Supporting Information

Dual-functional photocatalyst of CoS_x/Cd_{0.7}Zn_{0.3}S without noble metals for efficient selective benzaldehyde synthesis coupled with H₂ production

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Contents list

Characterizations

Photocatalytic performance tests

The principle of the photodeposition of CoS_x on CZS

Table S1 Comparison of activity for photocatalytic selective benzaldehyde synthesis coupled with H_2 production.

Table S2 The Co content in the as-prepared $m\%CoS_x/CZS$.

Table S3 The BET specific surface areas of CZS and 2%CoS_x/CZS.

Table S4 Exponential function fitted parameters of the TRPL decay spectra of the as-prepared samples.

Table S5 The photocatalytic performances of $2\%CoS_x/CZS$ for the selective oxidation of para-substituted benzyl alcohols.

Figure S1 Mott-Schottky plot of CZS.

Figure S2 N_2 absorption-desorption isotherms of CZS and 2%CoS_x/CZS.

Figure S3 HPLC results of photocatalytic products over 2%CoS_x/CZS.

Figure S4 Mass spectra of (a) BA and (b) BAD measured by gas chromatography-mass spectroscopy (GC-MS).

Figure S5 The XRD patterns of 2%CoS_x/CZS before and after photocatalytic cycling reaction.

Figure S6 The XPS spectra of 2%CoS_x/CZS before and after photocatalytic cycling reaction.

References

Characterizations

Powder X-ray diffraction (XRD) patterns are collected on Bruker D8 Advance diffractometer with Cu-Ka radiation. UV-vis diffuse reflectance spectra (DRS) are obtained with BaSO₄ as a reference on a Varian Cary 5000. The morphology and size are observed by a Hitachi SU 8010 field emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images are collected on a FEI TECNAI G2F20 instrument to obtain the morphologies and microstructures of the samples. X-ray photoelectron spectroscopy (XPS) is performed with a Thermo ESCALAB-250 spectrometer. Low temperature nitrogen adsorption-desorption is determined using Micromeritics ASAP 2020 equipment. Room temperature photoluminescence (PL) spectra and transient PL lifetime are collected at the spectrophotometer (Edinburgh Instrument, FLS-980) apparatus with excitation wavelength of 480 and 357 nm, respectively. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) is recorded on Avio 200. Electron paramagnetic resonance (EPR) data are recorded on the spectrometer (Bruker A300).

Photoelectrochemical measurements is carried out via PAR VMP3 workstation, the as prepared sample is coated on FTO glass as working electrode, Pt wire and Ag/AgCl electrode as counter electrode and reference electrode respectively. Electrochemical impedance spectroscopy (EIS) is detected with CHI-660E electrochemical workstation, with KCl (0.5 M) solution containing 0.01 M K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) as the electrolyte solution, while the photocurrent measurement, Mott-Schottky (M-S) curves and polarization curves measurements are conducted in 0.2 M Na₂SO₄ aqueous solution (pH = 6.8). A 300 W Xe lamp system equipped with a UV-CUT filter ($\lambda \ge 420$ nm) was used as a light source.

Photocatalytic performance Tests

The photocatalytic benzaldehyde (BAD) synthesis coupled with H₂ production is performed in a double-walled quartz reactor, and the reaction temperature is maintained at 20°C by circulating water in the sandwiched wall. Specifically, 10 mg samples are added into 10 mL of acetonitrile containing 100 µL of benzyl alcohol (BA), the suspension is purged with Ar gas for 0.5 h, then turn on the lamp, and the sample is analyzed after 3 hours irradiation. The light source used is a 300 W Xe lamp with a 420 nm cutoff filter (PLS-SXE 300D, Beijing Perfectlight Co., Ltd., $\lambda \ge 420$ nm, 810 mW·cm⁻²). The gas product is analyzed by a gas chromatograph (Shimadzu GC-8A 2014C), and the liquid products are monitored and analyzed by high-performance liquid chromatography (Agilent 1260 Infinity) and gas chromatography-mass spectroscopy (Agilent 7890B-5977A). The conversion of BA and the selectivity of BAD are obtained by the following equations:

Conversion (%) = $(n_0 - n_{BA})/n_0 \times 100\%$

Selectivity (%) = $n_{BAD}/(n_0-n_{BA}) \times 100\%$

Where n_0 stands for the initial moles of BA; n_{BA} and n_{BAD} is molar amount of the residual BA and BAD after the photoredox dual reaction, respectively.

The apparent quantum yield (AQY) of BAD generation on $2\%CoS_x/CZS$ is tested under the same reaction conditions except for the different wavelength monochromatic light irradiation. The AQY is calculated by the equation:

AQY (%) = $(N_h/N_p) \times 100\% = (2N_Ahcn_{BAD}) / (PS\lambda t) \times 100\%$

Where N_h stands for the number of reaction holes, N_p stands for the number of incident photons, N_A is Avogadro constant, h is the Planck constant, c is the speed of light, n_{BAD} represents for the molar amount of BAD, P is the intensity of the irradiation, S stands for the irradiation area, λ is the wavelength of incident light and t is the reaction time.

The principle of the photodeposition of CoS_x on CZS

The photodeposition process of CoS_x in the dispersion containing $Cd_{0.7}Zn_{0.3}S$, $Co(NO_3)_2 \cdot 6H_2O$, thiourea, and carbinol can be described by the following equations:

 $Cd_{0.7}Zn_{0.3}S + hv \rightarrow e^{-} + h^{+}$ (1)

$$\operatorname{Co}^{2+} + 2e^{-} \to \operatorname{Co}$$
 (2)

$$(NH_2)_2CS + 2H_2O \xrightarrow{hv} CO_2 + 2NH_3 + H_2S$$
(3)

$$H_2S \to H^+ + HS^- \tag{4}$$

$$\mathrm{HS}^{-} \to \mathrm{H}^{+} + \mathrm{S}^{2-} \tag{5}$$

$$S^{2-} + Co^{2+} \rightarrow CoS \tag{6}$$

 $Cd_{0.7}Zn_{0.3}S$ is excited to generate electrons and holes under light illumination (1). The photogenerated holes are captured and quenched by carbinol, while the photogenerated electrons react with Co^{2+} to form Co (2). Thiourea undergoes hydrolysis under irradiation to generate H₂S, which gradually releases S²⁻, and the released S²⁻ then combines with Co²⁺ to form CoS deposition (3-6). Therefore, the overall reaction process can be illustrated as follow:

$$Co^{2+} + (NH_2)_2CS + 2H_2O \xrightarrow{hv, carbinol} CO_2 + 2NH_3 + 2H^+ + CoS_x (x=0-1)$$
(7)

The CoS_x is deposited onto $Cd_{0.7}Zn_{0.3}S$ nanoparticles, resulting in the formation of $CoS_x/Cd_{0.7}Zn_{0.3}S$ composites.

Photocatalysts	BAD production (mmol	H ₂ production	Light source	Ref.
CoS _x /Cd _{0.7} Zn _{0.3} S	5.57	5.67	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	This work
Zn ₃ In ₂ S ₆ -W	1.83	1.77	300 W Xe-lamp $\lambda \ge$ 380 nm	1
CeO ₂ /ZnIn ₂ S ₄	0.66	1.49	300 W Xe-lamp AM 1.5 G	2
Ni: ZnIn ₂ S ₄	3.61	1.46	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	3
CdS/MIL-53(Fe)	1.41	1.17	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	4
CdS/BiVO ₄	4.40	4.56	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	5
PSO-Fe ₂ O ₃	4.62	5.90	300 W Xe-lamp	6
CdS/WO ₃	3.98	5.48	300 W Xe-lamp	7
Ni/(Au@CdS)	4.24	3.88	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	8
CCNuns	0.89	0.98	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	9
CN/BP@Ni	0.94	0.93	300 W Xe-lamp $\lambda \ge 400 \text{ nm}$	10
Au/ZnIn ₂ S ₄	1.76	1.63	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	11
$C/g-C_3N_4$	0.23	0.29	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	12
ZnS-Ni _x S _y	4.55	3.65	500 W Xe-lamp $\lambda \ge 200 \text{ nm}$	13
V _N -UP-CN	1.98	1.96	300 W Xe-lamp $\lambda \ge 420 \text{ nm}$	14
Ru/g-C ₃ N _{4-x}	5.07	6.42	300 W Xe-lamp $320 \le \lambda \le 850 \text{ nm}$	15

Table S1 Comparison of activity for photocatalytic selective benzaldehyde synthesis coupled with H₂ production.

Samular	Co content (<i>wt</i> %)			
Samples	Theoretical value	Actual value		
0.5%CoS _x /CZS	0.49	0.41		
1%CoS _x /CZS	0.98	0.88		
2%CoS _x /CZS	1.96	1.79		
5%CoS _x /CZS	4.77	4.36		

Table S2 The Co content in the as-prepared $m\%CoS_x/CZS$.

Table S3 The BET specific surface areas of CZS and 2%CoS_x/CZS.

Sample	CZS	2%CoS _x /CZS
S _{BET} (m ² /g)	23.54	17.71

Table S4 Exponential function fitted parameters of the TRPL decay spectra of the as-prepared samples.

	τ1 (ns)	A1 (%)	τ ₂ (ns)	A2 (%)	Average τ (ns)
CZS	0.67	47.71	4.40	52.29	4.32
2%CoS _x / CZS	0.17	69.57	0.86	30.43	0.80

For TRPL, the decay curves can be well fitted by the following biexponential equations:

 $I_{(t)} = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$

$$\tau\!=\!\left(A_{1}\tau_{1}{}^{2}\!+\!A_{2}\tau_{2}{}^{2}\right)/\left(A_{1}\tau_{1}\!+\!A_{2}\tau_{2}\right)$$

where the I₀ represents the baseline correction value, A₁ and A₂ are the pre-exponential factors, and τ_1 , τ_2 and τ

represent the lifetime (ns) in different processes and average lifetime.

Number	Aromatic alcohols	Conversion of aromatic alcohols (%)	Selectivity of aromatic aldehydes (%)
1	HO	18.1	96
2	HOCH ₃	16.5	95
3		16.2	94
4	HO	15.8	95
5	HO	8.5	88
6	HO	9.6	91
7	HO	11.5	92
8		6.5	83

 $\label{eq:solution} \begin{array}{l} \textbf{Table S5} \mbox{ The photocatalytic performances of $2\%CoS_x/CZS$ for the selective oxidation of para-substituted benzyl alcohols.} \end{array}$





Figure S2 N_2 absorption-desorption isotherms of CZS and 2%CoS_x/CZS.



Figure S3 HPLC results of photocatalytic products over 2%CoS_x/CZS.



Figure S4 Mass spectra of (a) BA and (b) BAD measured by gas chromatography-mass spectroscopy (GC-MS).



Figure S5 The XRD patterns of 2%CoS_x/CZS before and after photocatalytic cycling reaction.



Figure S6 The XPS spectra of 2%CoS_x/CZS before and after photocatalytic cycling reaction.

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