

Electronic Supplementary Information

Upcycling endogenous Fe from coal gasification slag waste into a cocatalyst for photocatalytic H₂ evolution reaction

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1. Experimental

1.1 Chemicals and materials

The coal gasification slag (CGS) powders were collected from the coal-to-methanol plant of the Ningdong Energy and Chemical Industry Base located at Yinchuan, Ningxia Hui Autonomous Region, China. Erythrosin B (ErB), Eosin Y (EY), Rose Bengal (RB), Fluorescein sodium (FS), and Rhodamine B were obtained from Tianjin Guangfu Fine Chemical Research Institute. Triethanolamine (TEOA, 99.8%) was purchased from Xilong Scientific Co., Ltd. TiO₂ (P25, ~25 nm, 80% anatase and 20% rutile) was purchased from Degussa. CdS nanoparticles were synthesized according to the reported methods.¹ All other reagents were of analytical grade and used as received. The ultrapure water (18.2 MΩ cm) used to prepare all the solutions.

1.2 Low-temperature phosphidation of CGS

The raw CGS powder was sieved (200 mesh), washed with water to remove the soluble impurities, and finally dried at 60 °C overnight. The 1.0 g of washed CGS was then mixed with 1.0 g of sodium hypophosphite (NaH₂PO₂) by extensive grinding and the resulting mixture was transferred into a tubular furnace and heated at 300 °C for 2 h at a ramping rate of 2.5 °C min⁻¹ in a N₂ flow. The obtained products, denoted as Fe₂P/CGS, were raised with water three times, and dried in a vacuum oven at 60 °C overnight.

1.3 Materials characterizations

Elemental analysis of the samples was carried out with an X-ray fluorescence (XRF) spectrometer (Thermo QUANT`X ED-XRF). X-ray diffraction (XRD) measurements were performed on a Rigaku Smartlab diffractometer using a nickel filtrated Cu K α radiation source at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were taken with a ZEISS Sigma 500 scanning electron microscope. Transmission

electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G²-F30 field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using a monochromatic Al K α X-ray source (1486.6 eV). The binding energies were referenced to the C 1s peak at 284.4 eV. The metal contents in the samples were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Agilent 5110). The specific surface areas of the samples were determined by nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method (Micromeritics ASAP 2460). UV-vis diffuse reflectance spectra (UV-vis-DRS) were recorded on a PerkinElmer Lambda-750 UV-vis-near-IR spectrometer equipped with an integrating sphere and BaSO₄ powder was used as the reflectance standard. Photoluminescence (PL) spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer.

1.4 Photocatalytic H₂ evolution experiments

Dye-sensitized photocatalytic H₂ evolution experiments were performed with a PCX50C Discover multichannel photocatalytic reaction system (Beijing Perfectlight Technology Co. Ltd.) with white-light LED lamps (10 W \times 9, 380 nm $\leq\lambda\leq$ 780 nm, 100 mW cm⁻²) as the light source. In a typical procedure, ErB and Fe₂P/CGS powders were added to a quartz reactor (60 mL) containing 25 mL of 10 vol.% TEOA aqueous solution under vigorous stirring. The pH values of the reaction solution were adjusted by addition of hydrochloric acid or sodium hydroxide. Then, the reaction solution was thoroughly degassed by repeated evacuation and N₂ refilling processes, and finally refilled with N₂ to reach an ambient pressure. After that, the reaction solution was irradiated under continuous stirring. The amount of H₂ produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with

a calibrated gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column (4 mm×5 m), and with N₂ as carrying gas.

The photocatalytic H₂ evolution experiments from ErB-sensitized Fe₂P/CGS system were also carried out under simulated AM1.5 solar light and natural sunlight irradiation. Typically, ErB (2.0 mM) and catalyst (CGS or Fe₂P/CGS) powders (100 mg) were added to a quartz reaction cell (150 mL) containing 100 mL of 10 vol% TEOA aqueous solution (pH 8). After removing the dissolved O₂ by repeated evacuation and N₂ refilling processes, the reaction was commenced under light irradiation. The simulated AM1.5 solar light was obtained with a 300-W Xe lamp equipped with a AM1.5 filter. The experiments under natural sunlight irradiation were carried out outside the room of chemistry department building (Yinchuan, Ningxia Province) between 10.30 a.m. and 15.30 p.m on 3 June 2023.

To evaluate the catalytic H₂ evolution activity of Fe₂P/CGS on CdS, a 300-W Xe lamp equipped with an optical cut-off filter ($\lambda \geq 420$ nm) was used as a light source. The reaction mixture solution was prepared by directly mixing CdS (100 mg) and Fe₂P/CGS (5 mg) powder in reaction cell containing 100 mL of 10 vol.% lactic acid (LA) under vigorous stirring. Then, the reaction solution was thoroughly degassed by repeated evacuation-N₂ filling, and finally refilled with N₂ to reach ambient pressure. During light irradiation, the reaction solution was continuously stirred and maintained at room temperature (25~30 °C) by a flow of cooling water. For the purpose of characterization, The reaction mixture was filtered, washed with water, and dried in a vacuum oven at 60 °C overnight. The obtained product was denoted as CdS-Fe₂P/CGS.

The TiO₂-Fe₂P/CGS was also prepared using the exact same process for the CdS-Fe₂P/CGS, and its H₂ evolution was tested using 10 vol.% CH₃OH as the sacrificial

agent under full-spectrum light irradiation from a 300-W Xe lamp.

1.5 Photocurrent measurements of CdS-Fe₂P/CGS

The photocurrent measurements of CdS-Fe₂P/CGS were carried out in a standard three-electrode electrochemical set-up using a CS3103 (Wuhan Corrtest Instruments Corp., Ltd) electrochemical workstation. The saturated Ag/AgCl and Pt mesh (1 cm×1 cm) graphite rod were used as reference electrode and counter electrode, respectively. For the fabrication of working electrode, the catalyst suspension was prepared by dispersing 10 mg of CdS-Fe₂P/CGS into 3 mL of ethanol/H₂O (1/2, v/v) mixed solution containing 20 μL of 1 wt% Nafion solution by ultrasonication for 15 min. Afterward, the 400 μL of as-prepared catalyst suspension was loaded onto conductive side of an indium-doped tin oxide (ITO) glass (1 cm×1 cm) and dried at 60 °C overnight. A 0.5 M Na₂SO₄ solution containing 10 vol.% LA was used as the supporting electrolyte. The transient photocurrent response of the CdS-Fe₂P/CGS loaded on ITO photoelectrode 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.

2. Additional figures

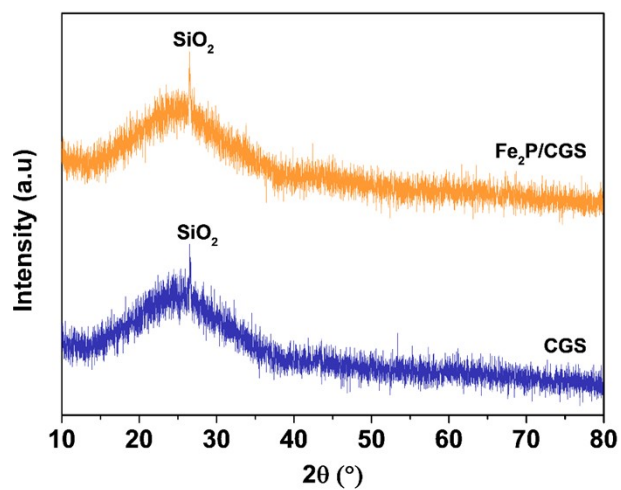


Fig. S1 XRD patterns of CGS and Fe₂P/CGS.

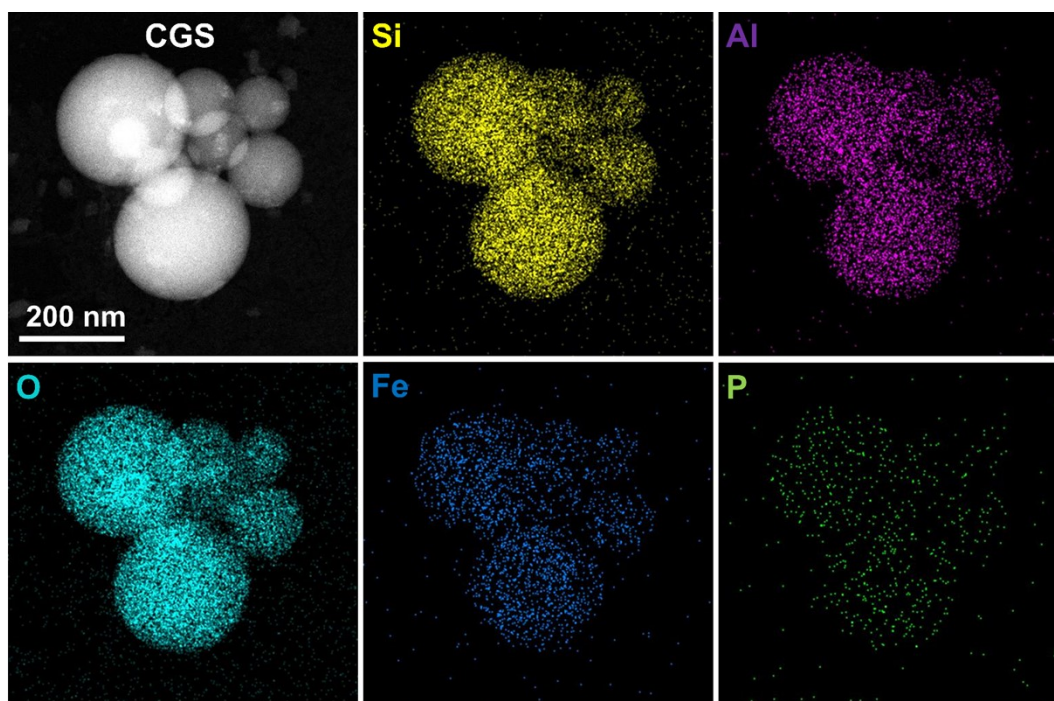


Fig. S2 HAADF-STEM images of CGS and the corresponding EDS mapping images of Si, Al, O, Fe, and P elements.

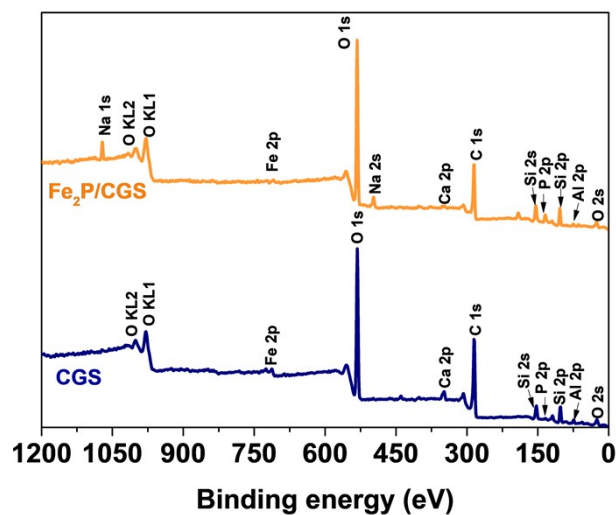


Fig. S3 XPS survey spectra of CGS and Fe₂P/CGS.

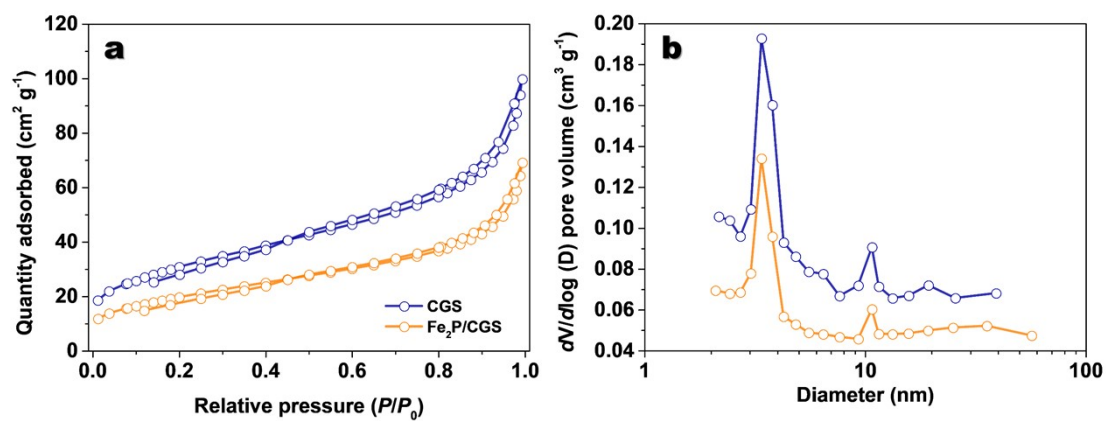


Fig. S4 (a) N₂ adsorption-desorption isotherms and (b) the corresponding pore size distribution curves of CGS and Fe₂P/CGS.

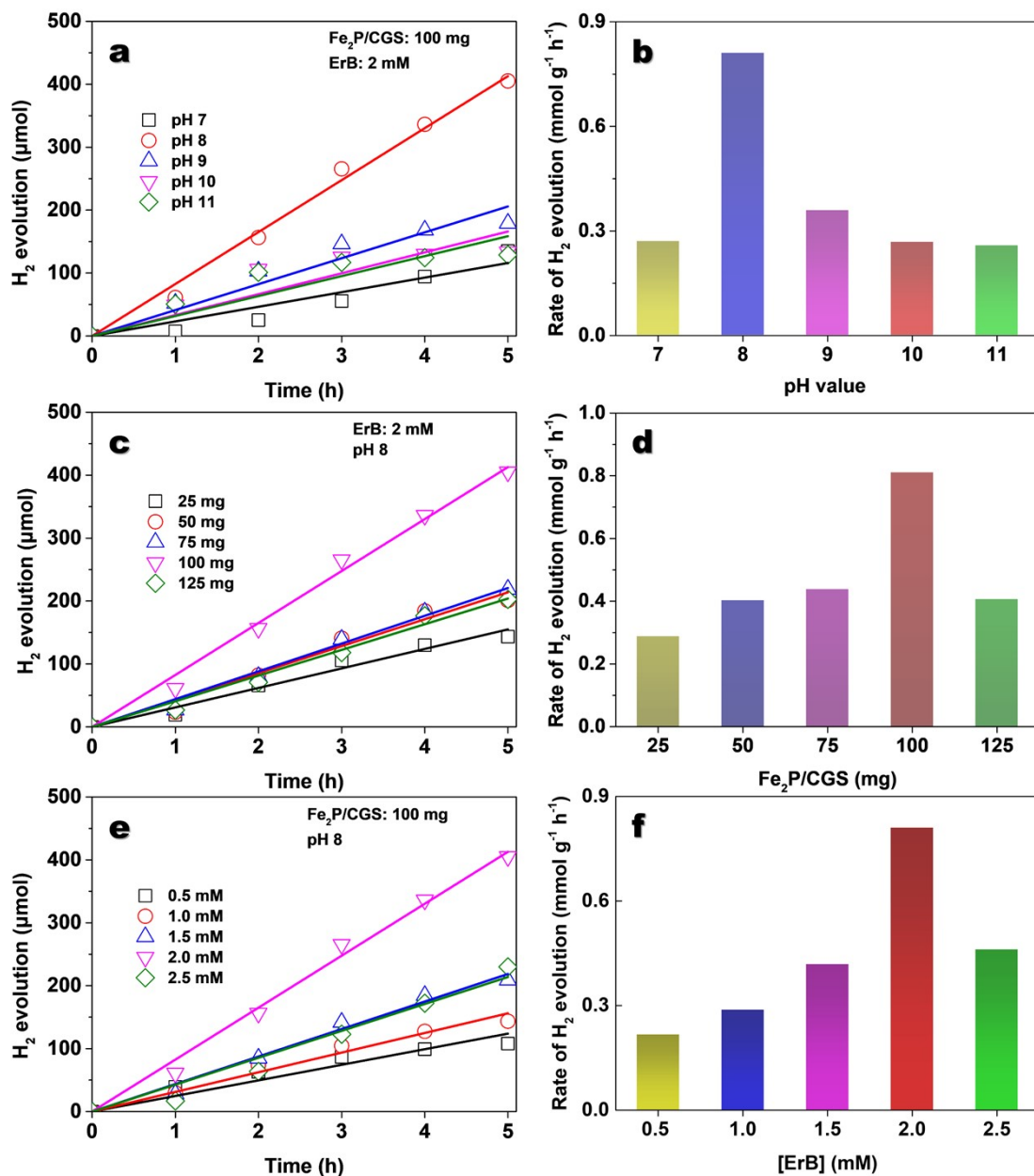


Fig. S5 Photocatalytic H_2 evolution catalyzed by $\text{Fe}_2\text{P/CGS}$ from ErB-TEOA system as a function of (a, b) pH value of TEOA solution, (c, d) $\text{Fe}_2\text{P/CGS}$ concentration, and (e, f) ErB concentration. Reaction conditions: light source, white LED lamp, $380 \text{ nm} \leq \lambda \leq 780 \text{ nm}$; TEOA solution, 25 mL, 10 vol%.

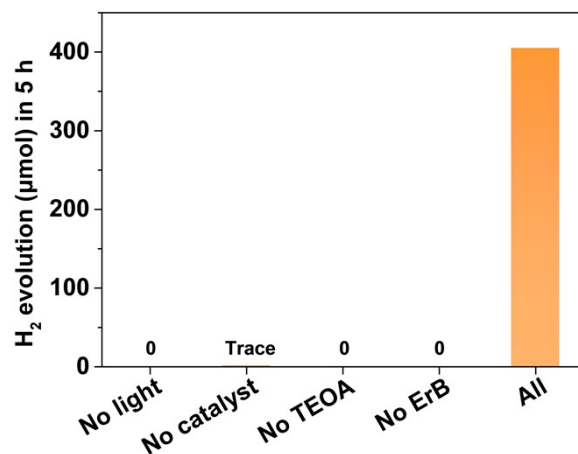


Fig. S6 The results of control experiments. Reaction conditions: light source: white LED lamp, $380\text{ nm} \leq \lambda \leq 780\text{ nm}$; ErB concentration: 2 mM; Fe₂P/CGS: 100 mg; TEOA solution: 25 mL, 10 vol%, pH 8.

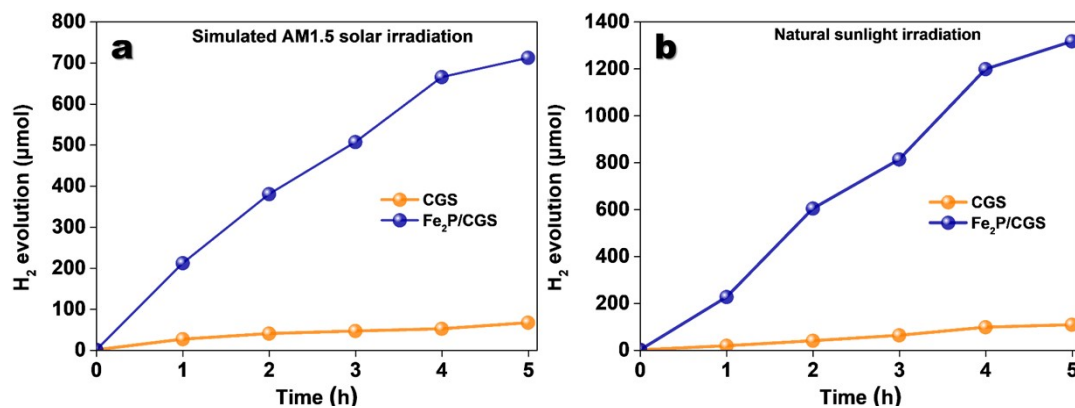


Fig. S7 Time courses of H₂ evolution catalyzed by Fe₂P/CGS from ErB-TEOA under (a) simulated AM1.5 solar light and (b) natural sunlight irradiation. Reaction conditions: ErB: 2 mM; Fe₂P/CGS: 100 mg; TEOA solution: 100 mL, 10 vol%, pH 8.

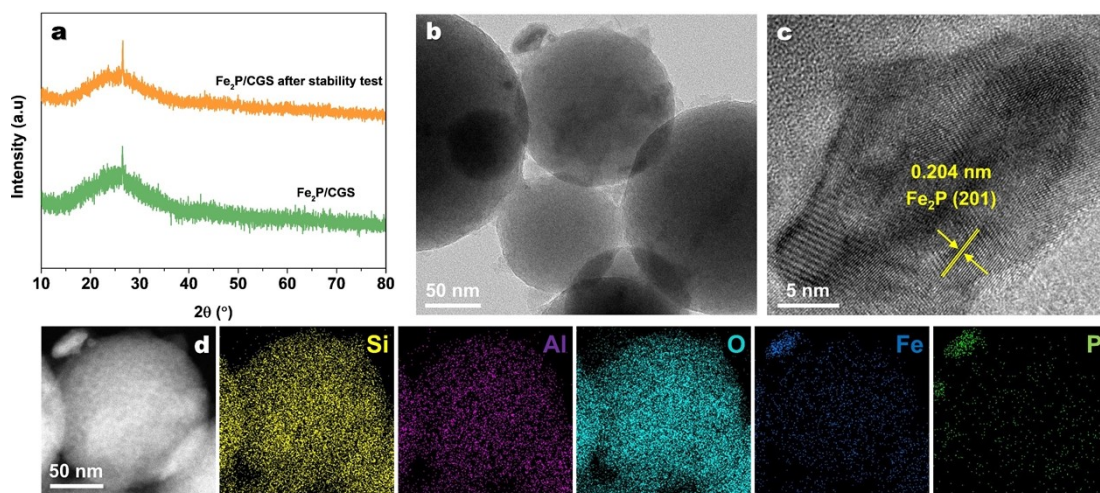


Fig. S8 (a) XRD patterns of Fe₂P/CGS before and after stability test. (b) TEM and (c) HRTEM images of used Fe₂P/CGS. (d) HAADF-STEM image and the corresponding EDX mapping images.

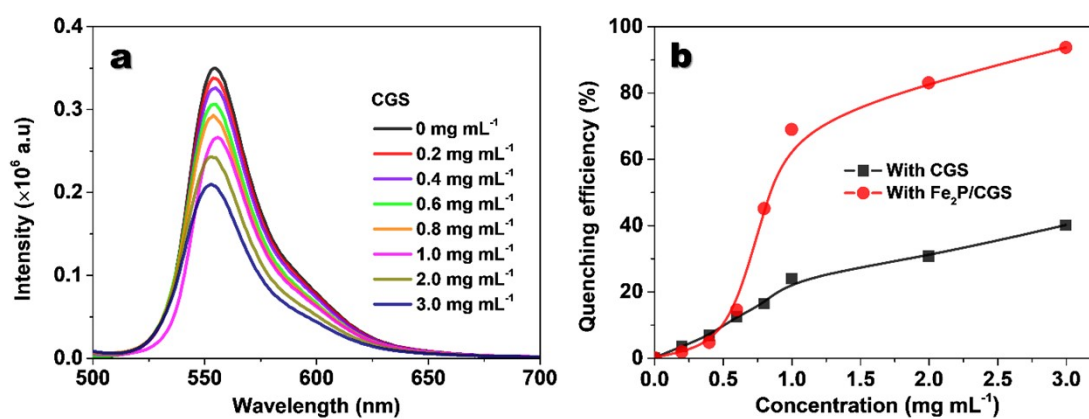


Fig. S9 (a) PL emission quenching of ErB solution (10 mM) with CGS. (b) Comparison of PL quenching efficiency of excited ErB by CGS and Fe₂P/CGS.

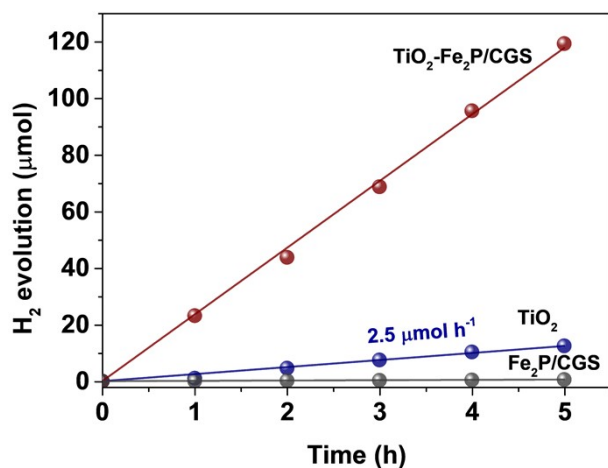


Fig. S10 Time courses of H₂ evolution over Fe₂P/CGS, pristine TiO₂, and TiO₂-Fe₂P/CGS. Reaction conditions: light source: 300-W Xe lamp; TiO₂: 100 mg; Fe₂P/CGS: 5 mg; CH₃OH: 100 mL, 10 vol%.

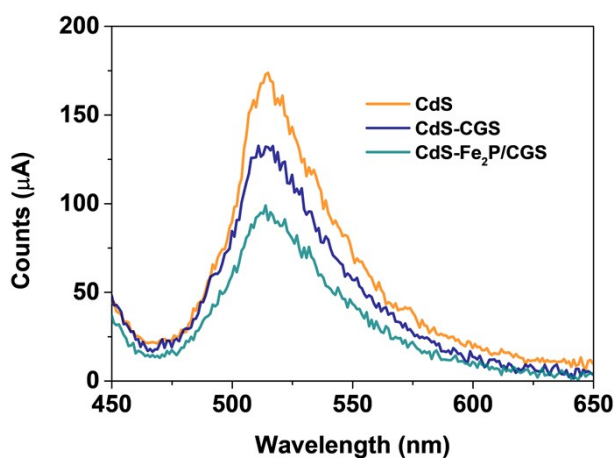


Fig. S11 PL emission spectra of CdS, CdS-CGS, and CdS-Fe₂P/CGS.

References

1. L. Tian, S. X. Min and F. Wang, *Appl. Catal. B: Environ.*, 2019, **259**, 118029.