

Supporting information

1 Experimental

1.1 Materials

Cerium dioxide (CeO₂, Macklin, 99.9%, 50 nm), cadmium chloride hydrate (CdCl₂·2.5H₂O), sublimed sulfur (S), zinc chloride (ZnCl₂), sodium sulfide (Na₂S·9H₂O), diethylenetriamine (DETA), sodium sulfite (Na₂SO₃), sodium sulfate (Na₂SO₄), Nafion, anhydrous ethanol, and distilled water were used in this work.

1.2 Characterization

Characterization techniques used include X-ray diffraction (XRD) on a Bruker D8 Advance, X-ray photoelectron spectroscopy (XPS) with an ESCALab MKII, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) on Hitachi S-8100 and FEI Tecnai G²-20, Fourier-transform infrared spectroscopy (FT-IR) and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) using IR-21 and Shimadzu UV-2450. Photoelectrochemical properties were assessed with a CHI-660D-controlled three-electrode cell. To prepare the working electrode, a slurry was made by mixing 10 mg of the catalyst with 10 μL of 5% Nafion and 0.1 mL of ethyl alcohol, then coated onto an ITO glass of 1.0 cm² in size.

1.3 Equations

The quantum efficiency (QE) was calculated according to equation:

$$QE = \frac{\text{number of evolved hydrogen atoms } (N_H)}{\text{number of incident photons } (N_P)} \times 100\% \quad (1)$$

$$N_P = \frac{A \cdot I}{E} \cdot t = \frac{A \cdot I}{(hc/\lambda)} \cdot t$$

$$N_H = 2 \times n_{H_2} \times L$$

where n_{H_2} is the moles of evolved hydrogen molecular (such as ZCS is 0.417 mmol); L is the Avogadro constant, $6.02 \times 10^{23} \text{ mol}^{-1}$; I is the light intensity at $\lambda=420 \text{ nm}$; $I=1.4 \text{ mW/cm}^2$; A is the illuminate area (here is 28.26 cm^2); E is the photon energy; h is the Plank constant, $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$; c is the light rate, $3 \times 10^8 \text{ m/s}$; $t=10800 \text{ s}$.

The band gap (E_g), valence band (E_{VB}) and conduction band (E_{CB}) of the photocatalysts can be obtained from the following equation:

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \quad (2)$$

$$E_{VB} = X - E^c + 0.5E_g \quad (3)$$

$$E_{CB} = E_{VB} - E_g \quad (4)$$

where α is the absorption coefficient, h represents Planck constant, ν represents light frequency and A is a constant. E^c is a constant with a value of 4.5 eV. The X values of CeO₂ and Cd_{7.23}Zn_{2.77}S₁₀ are 4.99 and 5.21 eV, respectively.

1.4 DFT calculations

We use density functional theory (DFT) to describe plane wave expansion of wave function, pseudopotential description of electron-nucleus interaction and first-principle pseudopotential of electron-electron interaction. We used Cambridge Serial Total Energy Package (CASTEP) in materials studio to calculate. The generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) is used to deal with forward variations and related interactions. A vacuum layer of 20 Å was constructed to eliminate interactions between periodic structures of surface models. Other parameters use default values.

1.5 Electrochemical testing methodology

Photocatalytic and electrochemical evaluations of the samples were conducted using a CH Instruments 660D electrochemical workstation. In this investigation, a 0.1 mol/L ascorbic acid solution was prepared with phosphate-buffered saline (PBS) as the solvent to serve as the electrolyte. A platinum wire was employed as the

counter electrode, Ag/AgCl as the reference electrode, and the synthesized photocatalyst constituted the working electrode. Specifically, the photocatalyst solution was deposited onto indium tin oxide (ITO) conductive glass substrates with a geometric area of 2 cm×1 cm, while the active deposition area of the sample was confined to 1 cm×1 cm. Photocurrent response measurements ($I-t$ curves) were primarily utilized to analyze the separation efficiency of photogenerated electron-hole pairs within the photocatalytic materials. The testing parameters were meticulously set to an initial potential of 0 V, a time interval of 0.1 s, a total testing duration of 350 s, a rest period of 0 s, and a sensitivity of one part per million. Concurrently, a 300 W xenon lamp was employed as the illumination source, irradiating the samples in 50-second intervals per cycle to ascertain the photocurrent density.

Electrochemical impedance spectroscopy (EIS) parameters were configured with an initial potential of 0 V, an amplitude of 5 mV, a high-frequency limit of 10000 Hz, a low-frequency limit of 0.1 Hz, and a relaxation time of 2 s, facilitating the assessment of the photocatalysts' charge transfer characteristics. Mott-Schottky analysis was conducted to elucidate the flat band potential of the photocatalysts, utilizing an electrochemical window ranging from -1 to 1 eV, frequencies of 500 Hz and 1000 Hz, and an alternating current (AC) amplitude of 50 mV. Through these comprehensive electrochemical testing methodologies, we were able to thoroughly evaluate the photocatalysts' performance in terms of photogenerated charge carrier separation, transport, and overall electrochemical properties. This multifaceted assessment provides critical insights for the optimization of photocatalyst structures and the enhancement of their photocatalytic efficacy under environmentally benign conditions.

Table S1 The amounts of chemicals for preparing Cd_{7.23}Zn_{2.77}S₁₀-DETA (ZCS) and 30%-CeO₂/Cd_{7.23}Zn_{2.77}S₁₀-DETA (EO/ZCS)

Sample	CeO ₂ /g	ZnCl ₂ /g	CdCl ₂ ·2.5H ₂ O/g	Sublimed sulfur/g	DETA/mL	H ₂ O/mL
ZCS	0	0.076	0.330	0.064	24	10
EO/ZCS	0.2	0.134	0.586	0.114	24	10

Table S2 The light intensity, H₂ production rates and QE of the photocatalysts

Sample	Light intensity/(mW·cm ⁻²)	H ₂ production rate/(mmol·g ⁻¹ ·h ⁻¹)	QE/%
ZCS	1.4	2.78	0.56
EO/ZCS	1.4	4.11	0.83
EO	1.4	0	0

Table S3 H₂ production rate of Ref. samples and this work

Sample	Light source	H ₂ production rate/(mmol·g ⁻¹ ·h ⁻¹)	Ref.
Cu ₃ BTC ₂ /ZIF-9(Co)/GDY-50	300 W Xe lamp	1.13	25
MnCo ₂ S ₄ /g-C ₃ N ₄	300 W Xe lamp	2.98	28
In ₂ O ₃ /CdSe-DETA	300 W Xe lamp	2.50	39
CuInS ₂ /CeO ₂	300 W Xe lamp	0.23	40
WO _{2.72} /Zn _{0.5} Cd _{0.5} S-DETA	300 W Xe lamp	3.94	41
ZCS	300 W Xe lamp	2.78	This work
EO/WO	300 W Xe lamp	4.11	This work

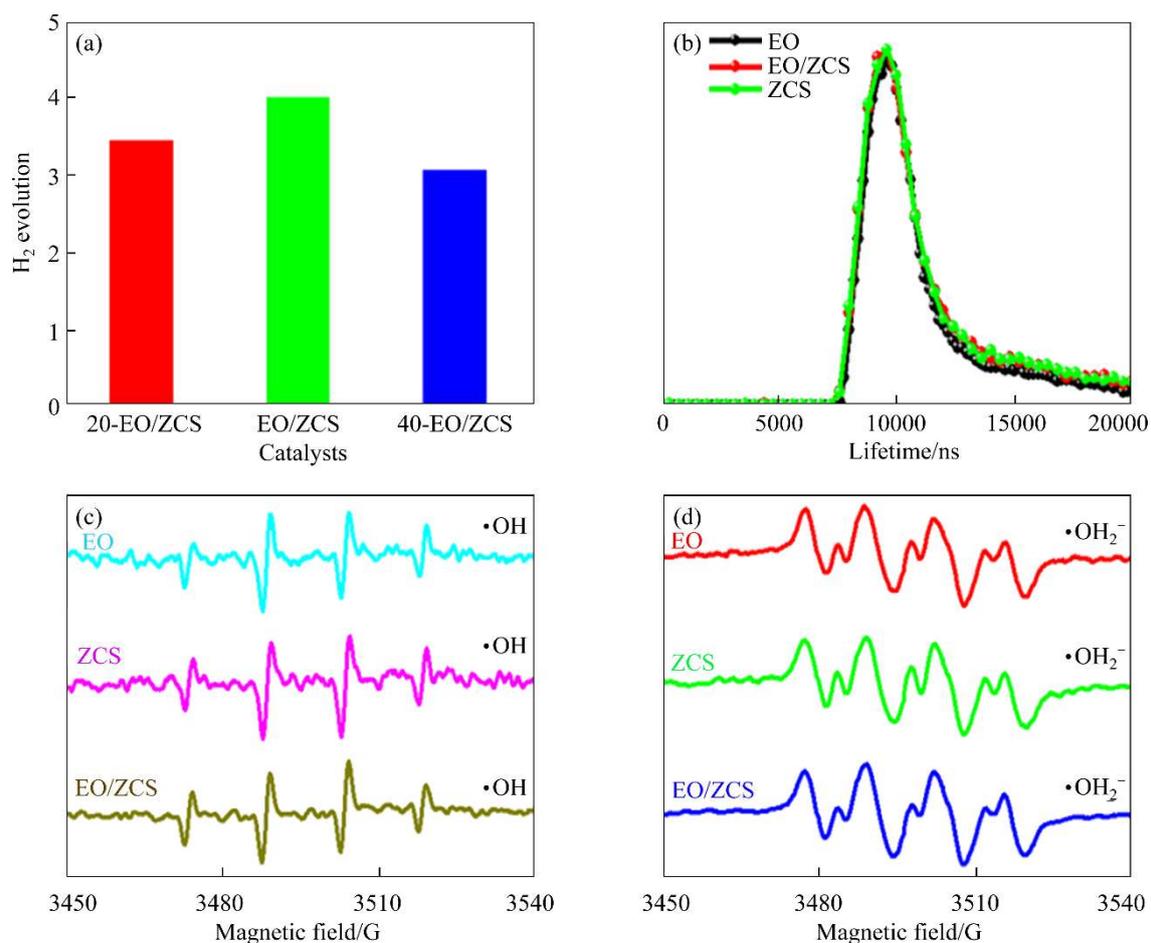


Figure S1 (a) H₂ evolution rates of 20-EO/ZCS, EO/ZCS and 40-EO/ZCS; (b) Photoluminescence decay profiles of EO, EO/ZCS and ZCS; (c) EPR spectra of DMPO-·OH radicals for EO, ZCS and EO/ZCS; (d) EPR spectra of DMPO-·O₂⁻ radicals for EO, ZCS and EO/ZCS