Electronic Supplementary Information for

In situ confinement of ultrahigh-density Co_2P nanoparticles within biomass-derived carbon nanosheet frameworks as efficient cocatalysts for solar H_2 production

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1. Experimental section

1.1 Chemicals and materials

All reagents used in this work were analytically pure and without further purification. The cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%) was purchased from Shanghai Titan Science. Sodium hypophosphite ($NaH_2PO_2 \cdot 2H_2O$, 99%) purchased from Shanghai Macklin Biochemical Co., Ltd. Triethanolamine (TEOA) was purchased from Xilong Scientific (>99.8%). Erythrosine B (ErB), Eosin Y (EY), and Fluorescein Sodium (NaFL) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Rose Bengal (RB) was obtained from Shanghai Zhongqin Chemical Reagent Co., Ltd. Rhodamine B (RhB) was purchased from Beijing Chemical Factory. The *Pleurotus eryngii* (PE) was purchased from a local vegetable market of Yinchuan, China. Natural basswood was purchased from Ruiyi Wood Industry Company (China). All solutions were prepared with ultrapure water (18.2 MΩ cm).

1.2 Materials preparation

1.2.1 Co/CPE

Raw *Pleurotus eryngii* (PE) was first cut into slice according to the growth direction, washed, and freezing-dried. Then the dry PE slices were soaked in a $Co(NO_3)_2$ solution (0.05-0.4 M) for 2 h to obtain Co^{2+}-adsorbed PE (Co^{2+}-PE) and freeze-dried overnight. Afterwards, the Co^{2+}-PE was successively carbonized in air at 260°C for 6 h and in an Ar atmosphere at 1000°C for 6 h to obtain Co/CPE.

1.2.2 Co_2P/CPE

500 mg of Co/CPE was mixed with 2 g of $NaH_2PO_2 \cdot 2H_2O$ and thoroughly ground. The resulting mixture was then transferred into a tubular furnace and heated at 300 °C for 2 h with a ramping rate of 2.5 °C min^{-1} under Ar atmosphere. The obtained samples were washed with deionized water three times and dried in a vacuum oven overnight to

obtain Co_2P/CPE.

1.2.3 Co_2P/CW

The carbonized wood supported Co_2P (Co_2P/CW) catalyst was prepared by using the exact same procedure for Co_2P/CPE except using natural wood powder instead of using PE.

1.2.4 Co_2P nanoparticles

The Co_2P nanoparticles were prepared by the direct phosphidation of $Co(NO_3)_2$ using NaH_2PO_2 following the procedures for the preparation of Co_2P/CPE.

1.3 Characterization

The phase structure of the samples was analyzed using a Rigaku Smartlab X-ray diffractometer (XRD) with Ni-filtered Cu Kα radiation. The morphology of the samples was observed with a ZEISS EVO 10 scanning electron microscope (SEM). The microstructure of the samples was observed with a JEM 2100F transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab-250Xi, Al Kα radiation) was analyzed to investigate the surface characteristics of the membrane electrodes. Inductively coupled plasma optical emission spectroscopy (ICP-OES) with an Agilent 5110 instrument was used to determine the Co and P contents in the samples. Photoluminescence (PL) spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. The excitation wavelengths for ErB sensitized systems and CdS-based systems are 480 and 370 nm, respectively.

1.4 Photocatalytic H_2 evolution experiments

1.4.1 Dye-sensitized photocatalytic H_2 evolution experiments

Photocatalytic H_2 evolution experiments were performed in a sealed Pyrex reactor (315 mL) with a top flat quartz window (38.47 cm^2) for light irradiation and a silicone rubber septum was fixed on its side for sampling the produced H_2. In a typical procedure, ErB and Co_2P/CPE were added to the reaction cell containing 100 mL of 10 vol.% TEOA (pH 8) aqueous solution under vigorous stirring. Then, the reaction solution was thoroughly degassed by repeated evacuation-N_2 filling, and finally refilled with N_2 to reach ambient pressure. After that, the reaction solution was irradiated by a 30 W white-light LED lamp with a 420 nm cut-off filter. During the reaction, the mixture solution was continuously stirred. The amount of H_2 produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column, and with N_2 as carrying gas. For evaluating the stability of the Co_2P/CPE, the Co_2P/CPE was separated by centrifugation, washed, and redispersed into the reaction solution containing fresh ErB and TEOA and the resulting system was subjected to light irradiation.

The monochromatic apparent quantum efficiencies (AQEs) of the H_2 evolution were measured under conditions similar to those in the above photocatalytic reaction except that the light source was equipped with various band-pass filters (450, 475, 500, 520 and 550 nm). The photon flux of incident light was determined using a ray virtual radiation actinometer (Apogee MQ-500, a silicon ray detector, light spectrum, 389–692 nm; measurement range, 0-4000 μmol m^{-2} s^{-1}). The AQE was calculated from the ratio of the number of reacted electrons during H_2 evolution to the number of incident photons according to equation (1) as follows:

$$\mathrm{AQE}(\%) = \frac{2 \times \text{number of evolved } \mathrm{H_2} \text{ molecules}}{\text{number of incident photons}} \times 100\% \tag{1}$$

1.4.2 Semiconductor-based photocatalytic H_2 evolution experiments

The semiconductor-based composite photocatalyst was prepared by simply mixing 5 mg of Co_2P/CPE or Co/CPE with 100 mg of CdS. The resulting composited photocatalysts (CdS-Co_2P/CPE and CdS-Co/CPE) were added into a reactor containing 100 mL of lactic acid (LA, 10 vol%), degassed by repeatedly vacuuming and filling N_2, and irradiated by a 300 W Xe lamp equipped with a 420 nm cut-off filter. During the reaction process, the reaction solution was continuously stirred and kept at room temperature by circulating with a flow of cooling water. The amount of H_2 produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column, and with N_2 as carrying gas.

1.5 Electrochemical and photoelectrochemical measurements

Photoelectrochemical measurements were carried out with a three-electrode system using an electrochemical workstation (CHI760E, Shanghai, China). The saturated Ag/AgCl electrode and Pt mesh (1 cm×1 cm) were used as reference electrode and counter electrode, respectively. For the fabrication of working electrode, the catalyst ink was prepared by dispersing 5 mg of catalyst into 2.5 mL of ethanol solution containing 25 μL of 5 wt% Nafion solution by ultrasonication for 15 min. Afterwards, 500 μL of as-prepared catalyst ink was loaded onto conductive side of an indium-doped tin oxide (ITO) glass (1 cm×1 cm) and dried at 60 °C overnight. A 0.2 M Na_2SO_4 solution containing 10 vol.% LA was used as the supporting electrolyte. The transient photocurrent response was recorded at a bias of 0.5 V vs. Ag/AgCl under chopped visible light irradiation. A 300-W Xe lamp equipped with a 420 nm cut-off filter was used as light source. The electrocatalytic H_2 evolution activity was measured using linear sweep voltammetry (LSV) with a scan rate of 5 mV s^{-1}.

2. Additional data

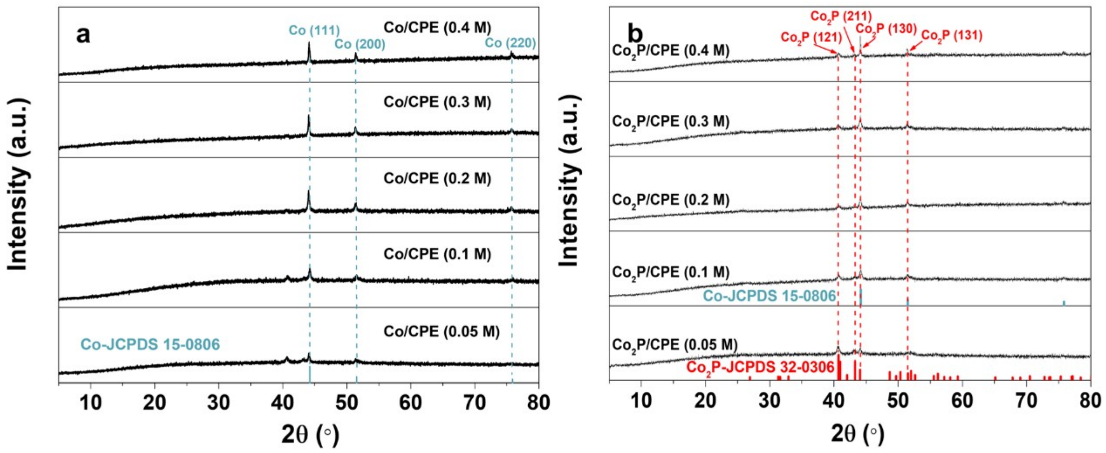

Fig. S1 XRD patterns of (a) Co/CPE and (b) Co_2P/CPE samples prepared using different concentrations of Co salt.

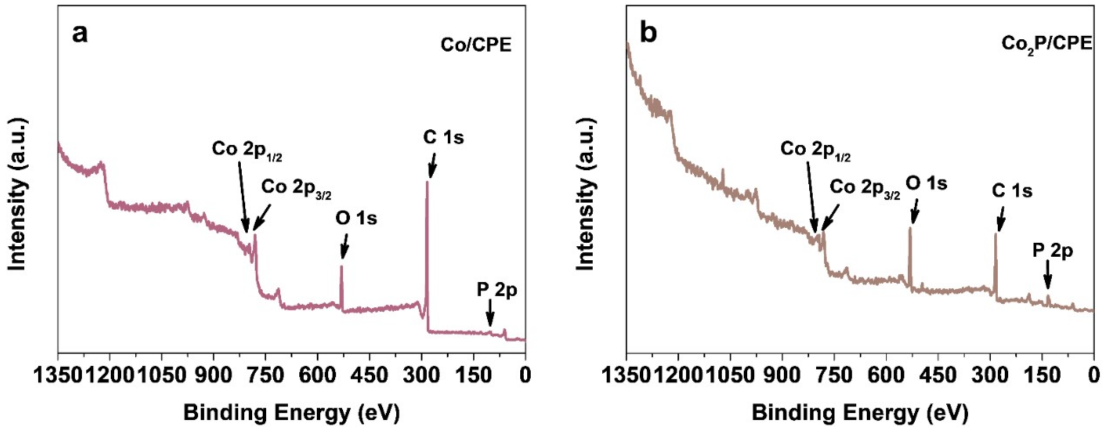

Fig. S2 XPS survey spectra of (a) Co/CPE and (b) Co_2P/CPE.

Table S1 Textual characteristics of Co/CPE and Co_2P/CPE.

Sample	Co (wt.%)^{a}	P (wt.%)^{a}	Surface area (cm^{2} g^{-1})^{b}	pore volume (cm^{3} g^{-1})^{c}	Pore size (nm)^{d}
Co/CPE	42.30	2.54	54.4	0.12	9.1
Co_2P/CPE	37.95	14.19	42.6	0.14	13.1

[a] The element content was determined by ICP-OES analysis.

[b] The specific surface area determined by N_2 adsorption-desorption measurements.

[c] Single point-total pore volume of the pores at P/P_0=0.99.

[d] Adsorption average pore width (4 V A^{-1} by BET).

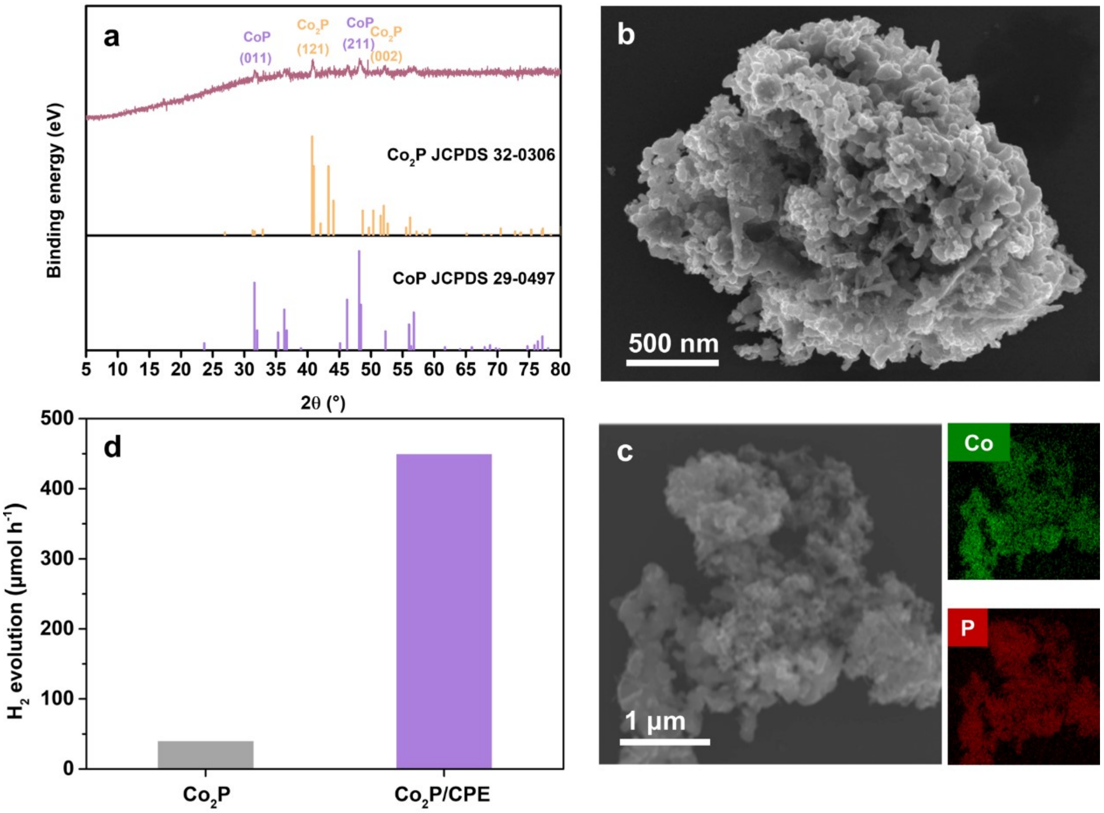

Fig. S3 (a) XRD patterns of free Co_2P nanoparticles. (b) SEM image and (c) the corresponding SEM-EDX maps of free Co_2P nanoparticles. (d) Photocatalytic H_2 evolution activities of free Co_2P nanoparticles and Co_2P/CPE in the ErB-TEOA system. Reaction conditions: light source: 30 W white-light LED lamp, λ≥420 nm; TEOA solution, 10 vol%, 100 mL, pH 8; ErB: 0.5 mM; Co_2P: 19 mg; Co_2P/CPE: 50 mg.

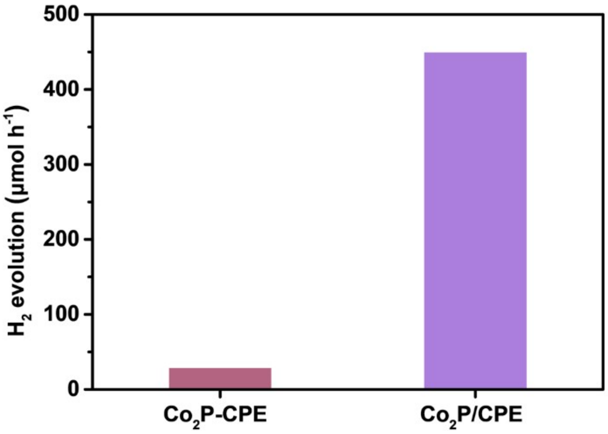

Fig. S4 Photocatalytic H_2 evolution activities of physically mixed Co_2P-CPE and Co_2P/CPE in the ErB-TEOA system. Reaction conditions: light source: 30 W white-light LED lamp, λ≥420 nm; TEOA solution, 10 vol%, 100 mL, pH 8; ErB: 0.5 mM; cocatalyst: 50 mg.

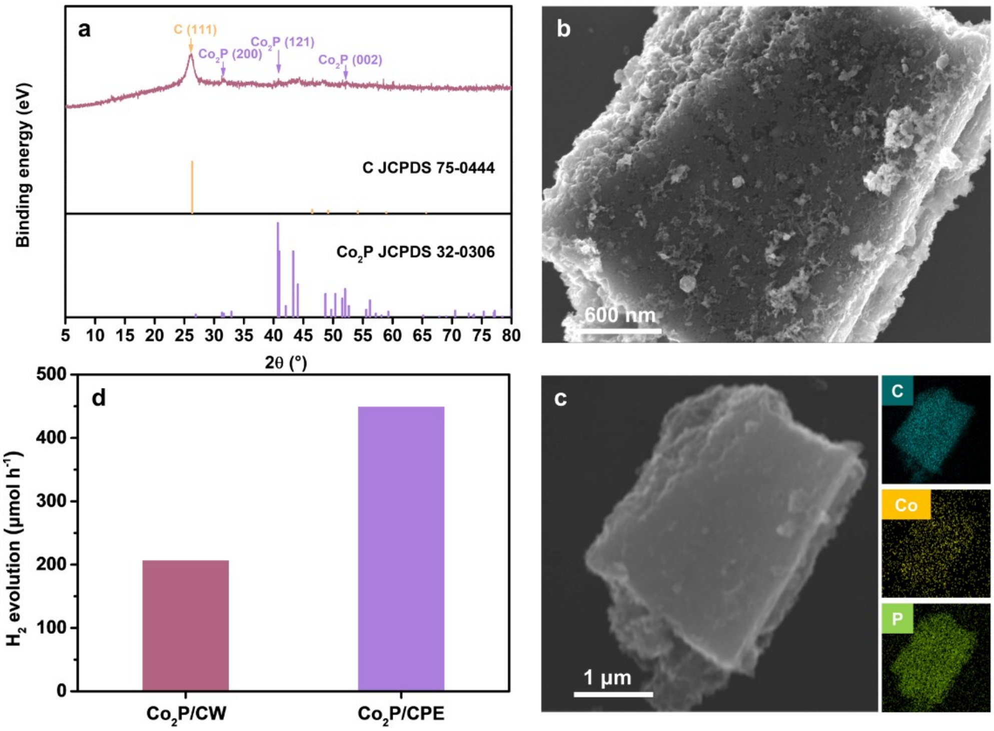

Fig. S5 (a) XRD patterns of Co_2P/CW. (b) SEM image and (c) the corresponding SEM-EDX maps of Co_2P/CW. (d) Photocatalytic H_2 evolution activities of Co_2P/CW in the ErB-TEOA system. Reaction conditions: light source: 30 W white-light LED lamp, λ≥420 nm; TEOA solution, 10 vol%, 100 mL, pH 8; ErB: 0.5 mM; cocatalyst: 50 mg.

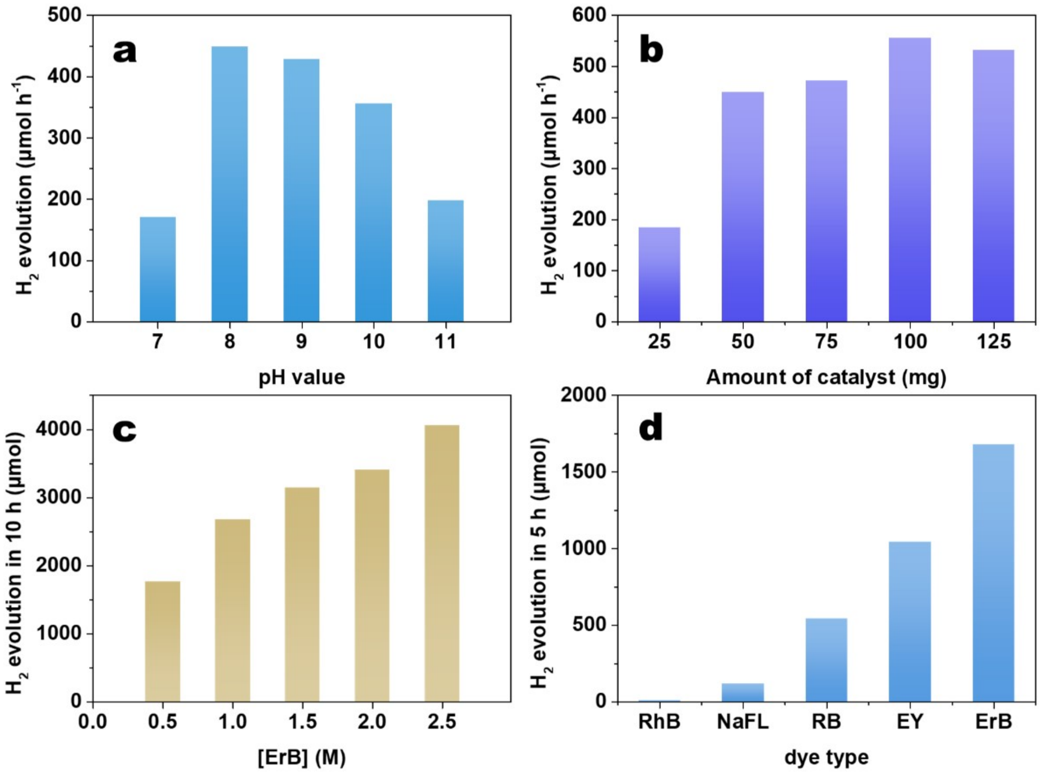

Fig. S6 Effects of (a) pH value of TEOA solution (ErB: 0.5 mM; Co_2P/CPE: 50 mg), (b) dosage of Co_2P/CPE (ErB: 0.5 mM; pH 8), (c) concentration of ErB (Co_2P/CPE: 50 mg pH 8), and (d) type of dye (dye: 0.5 mM; Co_2P/CPE: 50 mg; pH 8) on the photocatalytic HER performance of dye-sensitized Co_2P/CPE system under visible light. Reaction conditions: light source: 30 W white-light LED lamp, $\lambda \geq 420$ nm; TEOA solution, 10 vol%, 100 mL.

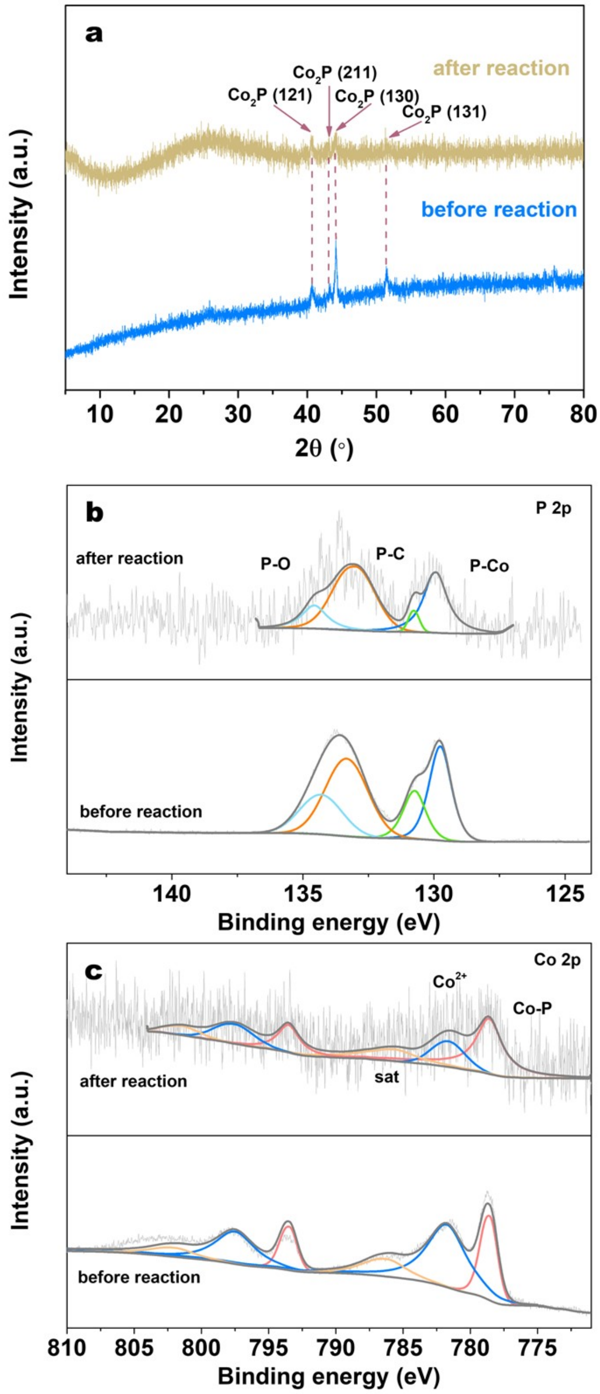

Fig. S7 (a) XRD spectra, (b) P 2p, and (c) Co 2p XPS spectra of Co_2P/CPE before and after cycling HER stability test.

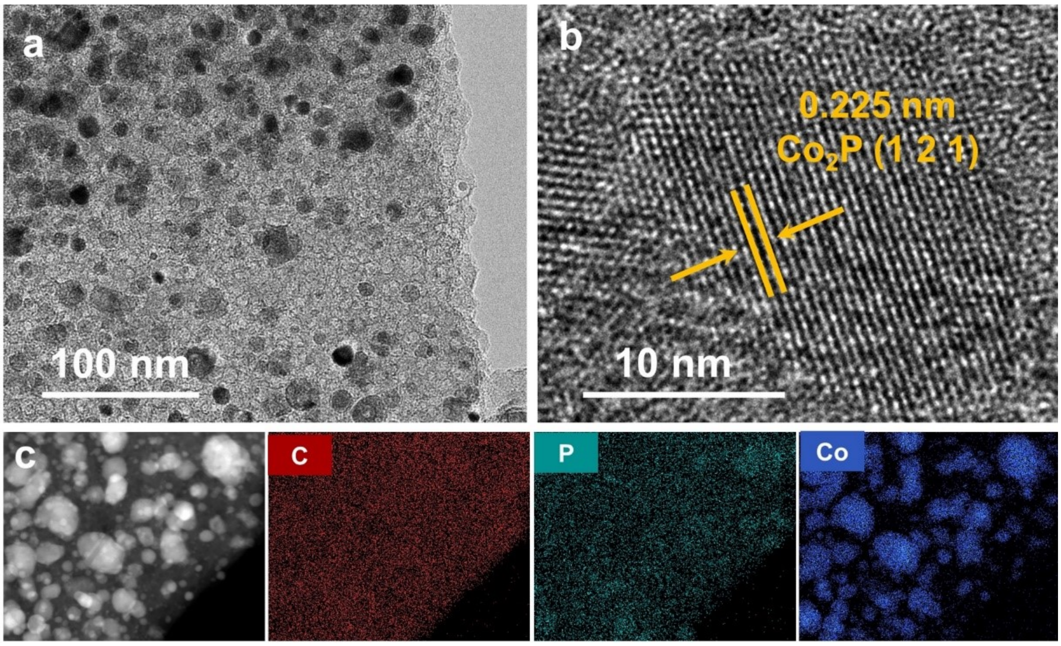

Fig. S8 (a) TEM and (b) HRTEM, (c) HAADF-STEM and the corresponding EDX images of Co_2P/CPE after cycling HER stability test.

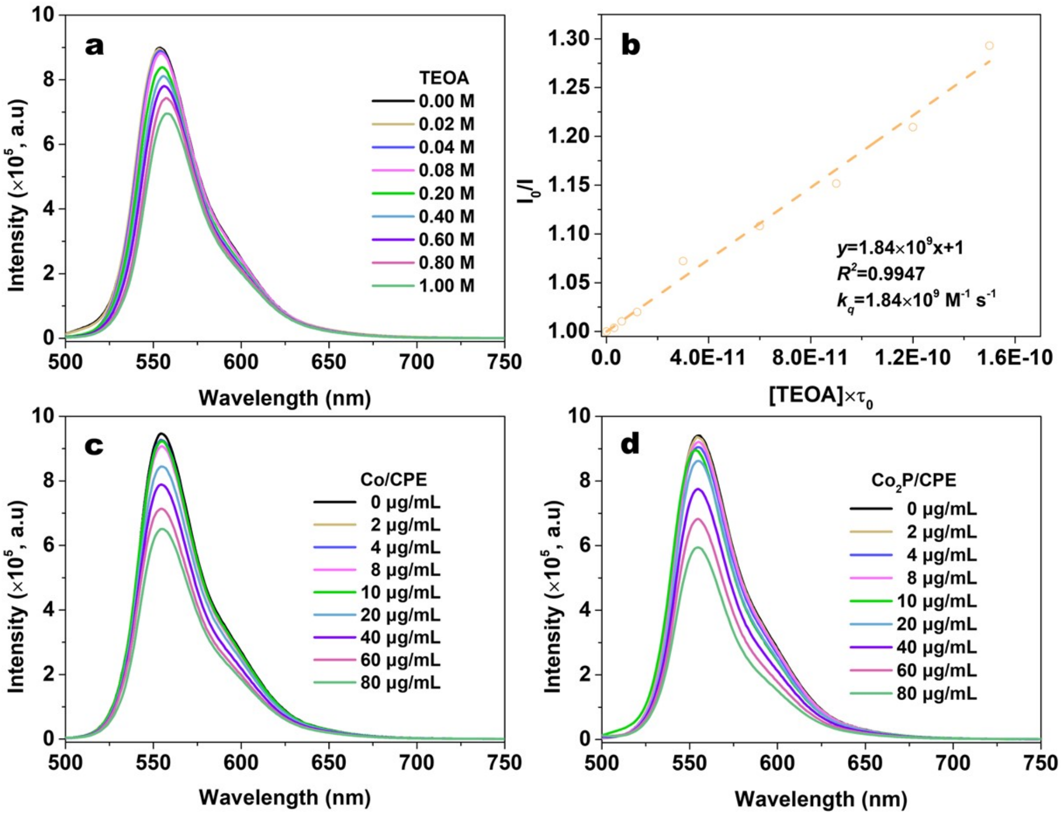

Fig. S9 PL emission quenching of excited ErB solution (10 mM) in the presence of (a) TEOA, (c) Co/CPE, and (d) Co_2P/CPE. (b) Stern–Volmer plot for PL emission quenching of excited ErB solution (10 mM) with TEOA (τ_{ErB}=0.15 ns).

Table S2: A comparison of the HER activity of CdS-Co_2P/CPE with previously reported metal phosphide cocatalyst–semiconductor composites for photocatalytic hydrogen evolution.

Entry	Catalysts	H_2 evolution rate (μmol·g^{-1} h^{-1})	Light sources	Sacrificial agents	Ref.
1	Ni_xP:CZS/NTO	27575	300-W Xe lamp (λ≥420 nm)	Na_2S/Na_2SO_3	1
2	CdS/CoP@AAH	54900	300-W Xe lamp (λ>400 nm)	Lactic acid	2
3	ZnCoP/$CdLa_2S_4$	10260	300-W Xe lamp (λ≥400 nm)	Na_2S/Na_2SO_3	3
4	PMCSFP	2937.11	300-W Xe lamp (λ≥420 nm)	Lactic acid	4
5	Fe_2P–Co_2P/g-C_3N_4	347	300-W Xe lamp (λ=420 nm)	TEOA	5
6	CdS-Co_2P/CPE	6098.1	300-W Xe lamp (λ≥420 nm)	Lactic acid	**This work**

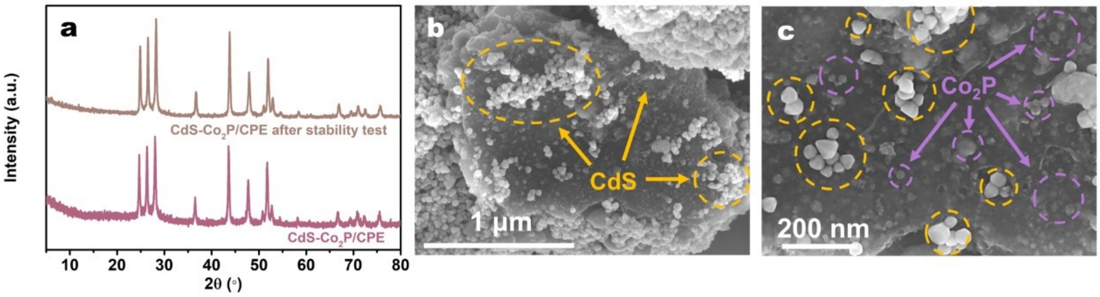

Fig. S10 (a) XRD patterns of CdS-Co$_2$P/CPE before and after stability test. (b) Low- and (c) high-magnification SEM images of CdS-Co$_2$P/CPE after stability test.

Supplementary references

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