

Supporting Information

Hybrid VS₂ cocatalyst and phosphorus dopant towards both surface and bulk modification of ZnCdS/CdS heterostructure

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1. Experimental Section

1.1 Chemicals: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CH}_4\text{N}_2\text{S}$, NaH_2PO_2 , Na_3VO_4 , Na_2MoO_4 , Na_2WO_4 and CH_3CSNH_2 (TAA) (Shanghai Macklin Biochemical Technology Co., Ltd) are analytical grade and used as received without further purification.

1.2 Sample preparation

1.2.1 Synthesis of P-ZnCdS/CdS precursors: P-ZnCdS/CdS nanoparticles were prepared using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CH}_4\text{N}_2\text{S}$ and NaH_2PO_2 as precursors by one-step hydrothermal method. In a typical process, 1.8 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.2 mmol $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and the corresponding ratios of S/P ($\text{CH}_4\text{N}_2\text{S} + \text{NaH}_2\text{PO}_2 = 8$ mmol) equal to 8:0, 7.6:0.4, 7.2:0.8, 6.4:1.6 were dissolved in 30 mL distilled water. The solutions were subsequently transferred into 50 mL teflon-lined autoclave and maintained for 20 h at temperatures of 180 °C. The final products were rinsed twice with distilled water and anhydrous ethanol respectively, and dried at 60 °C for overnight in a vacuum oven to evaporate the solvent.

1.2.2 Synthesis of the ZnCdS/CdS/VS₂: A hydrothermal method was adopted to fabricate ZnCdS/CdS/VS₂ nanoparticles. In a typical process, 100 mg ZnCdS/CdS, a suitable amount of Na_3VO_4 and TAA (the molar ratio of Na_3VO_4 and TAA is 3:16) were dissolved in 30 ml deionized water, and the solution was stirred vigorously for 1 hour. Then the as-prepared solution was transferred into 50 ml teflon-lined autoclave for 24 h at temperatures of 160 °C. Afterwards, the system was cooled down to room temperature slowly. The black precipitates were rinsed with deionized water and anhydrous ethanol several times, and collected by vacuum filtration, and then dried in a vacuum oven at 60 °C for 400 min. In this way, different amount of VS₂ with the quality ratios of VS₂/ZnCdS/CdS equal to 0.5, 1, 2, and 5 were obtained, respectively.

1.2.3 Synthesis of the P-ZnCdS/CdS-VS₂, MoS₂ and WS₂: In a typical process, 100 mg P-ZnCdS/CdS (P=10%), suitable amount of Na_3VO_4 and TAA (the molar ratio of Na_3VO_4 and TAA is 3:16) were dissolved in 30 ml deionized water, and the solution was stirred vigorously for 1 hour. Then the as-prepared solution was transferred into 50 ml teflon-lined autoclave for 24 h at temperatures of 160 °C. Afterwards, the system was cooled down to room temperature slowly.

The black precipitates were rinsed with deionized water and anhydrous ethanol several times, and collected by vacuum filtration, and then dried in a vacuum oven at 60 °C for 400 min. In this way, different amount of VS₂ with the quality ratios of VS₂/ P-ZnCdS/CdS (P=10%) equal to 0.5, 1, 2 and 5 were obtained, respectively. The MoS₂ and WS₂ loaded P-ZnCdS/CdS were prepared by the similar procedure, with the Na₃VO₄ replaced by similar molar content of Na₂MoO₄ and Na₂WO₄, respectively.

1.2.3 Synthesis of the VS₂: The VS₂ nano-sheet was prepared by the one-step hydrothermal method. In general, 6 mmol sodium orthovanadate (Na₃VO₄) and 32 mmol thioacetamide (TAA, CH₃CSNH₂) were dissolved in 50 ml deionized water, and the solution was stirred vigorously for 1 h. Then the as-prepared homogenous solution was transferred into a 100 ml Teflon-lined autoclave for 24 h at temperatures of 160 °C. Afterwards, the system was cooled down to room temperature. The final products were rinsed with deionized water and anhydrous ethanol several times, and collected by vacuum filtration, and then dried in a vacuum oven at 60 °C for 400 min.

2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$). Corresponding work voltage and current is 40 kV and 100 mA, respectively. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV. Element content analysis was tested on an inductively coupled plasma (ICP) spectroscope (Prodigy, Leeman, America). The atomic structure of the ZnCdS/CdS heterojunction was characterized using an ARM-200CF (JEOL, Tokyo, Japan) transmission electron microscope operated at 200 kV and equipped with double spherical aberration (Cs) correctors. Surface morphologies of the phase junction materials were examined by a scanning electron microscope (SEM, JSM-7600F) at an acceleration voltage of 10 kV. The UV–Vis absorption and diffused reflectance spectra were recorded using a Cary 5000 UV-Vis spectrometer (Viarian, USA) with BaSO₄ as a reflectance standard. XPS data was collected using an X-ray photoelectron spectrometer (XPS) by a scanning X-ray microprobe (PHI 5000 Versa, ULAC-PHI, Inc.) with Al K α radiation and the C1s peak at 284.6 eV as internal standard. Steady

photoluminescence (PL) emission spectra were tested by a luminescence spectrophotometer (QM-400, PTI) with 350 nm excitation wavelength. All the electrochemical measurements were conducted in a typical three-electrode setup with an electrolyte solution, a glassy carbon electrode (3 mm in diameter), an Ag/AgCl with saturated KCl, and a Pt wire were used as the working electrode, reference and counter electrode, respectively. Typically, a total of 4 mg of the catalysts were dispersed in 2 ml of 9:1 v/v water/Nafion solution by sonication to form a homogeneous ink. 5 μ l well-dispersed catalysts were covered on the glassy carbon electrode and then dried in an ambient environment for measurements. The electrocatalyst was prepared with a catalyst loading of 0.14 mg/cm². The transient photocurrent response measurements were performed with a CHI 660E electrochemical station (Shanghai Chenhua Co. Ltd, China) under irradiation of 300 W xenon arc lamp in 0.5 M Na₂SO₄ solutions. The electrochemical impedance spectra (EIS) data was carried out from 1,000 kHz to 100mHz with an amplitude of 10 mV at the open-circuit voltage using Electrochemical (Bio-Logic SP-150) workstation in 0.5 M Na₂SO₄ solutions. And electrochemical hydrogen evolution reaction reacts in 1 M KOH solution using a CHI 660E electrochemical station (Shanghai Chenhua Co. Ltd, China), with a flow of N₂ maintained over the electrolyte during the experiment to eliminate dissolved oxygen.

3. Photocatalytic Hydrogen Production

The photocatalytic H₂-production experiments were performed via a photocatalytic H₂-production activity evaluation system (CEL-SPH2N, CEAULight, China) in a 300 mL Pyrex flask, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp through a UV-cutoff filter with a wavelength range of 420 ~ 800 nm, which was positioned 13 cm away from the reaction solution, was used as a visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was ~ 200 mW·cm⁻², which was measured by a FZ-A visible-light radiometer (made in the photoelectric instrument factory of Beijing Normal University, China). In a typical photocatalytic H₂-production experiment, 5 mg of the as-prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing Na₂S (0.35 M) and Na₂SO₃ (0.25 M). Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A continuous magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst

particles in suspension during the experiments. H₂ content was analyzed by gas chromatography (GC-7900, CEALight, China). All glasswares were carefully rinsed with DI water prior to usage. The photocatalytic stability was performed in the same processing parameters. The sacrificial reagent was renewed every 18 h for the evaluation of the photocatalytic stability in vacuum.

4. Supporting Figures

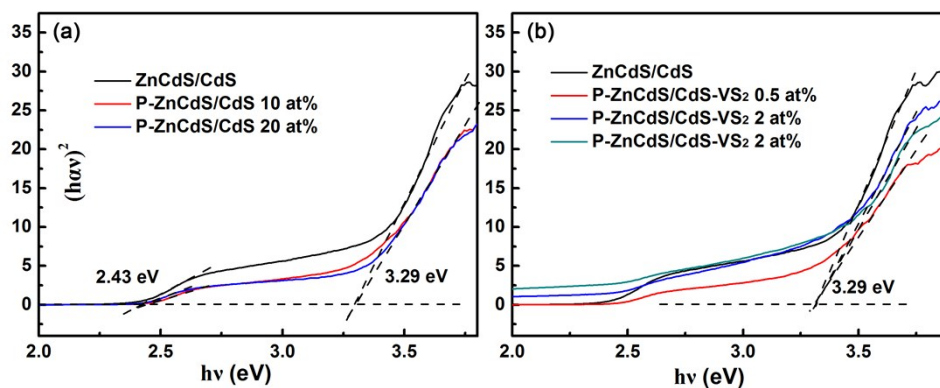


Fig. S1. Effect of the amount (a) P dopant and (b) VS₂ cocatalyst on the band gaps of the heterostructure samples.

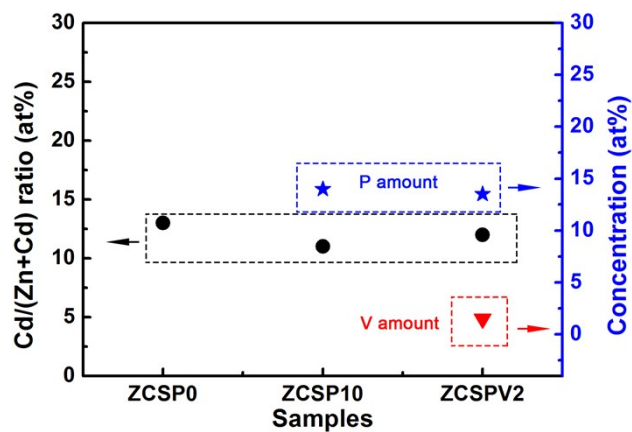


Fig. S2. The inductively coupled plasma (ICP) results for the ZnCdS/CdS, P-ZnCdS/CdS and P-ZnCdS/CdS-VS₂.

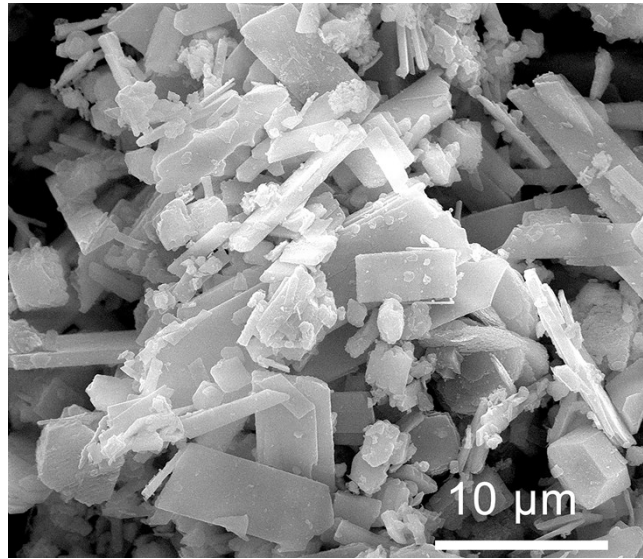


Fig. S3. The Scanning electron microscopy (SEM) image of the VS₂ nanosheet.

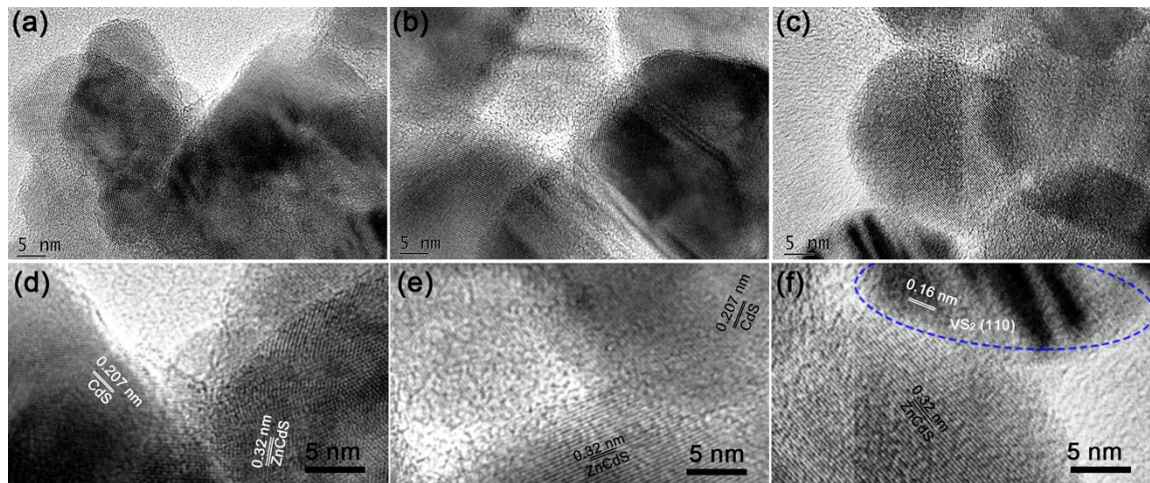


Fig. S4. The original and enlarged high resolution TEM (HRTEM) images of (a, d) ZnCdS/CdS, (b, e) P-ZnCdS/CdS, and (c, f) P-ZnCdS/CdS-VS₂.

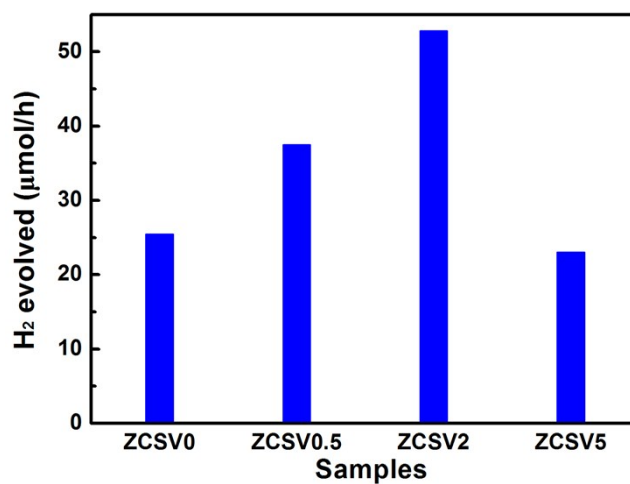


Fig. S5. Effect of the amount of VS₂ on the photocatalytic hydrogen evolution activity of the ZnCdS/CdS heterostructure.

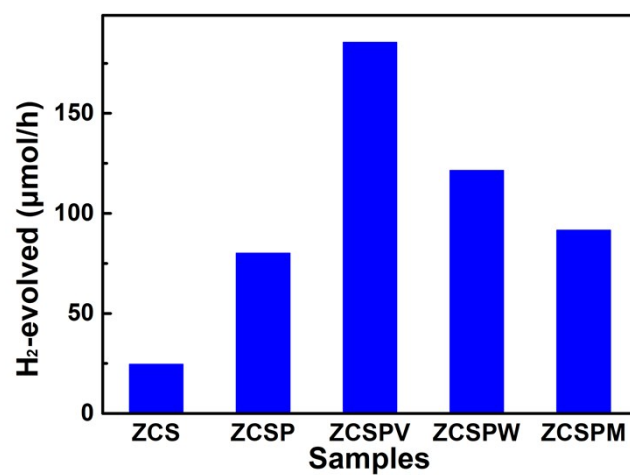


Fig. S6. The comparison results of the photocatalytic hydrogen evolution rate of the ZnCdS/CdS (ZCS), P-ZnCdS/CdS (ZCSP), and the P-ZnCdS/CdS loaded with VS₂, MoS₂ and WS₂.

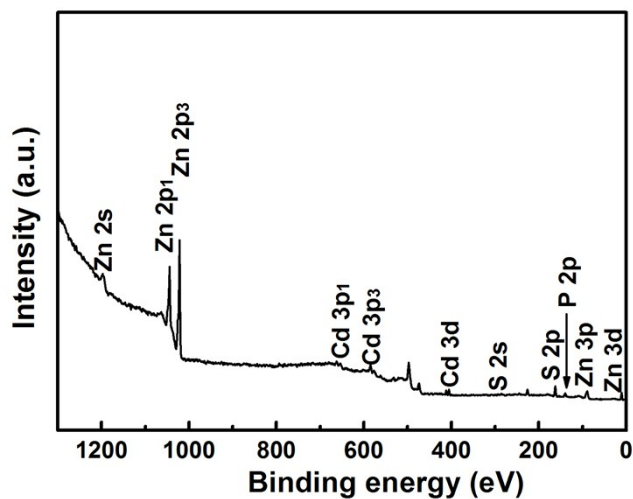


Fig. S7. XPS spectrum of P-ZnCdS/CdS nanocomposite.

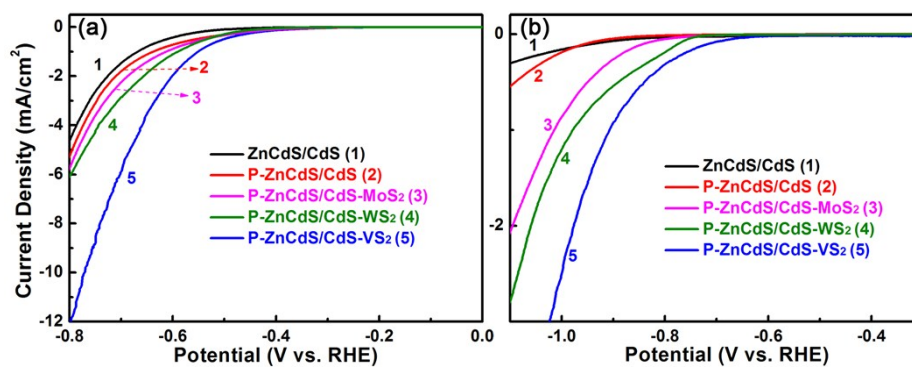


Fig. S8. The electrocatalytic HER performance of the ZnCdS/CdS, P-ZnCdS/CdS loaded with MoS₂, WS₂ and VS₂ in (a) KOH and (b) Na₂SO₄ solution, respectively.