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Supporting Information

Band energy engineering: Precise regulate the P-band centers reasonably construct S-scheme heterojunctions boosting photocatalytic hydrogen production

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1. Characterization

In this study, we employed X-ray diffraction technology (XRD: SmartlabSE, Rigaku Corporation, Japan) to analyze the structural characteristics of the photocatalyst. In the experiment, the diffraction angle range of the sample was set to 5°to 80°, and the scanning speed was 10° per minute. In addition, the PerkinElmer Lambda-750 UV visible spectrometer with a wavelength range of 250 to 800 nanometers was used for testing. The background correction of the sample was performed using barium sulfate ($BaSO_4$). Furthermore, we measured the photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra of the catalyst using a FluoroMAX-4 (Horiba, France) spectrometer. The Zeta potential of the photocatalyst was measured using a Litesizer 500. The surface morphology of the photocatalyst was characterized using scanning electron microscopy (SEM, SIGMA 500, Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100, Ricoh, Japan). The electron change state of the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The nitrogen adsorption desorption isotherm of the catalyst at 77 K was measured using ASAP2020M equipment. The photoelectrochemical properties of the catalyst were studied on the VersaStat 4-400 electrochemical workstation. Electronic paramagnetic resonance instrument model (E—500 CW ,Manufacturer Bruker, Germany).

2. Experimental section

2.1 Experiment

In the catalyst synthesis process, all drugs use analytic-grade chemicals and are not purified. Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 98%), Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot\cdot 6H_2O$, 98%), triethylamine (99.5%), ammonium metavanadate (NH_4VO_3, 99%), thiourea (CH_4N_2S, ≥99%), Ethylenediamine ($C_2H_8N_2$, 99 %), Anhydrous ethanol (CH_3CH_2OH, 99.7 %).

2.2 Preparation of CdS

CdS nanorods were synthesized using a hydrothermal method [45]. The specific steps involved dissolving 10.1 mmol of Cd $(NO_3)_2 \cdot 4H_2O$ and 30.3 mmol of thiourea in 70 mL of ethylenediamine and stirring for 15 minutes. Then, add the mixture to a 100 mL high-pressure vessel lined and heat it at 160 °C for 48 hours. After cooling the autoclave to room temperature, the yellow precipitate was collected by centrifugation, washed with anhydrous ethanol and deionized water several times, and dry at 62 °C for 10 hours.

2.3 Preparation of Co_2VO_4

Co_2VO_4 nanoparticles were synthesized according to the previous research protocol [46]. Simply put, dissolve 0.120 g of NH_4VO_3 in 50 mL of deionized water, stir at 80 °C for 1 hour, add 0.582 g of Co $(NO_3)_2 \cdot 6H_2O$, and adjust the pH to around 9 with triethylamine. The evenly dispersed solution was transferred into a 100 mL reactor and heated at 150 °C for 10 hours. It was then washed, centrifuged, and dried. Subsequently, the dried product was calcined in a tube furnace at 355 °C under an N_2 atmosphere for 2.5 hours to yield Co_2VO_4 nanoparticles, designated as CVO.

2.4 Preparation of X-Co_2VO_4/CdS

Taking 25- Co_2VO_4/CdS as an example, dissolve 50 mg CdS and 12.5 mg CVO in 40 mL anhydrous ethanol and sonicate for 17 minutes to achieve uniform dispersion. Transfer the solution to a magnetic stirrer and stir for 3.5 hours. After the reaction is complete, use an 80 °C constant temperature water bath to completely evaporate and dry ethanol to obtain the final product 25-Co_2VO_4/CdS (25-COCS).

3. Photocatalytic hydrogen production experiment

This work used a 9-channel reactor system to simulate the photocatalytic hydrogen production process. The experimental light source is a 10 W LED lamp. Firstly, accurately weigh and disperse 10 mg of catalyst into a solution containing 30 mL of lactic acid (LA) with a mass percentage of 10%. Subsequently, the hydrogen production bottle was ultrasonically treated for 4-5 minutes to ensure a uniform solution. Next, replace the gas inside the reaction vessel with nitrogen (N_2) for 4 minutes, place the reaction vessel under light irradiation, and continue the photocatalytic reaction for 5 hours. During the experiment, 0.5 mL of gas sample was taken from the reaction vessel every hour, and component analysis and data recording were performed using a gas chromatograph. In addition, in order to evaluate the stability and potential for cyclic use of the catalyst, stability experiments were conducted for four consecutive cycles. After each cycle, the hydrogen production reaction bottle was purged with an inert gas to maintain anaerobic experimental conditions.

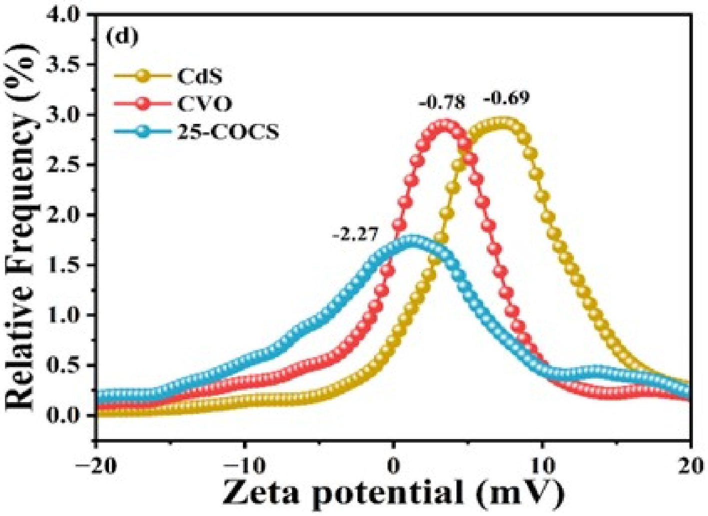

Fig. S1 Zeta potentials for CdS, CVO and 25-COCS.

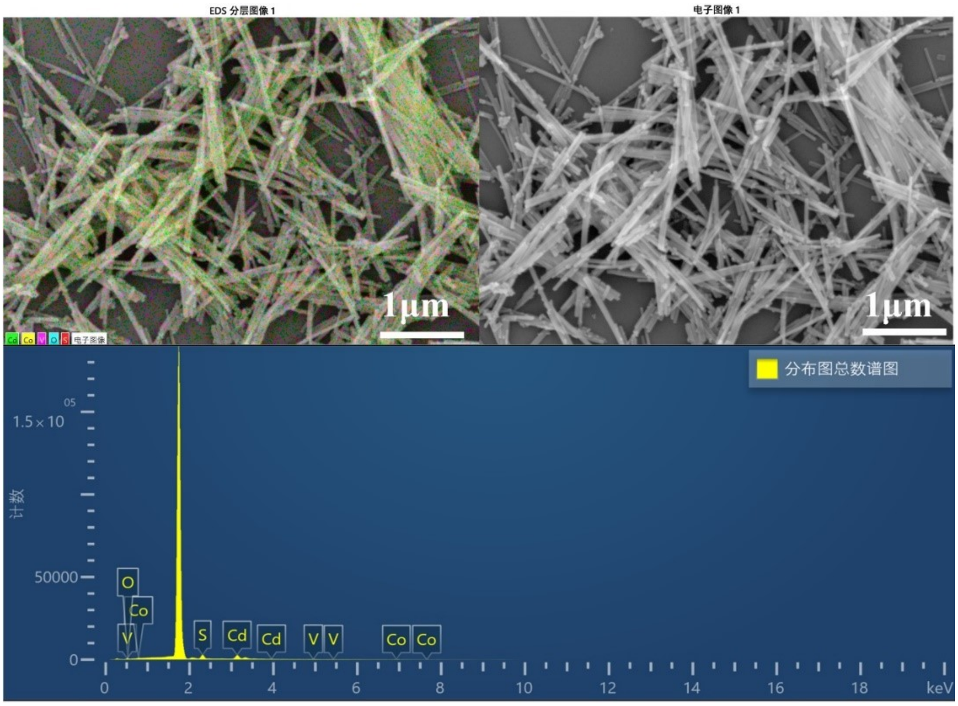

Fig. S2 EDS layered images, electron images and element distribution spectra of 25-COCS**.**

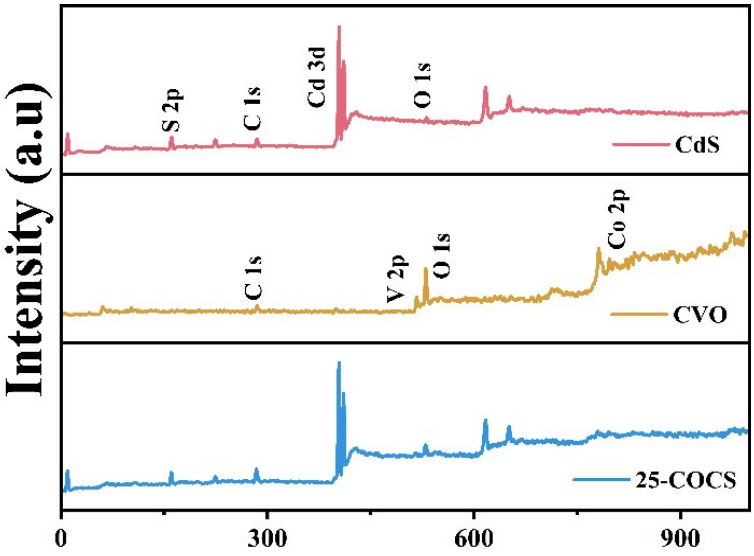

Fig. S3 XPS survey spectra for CdS, CVO and 25-COCS.

Table S1. Individual element content of 25-COCS.

Sample	Line type	wt%	Wt % Sigma	At%
O	K	13.52	0.91	41.03
S	K	18.27	0.35	27.66
V	K	0.81	0.39	0.77
Co	K	3.65	0.63	3.00
Cd	L	63.76	0.89	27.54
Total		100.00		100.00

Table S2. The S_{BET}, pore volume, and average pore size of CVO, CdS, and 25-COCS.

Sample	S_{BET} **(m^2 g^{-1})**	V_{pore} **(cm^3 g^{-1})**	D_{pore} **(nm)**
CVO	86.04	0.3434	15.0089
CdS	27.67	0.1785	23.0438
25-COCS	26.85	0.1637	13.67

Table S3. Fluorescence attenuation parameters of CVO, CdS, and 25-COCS.

Materials	Lifetime, τ (ns)	Rel (%)	<τ> (ns)	X^2
CVO	τ_1=4.95	A_1=28.10	1.55	1.43
	τ_2=126.05	A_2=24.53		
	τ_3=0.81	A_3=47.37		
CdS	τ_1=4.98	A_1=21.44	2.01	1.34
	τ_2=150.68	A_2=27.39		
	τ_3=1.14	A_3=57.52		
25-COCS	τ_1=4.17	A_1=25.96	1.45	1.37
	τ_2=136.95	A_2=25.67		
	τ_3=0.77	A_3=48.37		