Supporting Information

Photocatalytic hydrogen-evolution and simultaneously converting high-concentration of thiols into disulfides with excellent yield under visible-light

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Fig. S2 XPS full spectra (a) and individual spectra of (b) Cd 3d; (c) S 2p; (d) Ti 2p; (e) O 1s; (f) Ni 2p and (g) P 2p, respectively.



Fig. S3 Total amount of hydrogen production in 4.5 h with different pH.



Fig. S4 Total amount of hydrogen production in 4.5 h with different photocatalysts.



Fig. S5 The UV-vis spectra of the different supernates.



Fig. S6 Plot of hydrogen production versus reaction time from different substrates.



Fig. S7 Plot of hydrogen production versus reaction time under 0.06 M MPA.



Fig. S8 ¹H NMR spectrum of high-concentration liquid phase products.



Fig. S9 Plot of hydrogen production versus reaction time with 0.6 M MPA.



Fig. S10 The rate of hydrogen evolution under different concentration of MPA.



Fig. S11 Plot of hydrogen production versus reaction time with 0.3 MP.



Fig. S12 XRD patterns of S_1O_1P samples before and after the photocatalytic reaction.



Fig. S13 Photocurrent density of S_1O_1P and other photocatalysts.



Fig. S14 GC characterization for produced hydrogen: employing H_2O as the solvent.

Table S1 The loading amount of Ni₂P measured by X-ray photoelectron spectroscopy (XPS).

Photocatalysts	Mole Fraction (mol%)	
PN	0.77	
S_1O_1P	0.41	

 Table S2 Specific surface area and pore volume of samples.

	CdS	S_1O_1P	PN	P25	
BET area/m ² ·g ⁻¹	150.32	113.55	55.09	50.44	
Pore volume/cm ³ ·g ⁻¹	0.52	0.36	0.14	0.13	

Table S3 Optimal pH for conversion of MPA to 3,3'-dithiodipropanoic acid.

Entry ^[a]	рН [b]	Time (h)	Conversion Rate (%) ^[c]	Yield $H_2(mL)^{[d]}$
1	3	4.5	15.13	2.54
2	5	4.5	60.85	10.22
3	6	4.5	89.96	15.11
4	7	4.5	91.27	15.34
5	8	4.5	91.55	15.38
6	9	4.5	94.49	15.87
7	10	4.5	87.06	14.63
8	12	4.5	41.50	6.97

[a] Conditions: MPA (131 µL) and S₁O₃P (50 mg) in 50 mL reaction solution under a 300 W Xe

lamp, 8 °C. [b] Adjust with 1M NaOH solution. [c] Calculate with hydrogen: Conversion Rate (%) *Hydrogen produced (mL)*

= 16.8 . [d] Determined by GC with H₂as an internal standard.

Entry ^[a]	Catalysis (P25 : CdS ^[b])	Time (h)	Conversion rate ^[c] (%)	Yield H ₂ ^[d] (mL)
1	1:9	4.5	83.43	14.02
2	1:5	4.5	92.24	15.49
3	1:3	4.5	92.82	15.59
4	1:1	4.5	97.01 97.47 ^[e]	16.29
5	3:1	4.5	94.49	15.87
6	5:1	4.5	90.62	15.22
7	9:1	4.5	74.27	12.47
8	CdS	4.5	32.13	5.39
9	PN	4.5	2.02	0.34
10 ^[f]	1:1	4.5	0	0
11 ^[h]		4.5	0.60	0.10

Table S4 Optimal photocatalyst for conversion of mercapto propionic acid (MPA) to 3,3'-dithiodipropanoic acid.

[a] Conditions: Mercapto propionic acid (131 μL) and S_xO_yP (50 mg) in 50 mL reaction solution under a 300 W Xe lamp, 8 °C. [b] Molar ratio (P25 : CdS). [c] Calculate with hydrogen: Conversion Hydrogen produced (mL)

rate (%) =	16.8	. [d] Determined by GC with H ₂ as an internal standard. [e]		
			Product produced	l (mmol/L)
Calculate with	¹ H NMR spectrosco	opy: Conversion rate (%) =	15	 [f]
No	light.	[h]	No	catalyst.

Entry ^[a]	Substrate	Concentration	Time (h)	Conversion rate ^[b] (%)	Yield H ₂ ^[c] (mL)
1	$C_3H_6O_2S$	0.03 M	4.5	97.47	16.2983
2	$C_3H_6O_2S$	0.06 M	4.5	93.91	31.5533
3	$C_3H_6O_2S$	0.06 M	9	99.28	33.5297
4	$C_3H_6O_2S$	0.3 M	8.5	65.54	110.1117
5	$C_3H_6O_2S$	0.3 M	18	82.36	138.3698
6	$C_3H_6O_2S$	0.3 M	22	83.81	140.7978
7	$C_3H_6O_2S$	0.6 M	5	19.29	64.8297
8	$C_3H_6O_2S$	0.6 M	11	33.96	114.1152
9	$C_3H_6O_2S$	0.6 M	19	41.88	140.7037
10	$C_3H_6O_2S$	0.6 M	24	43.83	147.2626
11	C_3H_8OS	0.3 M	5	43.43	72.9705
12	C ₃ H ₈ OS	0.3 M	8.5	63.61	106.8637
13	C ₃ H ₈ OS	0.3 M	16	72.03	121.0169
14	C ₃ H ₈ OS	0.3 M	20	74.02	124.3521

Table S5 The conversion and H₂ of different concentrations of thiols at different times.

[a] Conditions: mercapto propionic acid and S1O1P (50 mg) in 50 mL reaction solution under a 300 W Xe lamp, pH = 9, 8 °C. [b] Calculate with hydrogen: Conversion rate (%) = *Hydrogen produced(mL)* 16.8

. [c] Determined by GC with H_2 as an internal standard.

Entry	Photocatalyst	H_2 production (µmol·h ⁻¹ ·g ⁻¹)	Catalyst dose (mg)	References
1	S_1O_1P	16697.86 (3 h)	50	Our Work
2	Pt/ZnCdS	1045	25	1
3	Ni@SGCN	23.58	20	2
4	Pt/PCN-777	586	10	3
5	$Zn_{0.5}Cd_{0.5}S$	419	1	4
6	^{NCN} CN _x -NiP	763	5	5
7	$Au/ZnIn_2S_4$	1760	50	6
8	$Pt/Zn_3In_2S_6$	927	180	7
9	CdS&P25-Ni ₂ P	1148	50	8

Table S6 Comparison of photocatalytic H_2 production rate reported in the literatureswith the transformation of organics and our work.

 Table S7 The simulation results of the EIS plots.

Photocatalysts	R_s/Ω	R_{ct}/Ω
S_1O_1P	145.82	5205
CdS	147.53	20120
PN	139.51	18200
P25	143.78	17160

Band gap (Eg) determination by UV-vis diffuse reflectance spectra

This article uses the Tauc plot method to estimate the band gap of the sample.⁹

 $(\alpha h v)^{1/n} = A(h v - E_g)$

where α , A, hv, h, v and E_g represents the absorption coefficient, constant, the photon energy, the Planck constant = $4.1356676969 \times 10^{-15}$ eV·s, the incident photon frequency the band gap. Direct semiconductors n = 2; Indirect semiconductors n=1/2.

 $hv = hc/\lambda$

where c is the velocity of light and λ is the wavelength of light.

The obtained UV-vis diffuse reflectance spectra are converted into the absorption spectra through the Kubelka-Munk equation. Calculate $(\alpha hv)^{1/n}$ and hv according to the equations and import the values of hv and $(\alpha hv)^{1/n}$ into origin, which are the X-axis and Y-axis, respectively. Find the straight-line segment on the graph and extend it to the X-axis. The intersection of the X-axis is the E_g.

¹H NMR spectrum analysis

Centrifuge the product obtained in the experiment, take 600 μ L supernatant in a 5 mL centrifuge tube, and then place the centrifuge tube in a vacuum drying oven at 30 °C for 24 h. Then 600 μ L D₂O (C₂D₆OS) was used to dissolve the solids and 10 μ L methanol solution was added to it as an internal standard. Finally, use MestReNova software to perform integration to calculate the concentration of disulfide in the products.¹⁰

$$c_p (mmol/L) = \frac{S_p * n_m * c_m}{S_m/n_n}$$

where S, n, c, m and p represents the integral area, number of H molecules, concentration, methanol and products.

¹H NMR spectra

MPA Colorless liquid; ¹H NMR (400 MHz, D₂O), δ 2.51 ppm (t, 2H), 2.73 ppm (t, 2H).

3,3'-Dithiodipropanoic Acid Colorless solid; ¹H NMR (400 MHz, D₂O), δ 2.94 ppm (t, 4H), 2.60 ppm (t, 4H). Internal standard: 0.031 M CH₃OH.

MP Colorless liquid; ¹H NMR (400 MHz, C_2D_6OS), δ 1.67 ppm (m, 2H), 2.22 ppm (t,

Bis (3-Mercapto-1-propanol) disulfide White solid powder; ¹H NMR (400 MHz,

1H), 2.51 ppm (q, 2H), 3.46 ppm (q, 2H), 4.46 ppm (t, 1H).

C₂D₆OS), δ 1.74 ppm (m, 4H), 2.72 ppm (t, 4H), 3.45 ppm (q, 4H), 4.52 ppm (t, 2H). Internal standard: 0.051 M CH₃OH.

Reduced Glutathione White solid powder; ¹H NMR (400 MHz, D₂O), δ 2.14 ppm (q, 2H), 2.55 ppm (m, 2H), 2.95 ppm (m, 2H), 3.78 ppm (m, 4H), 4.48 ppm (q, 1H).

Bis (Glutathione) disulfide White solid powder; ¹H NMR (400 MHz, D₂O), δ 2.14 ppm (q, 4H), 2.55 ppm (m, 4H), 2.93 ppm (m, 4H), 3.75 ppm (m, 8H), 4.54 ppm (q, 2H). Internal standard: 0.031 M CH₃OH.

L-Cysteine White crystal; ¹H NMR (400 MHz, D₂O), δ 3.00 ppm (q, 1H), 3.09 ppm (q, 1H), 3.97 ppm (t, 1H).

L-Cystine White solid powder; ¹H NMR (400 MHz, D₂O with NaOH), δ 2.86 ppm (q, 2H), 3.07 ppm (q, 2H), 3.53 ppm (q, 2H). Internal standard: 0.031 M CH₃OH.









Fig. S15 ¹H NMR spectra of substrates and corresponding products.

Apparent quantum yields (AQY) calculation

The photocatalytic quantum yield can be calculated by replacing the number of absorbed photons by the number of incident photons, which is called "apparent quantum yield" (AQY). The AQY is calculated using the following formula¹¹:

$$AQY = \frac{N_e}{N_p} \times 100\% = \frac{10^9 (n_{H_2} \times N_A \times K) \times (h \times c)}{(I \times A \times \lambda) \times t} \times 100\%$$

where N_e and N_p are the total number of electrons transferred by the reaction and number of incident photons; ${}^{n_{H_2}}$, N_A, K, h, c, I, A, λ and t represents amount of H₂ evolution (mol), Avogadro number (6.02 × 10²³ mol⁻¹), number of electrons transferred in the reaction, Planck constant (6.62 × 10⁻³⁴ J·s), velocity of light (3 × 10⁸ m·s), optical power density (W·m⁻²), incident illumination area (m²), wavelength of incident light (nm) and reaction time (s), respectively.

Detailed steps of electrochemical testing

Photoelectric chemical properties of catalysts have been investigated using a threeelectrode potential station (CHI 660E) with a saturated Ag/AgCl as a reference electrode and a platinum sheet as the counter electrode.

Under AM 1.5G simulated solar light illumination (100 mW/cm^2) from a Xe lamp (300 W), 0.03 M MPA solution (pH = 9) has been used as electrolyte with 30 min N₂ bubbling. LSV and CV are conducted at a scan rate of 10 mV/s. Mott-Schottky diagrams are obtained at 1 kHz. EIS is measured in the frequency domain from 1 Hz to 100 kHz and modulation amplitude of 10 mV.

The conductive glass (FTO) selected in this experiment was purchased from Opivite New Energy Co., Ltd., Yingkou City, Liaoning Province, and the working electrode was made by coating the catalyst sample with FTO. The specific main experimental steps are as follows:

1. FTO surface pretreatment. The conductive glass was cut into a shape of 1 cm*3 cm, and ultrasonically cleaned in isopropanol, absolute ethanol, and deionized water for 15 minutes in order. Dry the ultrasonically cleaned FTO naturally for later use.

2. Preparation of catalyst dispersion. Weigh 4 mg of the catalyst sample and disperse it in a mixed solution of 2 mL deionized water and isopropanol (volume ratio 1:1) containing 5 μ L Nafion, and ultrasonicate for 30 minutes to obtain a uniform dispersion.

3. Electrode coating. Cover one side of the conductive surface of the FTO with

transparent tape, leaving a coating area of 1 cm*1 cm to prevent it from being covered completely and affecting the conductivity of the electrode and the experimental effect. Take 25 μ L of the dispersion and drop it vertically on the exposed 1 cm² FTO. After the droplets are spread out and evenly cover the entire electrode of the sample, test after drying at room temperature.



Fig. S16 Schematic illustration of the experimental device of photoelectric catalytic performance

Supplementary References

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