

Electronic Supplementary Information

Material synthesis

Synthesis of ZIF-67 polyhedrons: In a typical synthesis, two solutions were prepared by dissolving 291 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 328 mg of 2-methylimidazole in 30 mL of methanol, respectively. Afterward, the two solutions were mixed rapidly and aged for 24 h at room temperature. The produced ZIF-67 precipitate was washed with ethanol 4 times and then dispersed in 20 mL of ethanol for further use.

Synthesis of dodecahedral Co_9S_8 cages: 10 mL of the obtained ZIF-67 mixture was added into 10 mL of an ethanol solution containing 100 mg of thioacetamide, and stirred for 2 min. Then, the resultant mixture was transferred into a Teflon-lined autoclave (40 mL in capacity) and maintained at a preheated oven at 180 °C for 3 h. After cooling down to room temperature, the precipitate was collected by centrifugation (3000 rpm, 5 min) with ethanol several times and dried at 60 °C, yielding the cobalt sulfide CoS_x cages.

Synthesis of dodecahedral Co_9S_8 cages: The Co_9S_8 dodecahedral cages were produced by heating the CoS_x material in an argon flow at 600 °C for 2 h with a heating rate of 5 °C min⁻¹.

Materials characterization

X-ray diffraction (XRD) characterizations were carried out to study the crystal phases of materials on a Bruker D8 Advance X-ray instrument (Cu $K_{\alpha 1}$ radiation, $\lambda=1.5406 \text{ \AA}$)

with the voltage and current of 40 kV and 40 mA, respectively. Field-emission scanning electron microscope (FESEM; JEOL JSM 6700) and transmission electron microscope (TEM; JEOL, JEM-2010) were employed to investigate the morphologies and microstructures of samples. The compositions of samples were determined by an energy-dispersive X-ray spectroscopy (EDX) attached to the field-emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) tests were carried out on a PHI Quantum 2000 XPS system with C 1s binding energy (284.6 eV) as the reference and He I excitation energy (21.22 eV) as the monochromatic light source. N₂ adsorption-desorption isotherms were obtained on a Micromeritics ASAP2020 under liquid nitrogen temperature (77 K). UV-vis diffuse reflectance spectra (DRS) were captured using a Varian Cary 500 UV-vis spectrometer with BaSO₄ as a reference. The photoluminescence (PL) measurements were executed on a Hitachi F-7000 spectrophotometer at room temperature. The thermo analysis was conducted by NETZSCH STA-449F3 thermoanalyzer with a heating rate of 5 °C/min under a nitrogen atmosphere. The electrochemical tests were carried out on Metrohm Autolab Electrochemical System, using a conventional three electrodes cell with Pt electrode and Ag/AgCl electrode as the counter electrode and reference electrode, respectively. Typically, 5 mg of the sample was dispersed in N, N-dimethylformamide (1 mL) by sonication to obtain a mixture. Then, the mixture was spread on the FTO glass with an area of ca. 0.25 cm² and dried at room temperature in the air. The transient photocurrent response spectra were conducted in Na₂SO₄ aqueous solution (0.2 M) with a 300 W xenon lamp ($\lambda \geq 420$ nm) as the light source.

Photocatalytic CO₂ reduction

The photocatalytic CO₂ reduction reaction was conducted in a 80 mL reactor containing 1 mg of Co₉S₈ as the cocatalyst, 8 mg of Ru(bpy)₃Cl₂•6H₂O as the photosensitizer (abbreviated as **Ru**, bpy = 2'2-bipyridine), 1 mL of triethanolamine (TEOA) as the electron donor, 2 mL of water and 3 mL of acetonitrile as the reaction solvents. Before initiating the reaction, the air in the reaction of removed completely by flowing high-purity CO₂ gas, and finally, the reactor was filled by the CO₂ gas with a partial pressure of 1 atm. The reaction temperature was kept at 30 °C controlled by a circulating condensed water system. A 300 W Xe lamp with a 420 nm cut-off filter was used to provide the simulated sunlight irradiation to drive the CO₂ reduction reaction. During the reaction, the reaction mixture was vigorously stirred by a magnetic stirrer. After the reaction, the gas products were extracted from the reactor and analyzed by an Agilent 7820 A gas chromatograph (GC). The liquid products (CH₃OH, CH₂O and CH₃CH₂OH) were determined by gas chromatography-mass spectrometer (GC-MS, HP-5973, Agilent) with a HP-5 capillary column, high performance liquid chromatography (HPLC, Waters) and nuclear magnetic resonance spectrometer (NMR, JNM-ECZ600R). The formic acid product was detected by an ion chromatography (IC, Dionex Aquion, Thermo Scientific). After the photocatalytic reaction, the heterogeneous Co₉S₈ catalyst was separated from the reaction mixture by filtration, then washed by acetonitrile and finally re-dispersed into a fresh reaction mixture for next activity test.

Computational methods

All structure optimizations were performed via spin-polarized DFT using the Vienna ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method.¹⁻³ The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) was used to describe exchange-correlation energy.⁴ The Co₉S₈(311) surface was constructed using a (1 × 2) unit cell with a vacuum space of 15 Å to avoid electronic interactions between vertically neighboring cells. A cutoff energy of 500 eV was utilized to expansion the wave functions, and Brillouin zone was sampled with a 1 × 1 × 1 Monkhorst-Pack mesh of k points.⁵ The convergence criterions of force and energy are set to be 0.03 eV/Å and 1×10⁻⁵ eV/atom, respectively. A DFT-D2 empirical correction was adopted to describe the dispersion interaction.⁶ Furthermore, dipole correction was used to correct for potential spurious terms caused by the asymmetry of the slabs.⁷ The implicit solvation model in VASPsol was carried out to deal with solvation effect.⁸

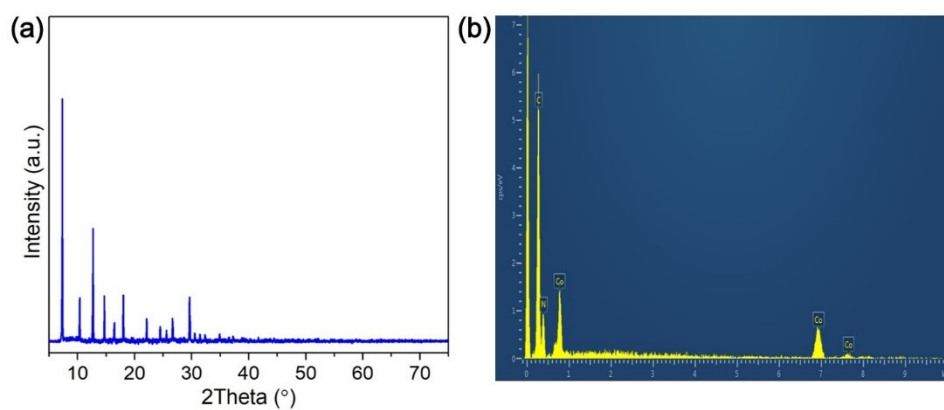


Fig. S1 (a) XRD pattern and (b) EDX spectrum of ZIF-67 precursor.

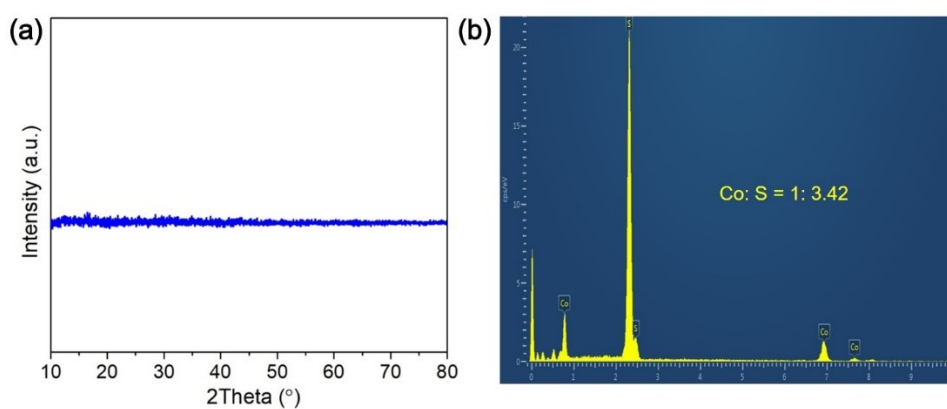


Fig. S2 (a) XRD pattern and (b) EDX spectrum of CoS_x cages.

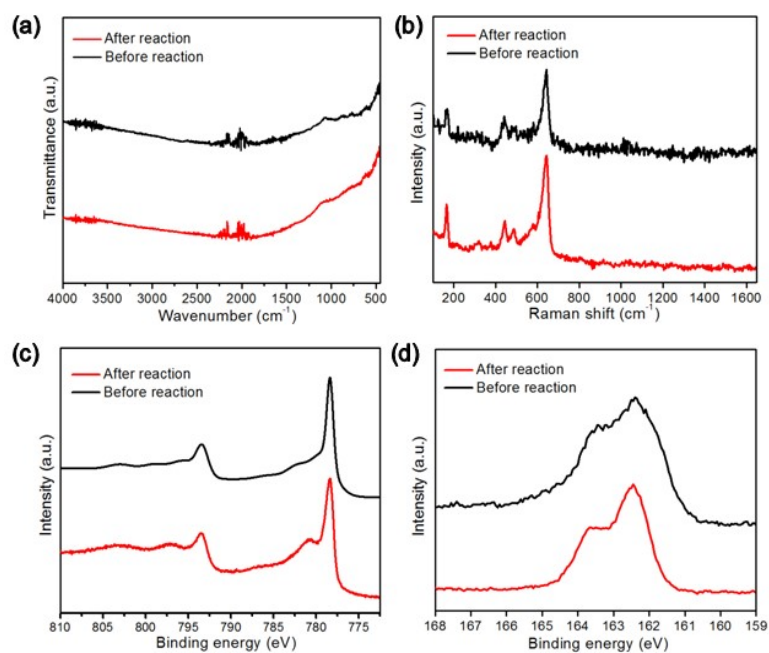


Fig. S3 (a) FT-IR, (b) Raman, (c) Co 2p XPS spectrum and (d) S 2p XPS spectrum of Co_9S_8 cocatalyst before and after CO_2 reduction reactions.

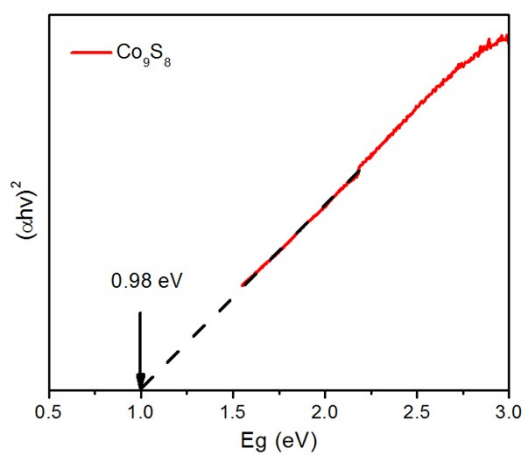


Fig. S4 Tauc curve of Co_9S_8 .

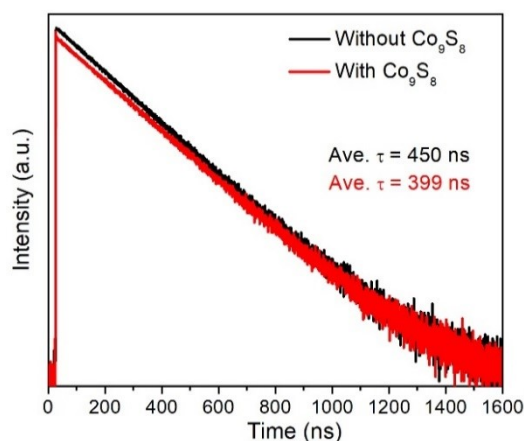


Fig. S5 The time-resolved PL (TRPL) spectra of the reaction mixtures with and without the Co_9S_8 cocatalyst.

References

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