

$$\varphi = W_f = E_v - E_f \qquad \text{(Formula S7)}$$

where *Wf* represents work function, *Ef* represents Fermi level and *Ev* represents the vacuum level and *Wf* is the energy difference between the *Ef* and *Ev*.

The φ, *Ef*, and *Ev* values for ZnO (101), ZnS (111), and CdS QDs (111) calculated using the above formula are shown in Table S2. The crystal model structures are depicted in Fig. S6.

Appendix of the references:

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Table S1 Results of inductively coupled plasma emission spectrometry test of CdS QDs@ZnS/ZnO-0.15 photocatalyst

Sample number	Sampling volume V（mL)	Constant volume V_0（mL)	Test element	Test the concentration of elements in the solution C_0（mg·L^{-1})	Dilution factor f	Element concentration of digestion solution/original sample solution C_1（mg·L^{-1})	Element content of the sample C_x（mg·L^{-1})
1	5.000	25	Cd	4.0701	1	4.0701	20.3504
2	5.000	25	Cd	4.0669	1	4.0669	20.3346
3	5.000	25	Cd	4.1485	1	4.1485	20.7424
4	5.000	25	Zn	3.0328	1	3.0328	15.1641
5	5.000	25	Zn	3.0324	1	3.0324	15.1618
6	5.000	25	Zn	3.0777	1	3.0777	15.3883

Table S2 Values of φ, Ef, and Ev for ZnO, ZnS, and CdS QDs

Semiconductor	φ(eV)	Ef (eV)	Ev (eV)
ZnO (101)	5.37	-3.32	2.05
ZnS (111)	4.91	-1.81	3.10
CdS QDs (111)	4.98	-2.01	2.97

Table S3 Comparison table of photocatalytic properties of CdS QDs@ZnS/ZnO-0.15 composite materials

Photocatalyst	Pollutant	Light irradiation	Irradiation time(min)	Degradation(%)	Hydrogen production rate (μmol·g^{-1}·h^{-1})	Ref
CdS QDs@ZnS/ZnO-0.15	RhB	Simulated sunlight	120	91.31	1472.1	Here
		Visible light	120	59.51	-	
		UV light	120	87.92	-	
3-Ag-CS/BO	-	Simulated sunlight	-	-	1276.8	[1]
$PbTiO_3$/CdS-10%	-	Simulated sunlight	-	-	849	[2]
CdO–ZnO–MgO	MB	Simulated sunlight	120	91.00	-	[3]
g-C_3N_4/Ag/ZnO	RhB	Simulated sunlight	180	89.00	-	[4]
$SRP_{0.03}$/CdS HNS	RhB	Simulated sunlight	120	88.00	-	[5]
CdS/ZnO	RhB	Simulated sunlight	150	91.50	-	[6]

Appendix of the references:

1 G.L. Zuo, H.Y. Ye, Y.H. Fang, J. Du, X. Ding, Photocatalytic hydrogen production performance of Ag-modified S-scheme CdS/Bi_2O_3 heterojunction composites, *Catal. Lett.*, 2025, **155**(9), 294.

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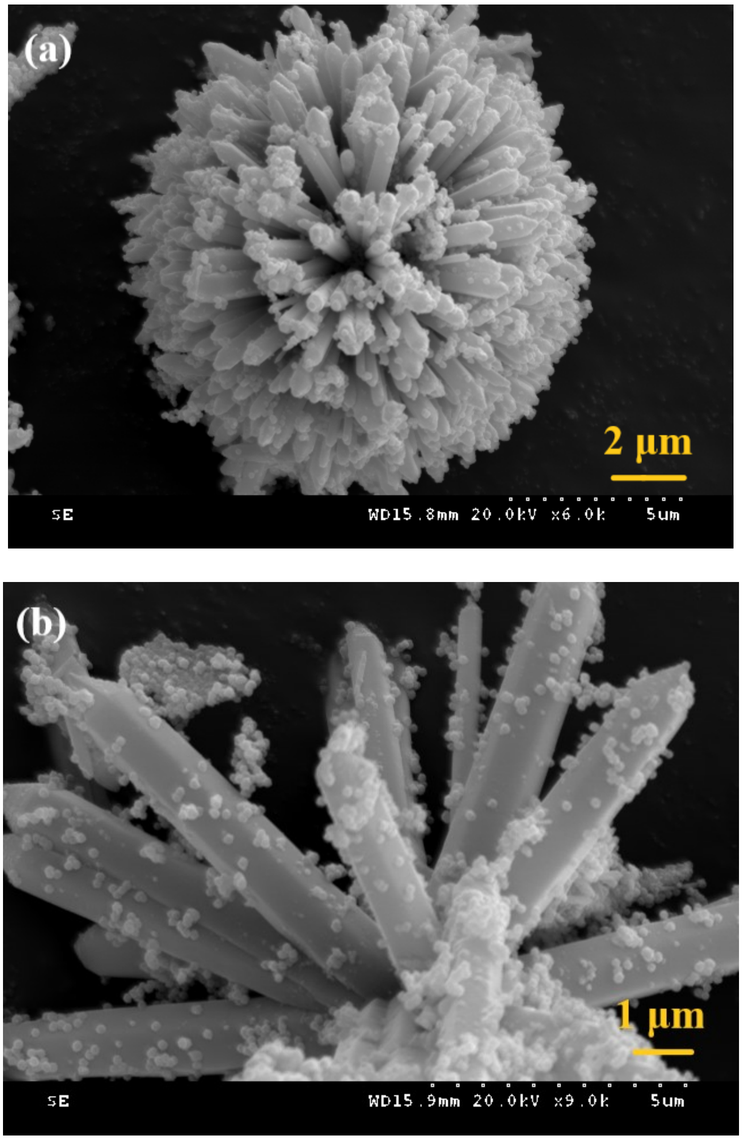

Fig. S1 SEM images of ZnS/ZnO composites (a, b)

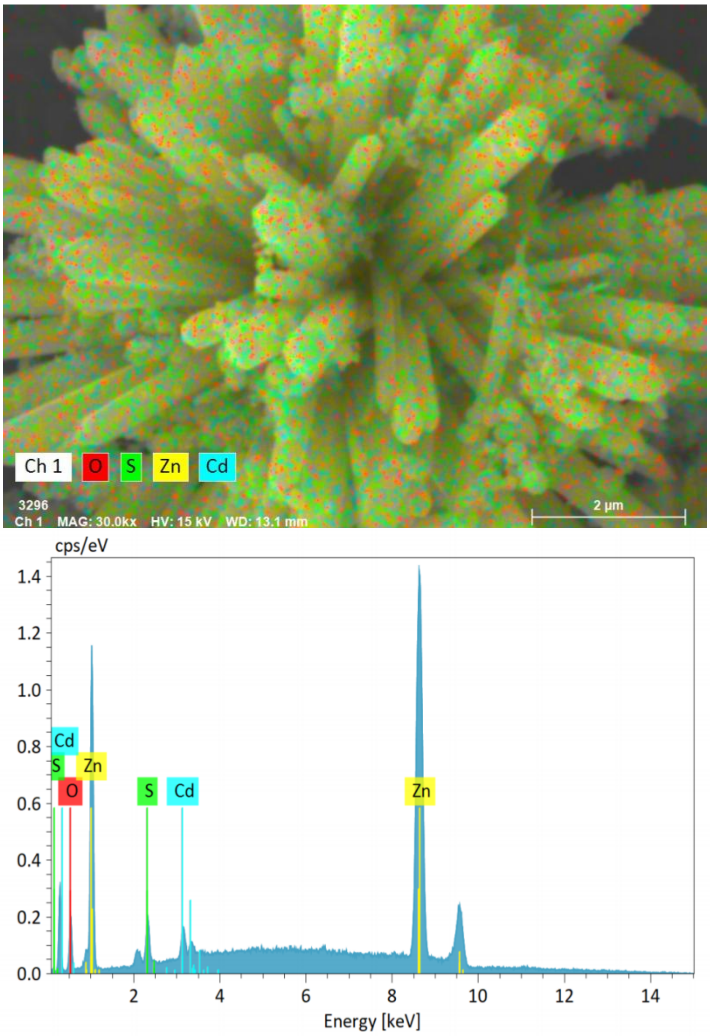

Fig. S2 Contents of elements in CdS QDs@ZnS/ZnO-0.15 composites

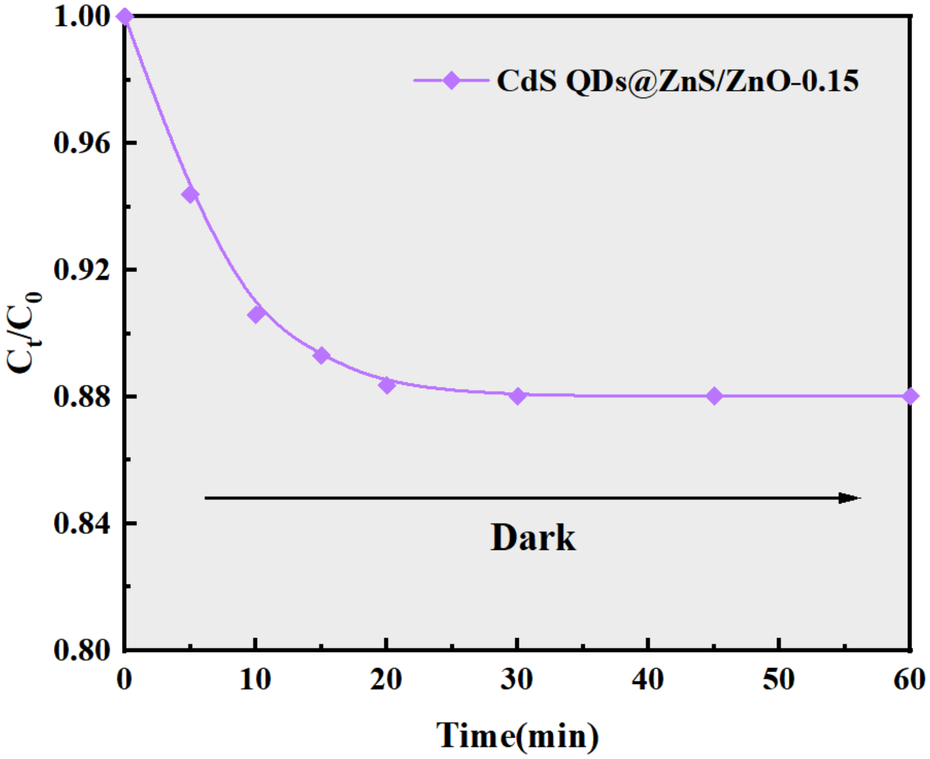

Fig. S3 Experimental results of the dark reaction for CdS-QDs@ZnS/ZnO-0.15

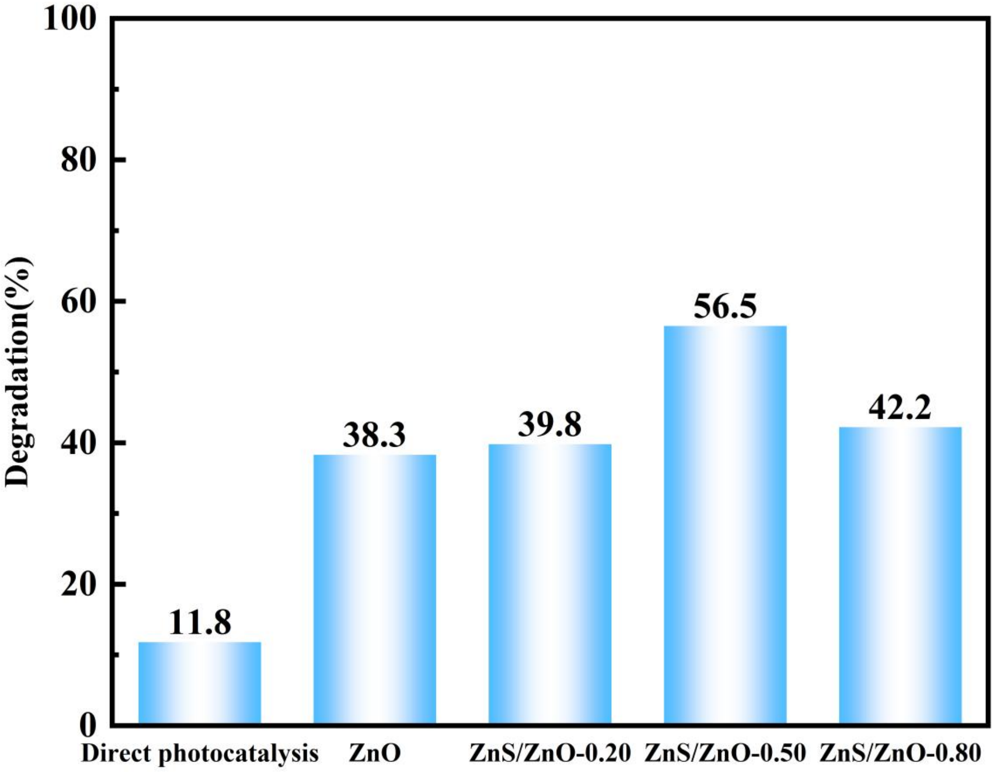

Fig. S4 Results of photocatalytic degradation of RhB with different catalysts under simulated daylight conditions (300 W xenon lamp, t=120 min)

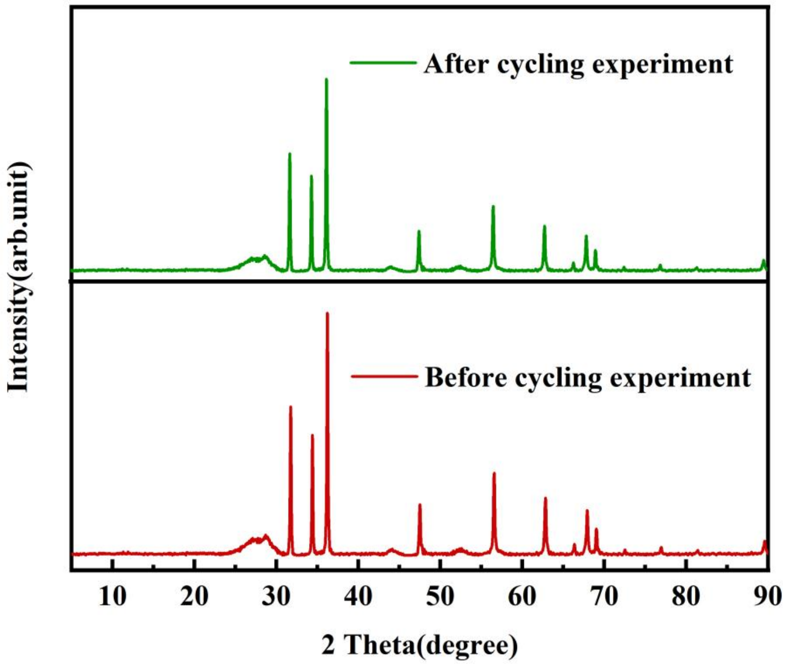

Fig. S5 XRD comparison of composites before and after cycling

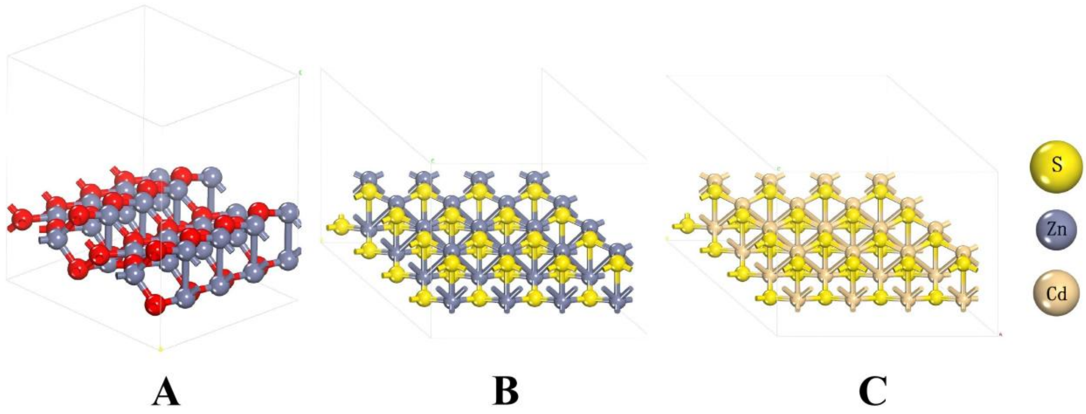

Fig S6 Crystal structure models of ZnO (A), ZnS (B), and CdS QDs (C)