Supporting Information

1. Experimental section

Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2·2H_2O$, ≥99.0%), cadmium acetate dihydrate ($Cd(CH_3COO)_2·2H_2O$, ≥99.9%), ethylenediamine ($C_2H_8N_2$, ≥99%), thioacetamide (TAA, C_2H_5NS, ≥99%), hydrazine hydrate ($N_2H_4·H_2O$, 85 wt%), anhydrous ferric acetate ($Fe(CH_3COO)_3$, reagent grade), thiourea (≥99%), isopropanol (IPA, ≥99.7%), polyvinylpyrrolidone (PVP, K90), and acetone (analytical reagent, ≥99.5%) were used as received. Deionized water was used in all experiments. All chemicals were purchased from commercial suppliers. Hydrazine hydrate was handled in a fume hood with appropriate personal protective equipment.

Catalyst preparation

Preparation of $Zn_{0.4}Cd_{0.6}S$ (ZCS)

In a typical synthesis, 4 mmol of $Zn(CH_3COO)_2·2H_2O$ was dissolved in 25 mL of ethylenediamine and 25 mL of deionized water under magnetic stirring. Then 6 mmol of $Cd(CH_3COO)_2·2H_2O$ was added and the mixture was stirred until homogeneous. After the solution became clear, 13 mmol of thioacetamide (TAA) was introduced and the mixture was stirred for 30 min, giving a light-yellow suspension. The suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclave, sealed and heated at 220 °C for 24 h. After naturally cooling to room temperature, the product was collected by centrifugation (8000 rpm, 3 min), washed several times with deionized water and ethanol, and dried in a vacuum oven at 60 °C for 12 h. The obtained pale-yellow powder was labeled $Zn_{0.4}Cd_{0.6}S$ (ZCS).

Preparation of S_V-$Zn_{0.4}Cd_{0.6}S$ (S_V-ZCS)

100 mg of as-prepared ZCS was dispersed in 20 mL of deionized water and sonicated for 1 h to obtain a uniform suspension. Then 5 mL of hydrazine hydrate ($N_2H_4·H_2O$, 85 wt%) was added dropwise and the mixture was stirred for 30 min at room temperature. The resulting mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave, sealed and heated at 240 °C for 5 h. After natural cooling to room temperature, the product was collected by centrifugation (8000 rpm, 3 min), washed several times with deionized water and ethanol, and dried at 60 °C for 10 h to yield a pale-yellow powder designated S_V-$Zn_{0.4}Cd_{0.6}S$ (S_V-ZCS).

Preparation of Fe-S_V-$Zn_{0.4}Cd_{0.6}S$ (Fe-S_V-ZCS)

Solution A: Dissolve 2 mmol of anhydrous ferric acetate ($Fe(CH_3COO)_3$, reagent grade) and 5 mmol of thiourea in 10 mL deionized water. Sonicate the solution until fully

dissolved and allow it to stand at room temperature overnight to promote complex formation.

Solution B: Disperse 50 mg of S_V-ZCS in a mixed solvent of 15 mL isopropanol and 35 mL deionized water and stir until homogeneous. Under continuous stirring, slowly add Solution A into Solution B. Add 50 mg of polyvinylpyrrolidone (PVP, K90) to the resulting mixture, sonicate for 1 h, then continue stirring at room temperature for an additional 12 h. Collect the solid by centrifugation (8000 rpm, 3 min), wash several times with deionized water and ethanol, and dry at 60 °C for 10 h to obtain a yellowish-brown powder denoted Fe-S_V-$Zn_{0.4}Cd_{0.6}S$ (Fe-S_V-ZCS). A control sample prepared by the same procedure but without adding $Fe(CH_3COO)_3$ is labeled S-S_V-ZCS.

Photocatalytic Conversion Experiment of Cyclohexene

Photocatalytic Reaction Process

In a typical run, 5 mg of catalyst was added to a glass reaction tube. Acetone (3 mL) was used as solvent, and cyclohexene (0.15 mmol) was introduced by micro syringe; 0.10 mL of deionized water was also added. The suspension was sonicated for 5 min before light irradiation to ensure uniform dispersion. Prior to irradiation, the reaction tube was purged with oxygen by five evacuation–refill cycles using an O_2 balloon; the tube was then sealed with Parafilm for irradiation and stirring was maintained during the process. The suspension was irradiated from the front with a 405 nm LED lamp (30 W) positioned at a distance of 10 cm from the sample. Unless otherwise specified, all reactions were performed at room temperature (~25 °C).

Inert atmosphere photocatalysis

For the argon (Ar) experiment, the reactor was subjected to five vacuum-inflation cycles using an argon-filled balloon before exposure to light, in order to eliminate the air within the reactor. All other procedures and conditions were identical to those in the experiment conducted under an oxygen atmosphere.

Extraction procedure for cyclohexene and its oxidation products

The extraction process was carried out as follows: After completion of the reaction, 2 mL of reaction mixture was transferred from each reaction tube using a pipette into a centrifuge tube. An appropriate amount of $CaCO_3$ and Na_2SO_4 powder was then added to remove the water. The mixture was centrifuged at 8000 rpm for 3 minutes. Subsequently, 1 mL of the resulting supernatant was carefully aspirated using a pipette and transferred into an injection vial for subsequent analysis via gas chromatography.

GC analysis

Quantitative analysis was performed by GC-FID (column: RB-WAX, 30 m * 0.32 mm * 0.5 μm). Typical GC conditions: injector temperature 200 °C, FID temperature 220 °C, carrier

gas Ar at 1.5 mL·min^{-1}, split ratio 20:1, injection volume 0.4 μL. Oven program example: 80 °C (2 min) → ramp 10 °C·min^{-1} to 200 °C, hold 3 min. Calibration curves for cyclohexene and each product (cyclohexene oxide, 2-Cyclohexen-1-ol, 2-Cyclohexen-1-one) were prepared using authentic standards and the selected internal standard; all concentrations were determined from the calibration plots (Fig. S1–S3).

Data processing and definitions

Conversion (%) and selectivity (%) were calculated as:

$$\text{Conversion (\%)} = \frac{n_{initial\ substrate} - n_{remaining\ substrate}}{n_{initial\ substrate}} * 100\%$$

$$\text{Selectivity to product } i \text{ (\%)} = \frac{n_{product\ i}}{\sum n_{all\ products\ formed}} * 100\%$$

Where mole numbers n are obtained from GC quantification using the internal standard and calibration curves.

2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser diffractometer using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA. Data were collected in the 2θ range of 10–80° with a step size of 0.02° and a scan speed of 2°·min^{-1}. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7001F field-emission SEM at an accelerating voltage of 15 kV; secondary-electron (SE) images were mainly used and backscattered-electron (BSE) images were taken when compositional contrast was needed. Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental maps were acquired on a JEOL JEM-2100 transmission electron microscope operated at 200 kV. Mapping was performed with a probe current of ~0.8 nA and a dwell time of ~5 μs per pixel. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha instrument with Al Kα radiation (hv = 1486.6 eV). Survey spectra were recorded with a pass energy of 150 eV and high-resolution spectra with a pass energy of 20 eV. All binding energies were calibrated by referencing the C 1s peak to 284.80 eV. XPS data were processed using Avantage with a Shirley background and Gaussian-Lorentzian peak shapes for fitting. Diffuse reflectance UV-Vis spectra (DRS) were measured on a Shimadzu UV-2550 spectrometer equipped with an integrating sphere; $BaSO_4$ was used as the reference. The reflectance data were converted to the Kubelka-Munk function for band-gap estimation. Photoluminescence (PL) spectra were collected on a JASCO FP-6500 fluorescence spectrophotometer using an excitation wavelength of 325 nm and slit widths of 5 nm for both excitation and emission.

Photoelectrochemical measurements were carried out on a CHI660B potentiostat in a conventional three-electrode configuration with a Pt plate counter electrode and an Ag/AgCl (saturated KCl) reference electrode. Working electrodes were prepared by drop-casting a catalyst suspension (5 mg catalyst in 1 mL ethanol) onto fluorine-doped tin oxide (FTO) glass (active area = 1.0 cm^2) and drying at 60 °C; the resulting catalyst loading was approximately 5 $mg \cdot cm^{-2}$. Transient photocurrent responses were recorded under chopped AM1.5G-simulated illumination (300 W Xe lamp with AM1.5G filter, 100 $mW \cdot cm^{-2}$) using 10 s on / 10 s off cycles at 0 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potential with an AC amplitude of 10 mV over the frequency range 100 kHz–0.1 Hz in 0.1 M Na_2SO_4.

In this work, the Nernst equation is used to convert the saturated Ag/AgCl electrode potential to the reversible hydrogen electrode (RHE). The conversion formula is shown in Eq. (1)

$$V_{RHE} = E_{Ag/Agcl} + 0.059 * pH + 0.197\#\ (1)$$

Mott–Schottky measurements were performed in the dark at 600 Hz on FTO-supported films (geometric area A =1.76 cm^2). The areal form of the Mott–Schottky relation was used to extract apparent donor densities N_D. The plotting formula is shown in Eq. (2)

$$\frac{1}{C'^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_D}\left(V - V_{fb} - \frac{kT}{e}\right)\#(2)$$

where C' is the space-charge capacitance per unit area ($F \cdot cm^{-2}$), ε_0 is the vacuum permittivity, ε_r the relative permittivity of the semiconductor, and other symbols have their usual meanings. We estimated ε_r($Zn_{0.4}Cd_{0.6}S$) ≈8.6 by linear interpolation between reported static permittivities of ZnS (≈8.2) and CdS (≈8.9). Using this ε_r and the fitted MS slopes yields apparent donor densities of ≈6.66×10^{20} cm^{-3} for S_V-ZCS and ≈4.25×10^{20} cm^{-3} for Fe-S_V-ZCS. These values are reported as **apparent** N_D because Mott–Schottky analysis can be affected by surface states, film porosity, frequency choice and non-ideal capacitive contributions.

$$AQE\ (\%) = \frac{N_{reacted\ electrons}}{N_{incident\ photons}} \times 100 = \frac{n_{product} \times e^{-}\ per\ product}{N_{photons}} \times 100$$

TRPL decay curves were fitted using a bi-exponential mode, and average lifetimes (τ_{ave}) were calculated using the formula below.

$$\tau_{\mathrm{ave}} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

3. Supplementary figures

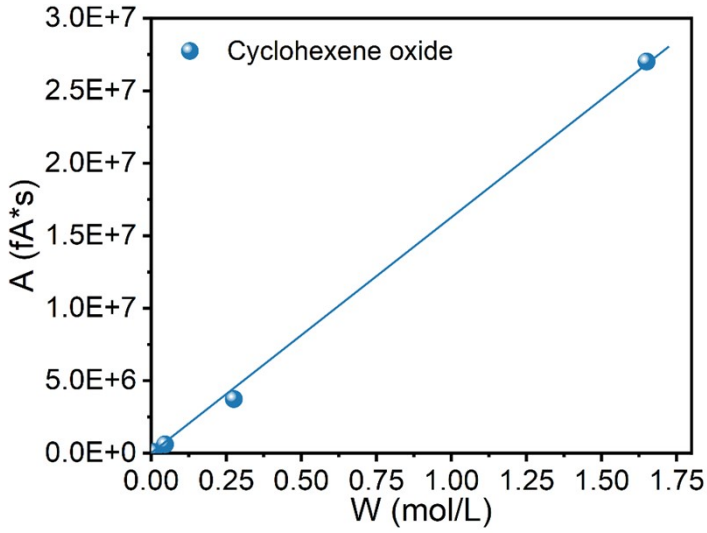

Figure S1. Calibration image of cyclohexene oxide. *A* curve equation: *A* = -224425.062500 + 16453983 * *W*, correlation coefficient: 0.99924.

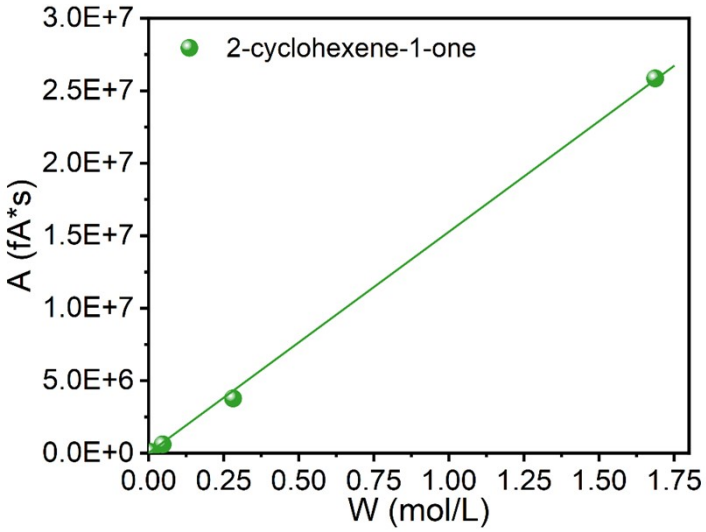

Figure S2. Calibration image of 2-cyclohexene-1-one. *A* curve equation: *A* = -157081.140625 + 15381781 * *W*, correlation coefficient: 0.99961.

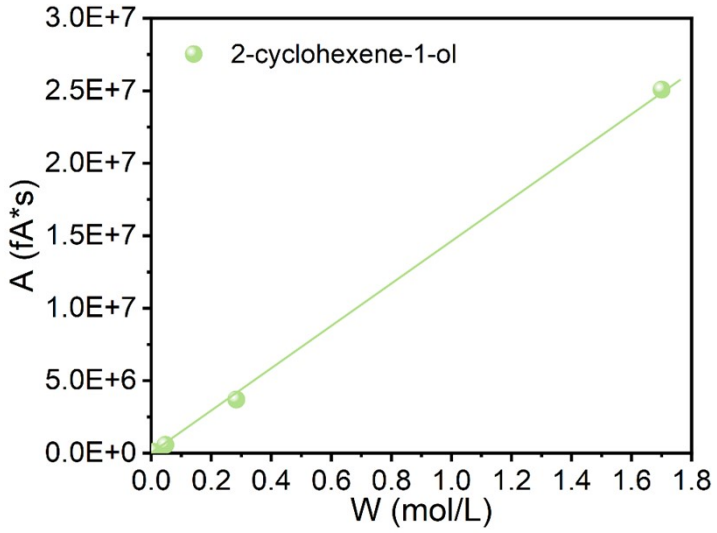

Figure S3. Calibration image of 2-cyclohexene-1-ol. *A* curve equation: *A* = -147241.093750 + 11811155 * *W*, correlation coefficient: 0.99967.

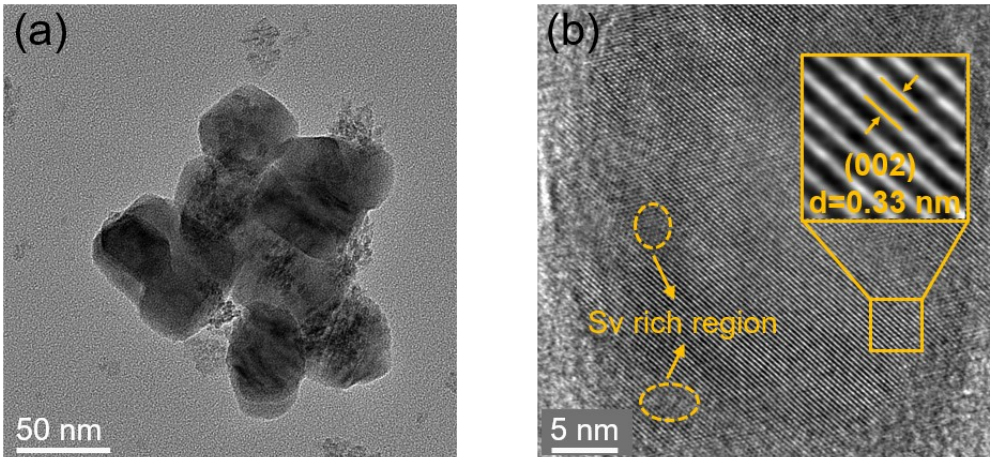

Figure S4. (a) TEM image and (b) HRTEM image of Fe-S_V-ZCS.

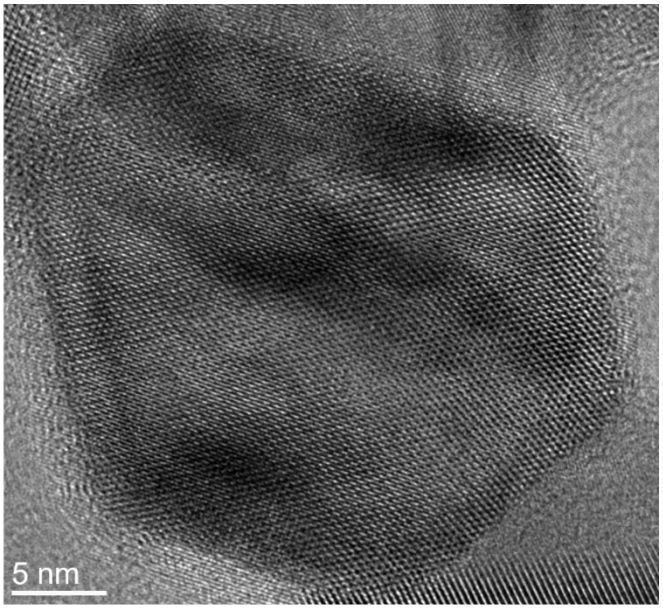

Figure S5. TEM image of S_V-ZCS.

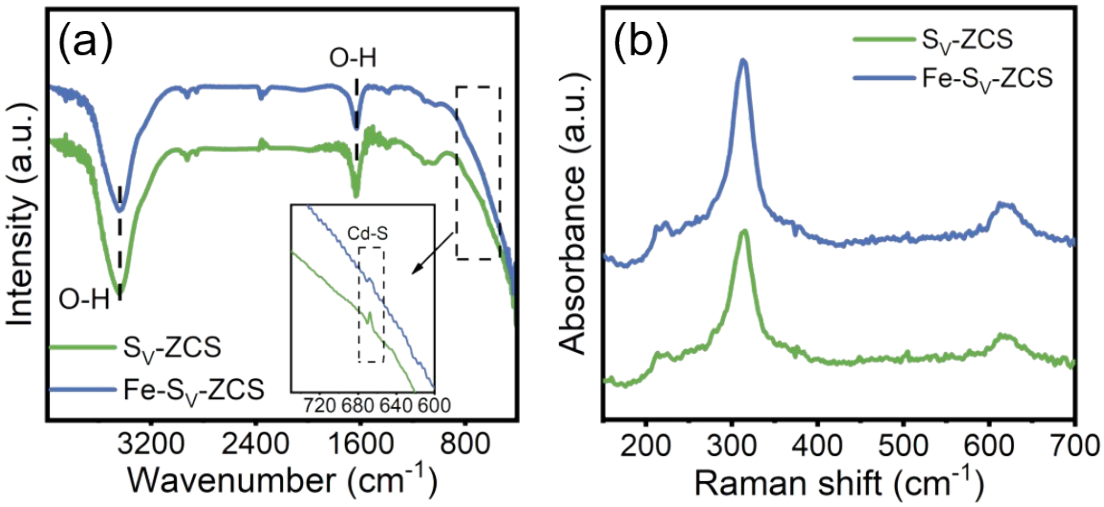

Figure S6. (a) FT-IR spectra and (b) Raman spectra of S_V-ZCS and Fe-S_V-ZCS.

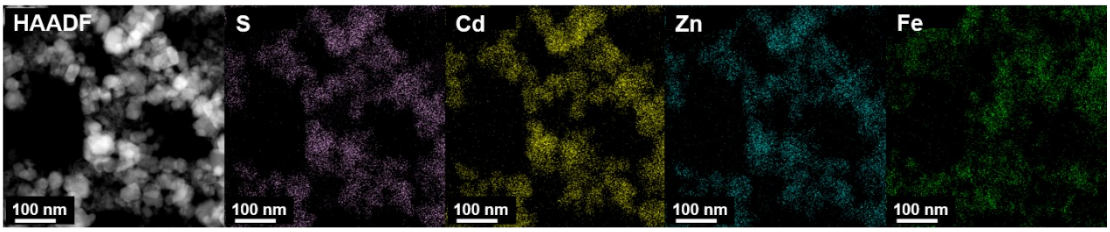

Figure S7. HAADF-STEM image and corresponding EDS elemental maps of Fe-S_V-ZCS.

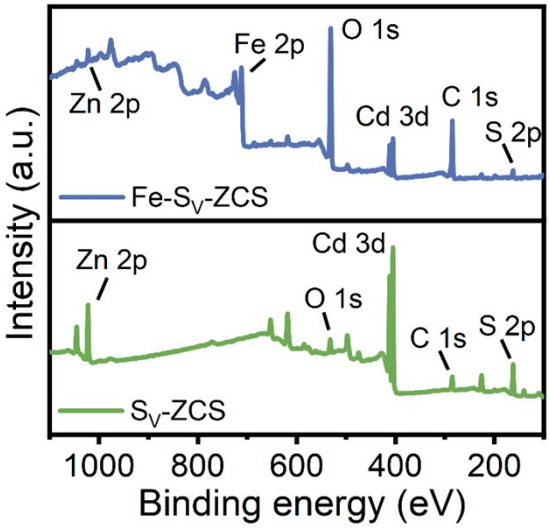

Figure S8. Survey spectrum of Fe-S$_V$-ZCS.

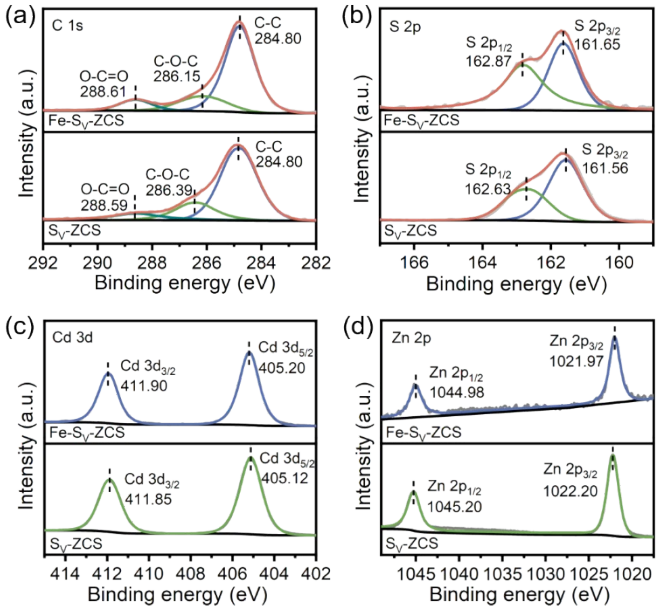

Figure S9. (a–d) High-resolution C 1s, S 2p, Cd 3d and Zn 2p spectra comparing S$_V$-ZCS and Fe-S$_V$-ZCS.

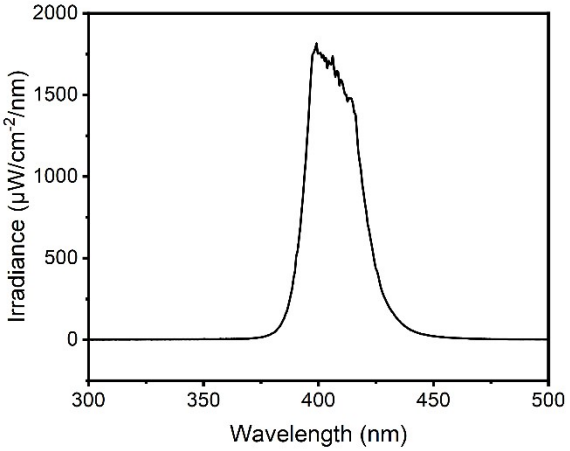

Figure S10. The irradiance spectrum of 30 W 405 nm LED light source.

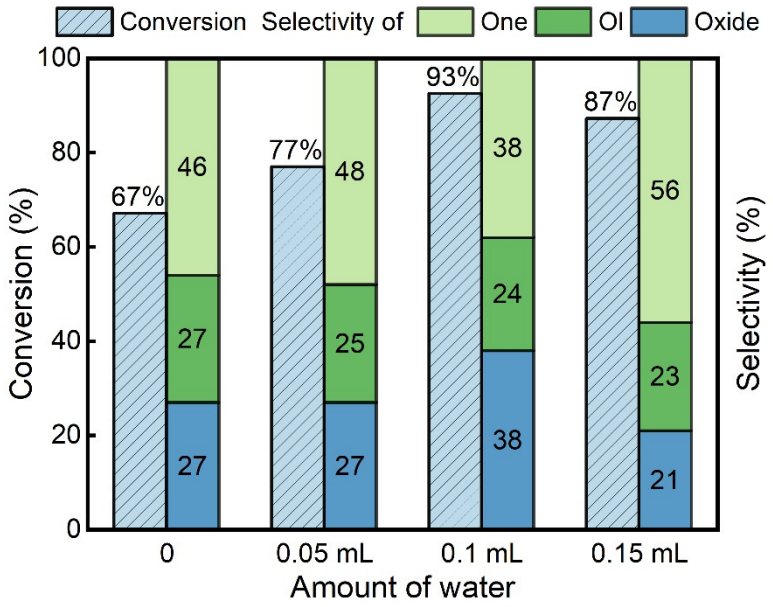

Figure S11. Performance and selectivity affected by the amount of deionized water added.

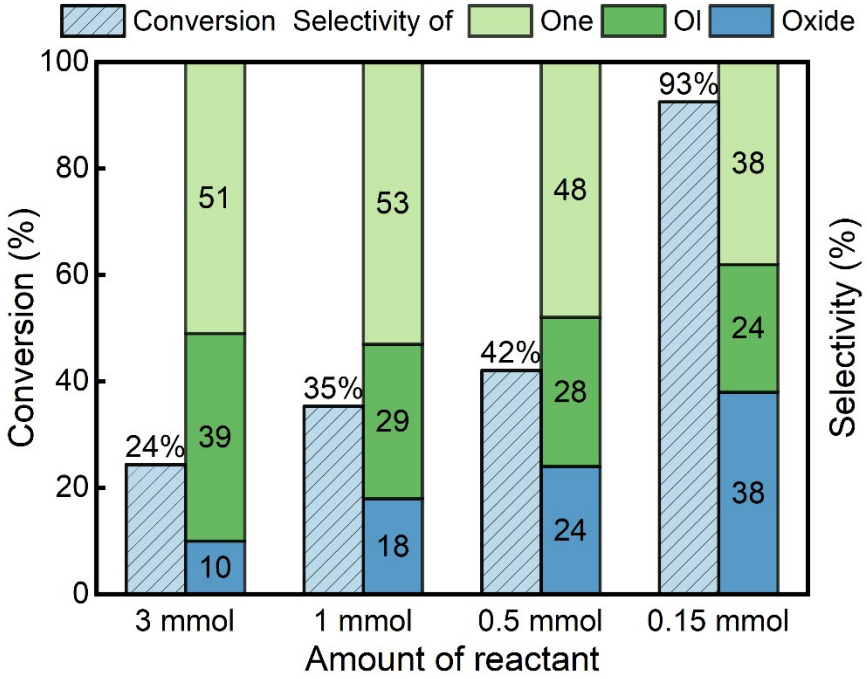

Figure S12. Effect of substrate loading.

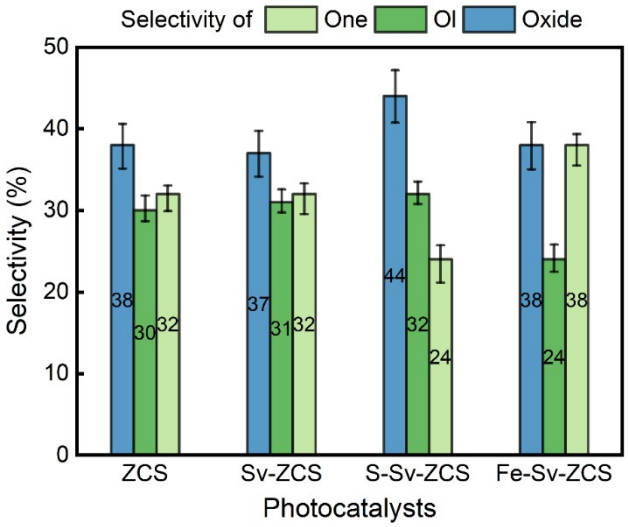

Figure S13. Catalytic selectivity performance of ZCS, S_V-ZCS, S-S_V-ZCS, and Fe-S_V-ZCS. Data are presented as mean ± standard deviation (error bars) from three independent experiments (n = 3).

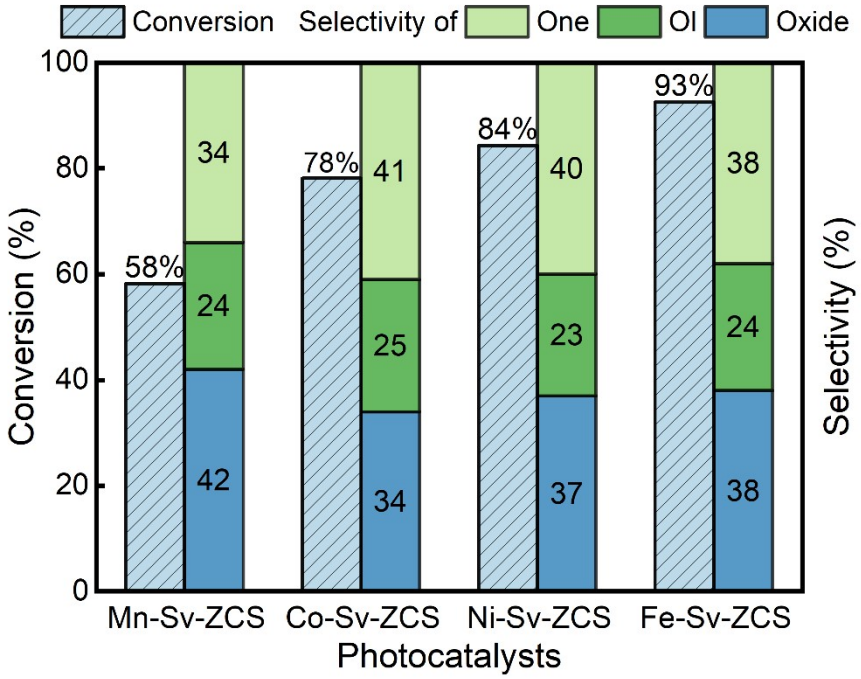

Figure S14. Performance of Mn-, Co-, Ni-, and Fe-loaded samples.

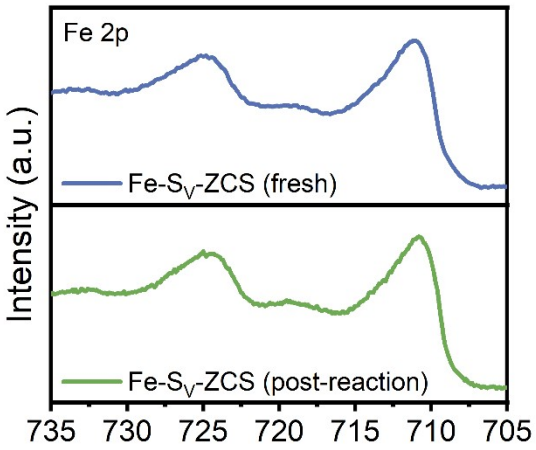

Figure S15. Fe 2p XPS spectra of the catalyst before and after reaction.

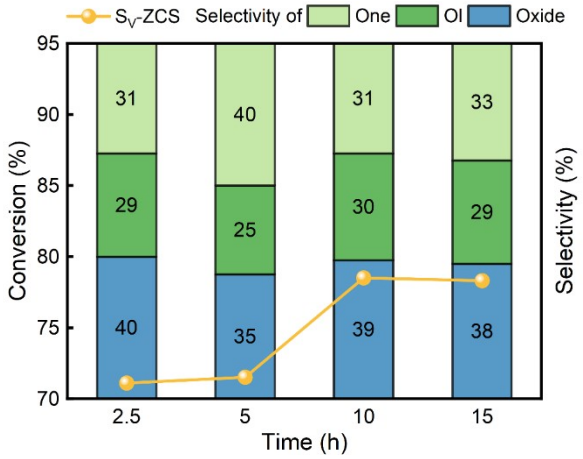

Figure S16. Time-dependent conversion and selectivity of S$_V$-ZCS.

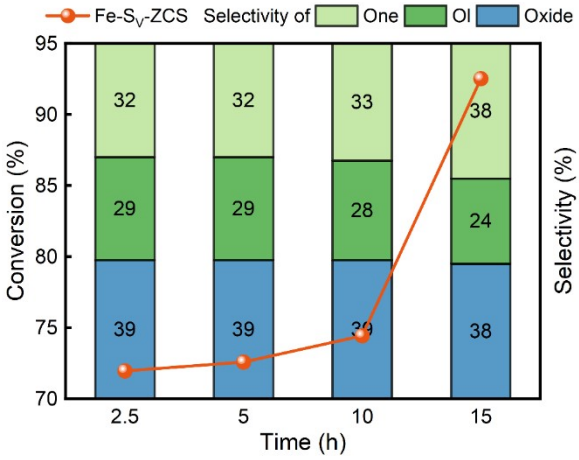

Figure S17. Time-dependent conversion and selectivity of Fe-S$_V$-ZCS.

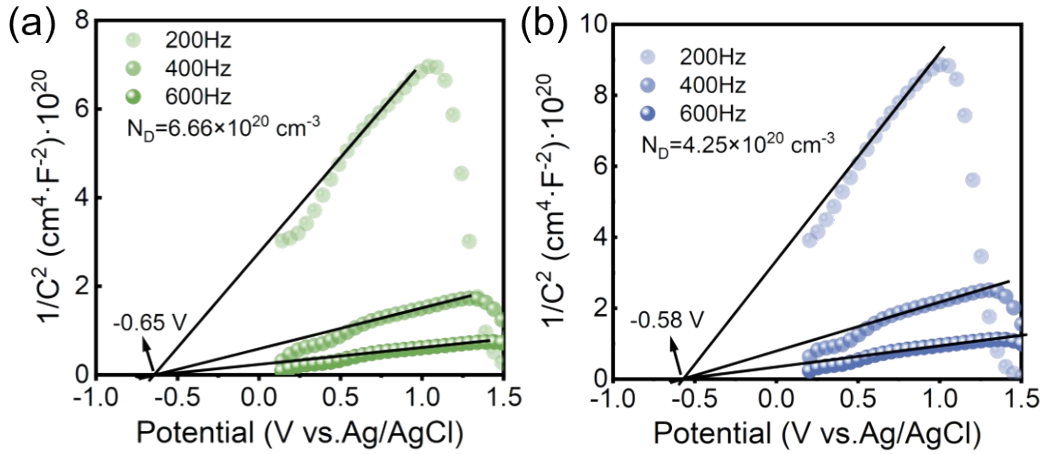

Figure S18. (a) Mott–Schottky plot of S_V-ZCS. (b) Mott–Schottky plot of Fe-S_V-ZCS.

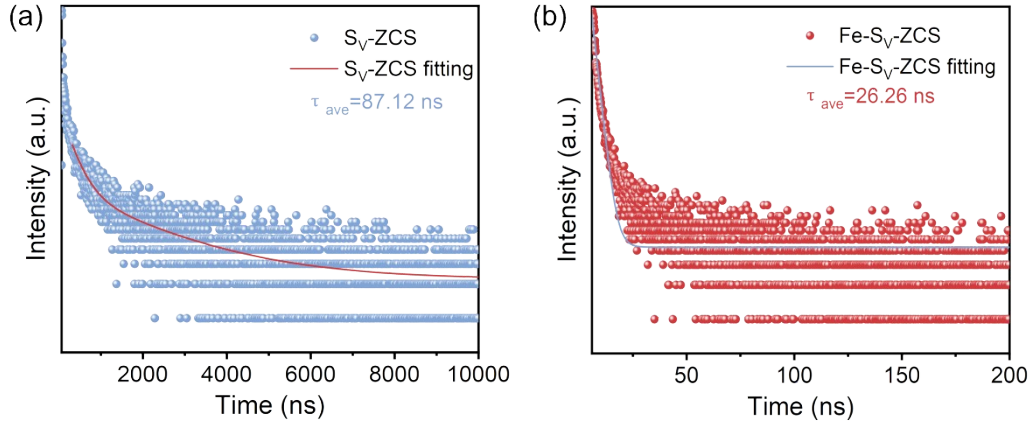

Figure S19. Time-resolved photoluminescence decay curves for (a) S_V-ZCS and (b) Fe-S_V-ZCS. The fitted average lifetimes are τ_{ave} ≈ 87.12 ns (S_V-ZCS) and τ_{ave} ≈ 26.26 ns (Fe-S_V-ZCS).

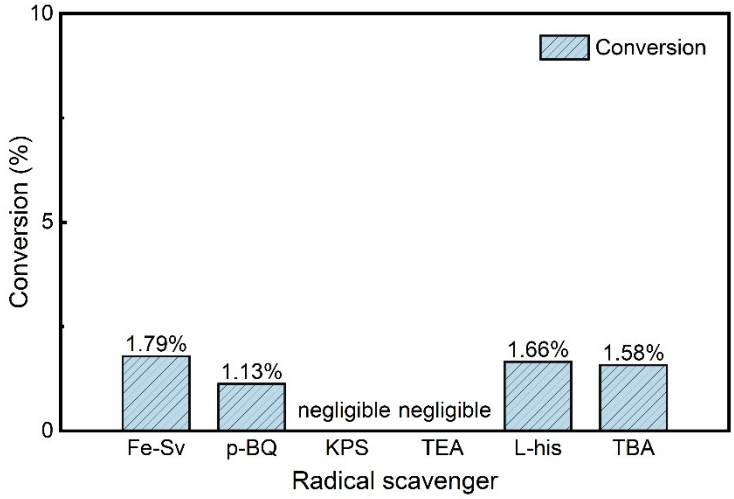

Figure S20. Photocatalytic performance of Fe-S_V-ZCS in the dark: blank experiment and tests in the presence of p-BQ, KPS, TEA, L-His and TBA.

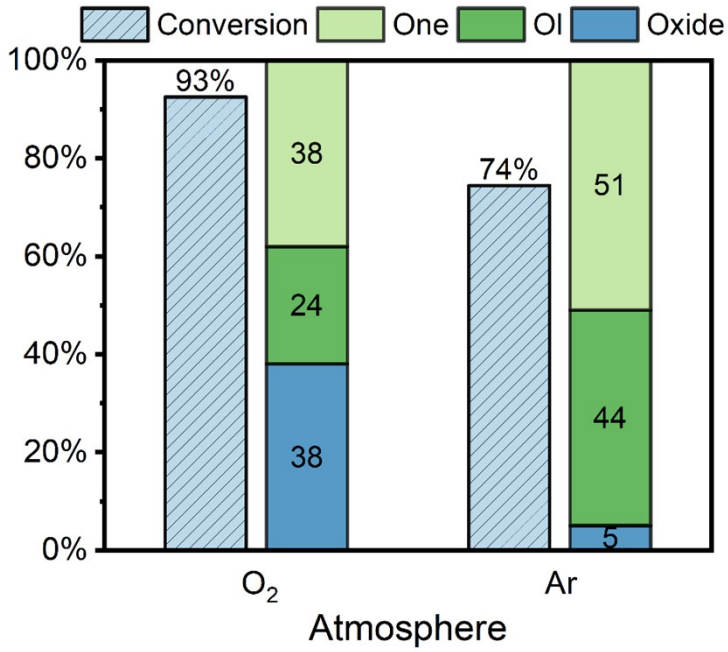

Figure S21. Atmosphere-dependent conversion and selectivity of Fe-S_V-ZCS.

4. Supplementary table

Table S1. Bulk Fe content in the samples determined by ICP-OES. Fe-S_V-ZCS: 29.34 ± 0.45 wt%.

Number	Quality m_0 (g)	Elements tested	Element content C_X (mg/kg)	Element content W (%)	Average element content W_0 (%)
1	0.0517	Fe	297630.56	29.76	
2	0.0517	Fe	288684.72	28.87	29.34
3	0.0517	Fe	294003.87	29.40	

Table S2. Fe concentration in the reaction supernatant determined by ICP-MS (n = 3).

Sample number	Sample volume V (mL)	Constant volume V_0 (mL)	Element concentration of solution C_0 (μg/L)	Element concentration of digestion solution C_1 (μg/L)	Element content of sample C_X (μg/L)	Average element content C (μg/L)
1	5.000	25	196.1430	196.1430	980.7148	
2	5.000	25	195.5525	195.5525	977.7627	988.3553
3	5.000	25	201.3177	201.3177	1006.5885	

Table S3. Raw data on the catalytic performance of ZCS, S_V-ZCS, S-S_V-ZCS, and Fe-S_V-ZCS

Photocatalyst	Number of tests	Conversion (%)	Average Conversion (%)	Cyclohexene oxide (%)	Average selectivity (%)	2-cyclohexene-1-ol (%)	Average selectivity (%)	2-cyclohexene-1-one (%)	Average selectivity (%)
ZCS	1	66.21	70.26	35.28	38.15	32.05	30.23	32.67	31.62
	2	71.28		38.42		28.91		32.67	
	3	73.29		40.75		29.73		29.52	
S_V-ZCS	1	78.52	81.04	34.38	37.24	32.64	31.08	32.98	31.68
	2	81.29		37.36		29.82		32.82	
	3	83.31		39.98		30.78		29.24	
S-S_V-ZCS	1	50.12	53.46	40.85	44.11	33.42	31.88	25.73	24.01
	2	54.89		44.20		30.67		25.13	
	3	55.37		47.28		31.55		21.17	
Fe-S_V-ZCS	1	91.04	92.52	34.72	37.69	26.11	24.30	39.17	38.01
	2	93.07		37.85		22.79		39.36	
	3	93.45		40.50		24.00		35.50	