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Electronic Supplementary Information

A Stable ZnCo_2O_4 Cocatalyst for Photocatalytic CO_2 Reduction

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Experimental section

Materials synthesis

All the chemical reagents were analytical grade, purchased from Aladdin Chemical Company, and used as received without any further purification.

In the typical synthesis of ZnCo_2O_4 nanorods, 2 mmol zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, 4 mmol cobalt nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, 4 mmol ammonium fluoride (NH_4F), and 10 mmol urea $[\text{CO}(\text{NH}_2)_2]$ were added to 70 ml distilled water and the mixture was stirred intensely for 1 h to form a homogeneous solution. Then, the solution was transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and heated at 120 °C. After for 5 h, the autoclave cooled down to room temperature naturally. The product was collected, washed by distilled water for several time to remove the unreacted ions, and dried at 60 °C in an oven for 12h. At last, the sample was thermal treated at 400 °C for 2 h with a ramping rate of 2 °C min⁻¹.

Materials characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance instrument (Cu K α 1 irradiation, $\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and the applied current were 40 KV and 40 mA, respectively. Data were recorded at a scanning rate of 0.02° 2 θ s⁻¹ in the 2 θ region of 15–80°. Hitachi New Generation SU8010 field emission scanning electron microscope (SEM) was employed to obtain the SEM images, energy dispersive X-ray (EDX) spectrum, and the corresponding EDX elemental mappings of the samples. Transmission electron microscopy (TEM) measurements were conducted using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV with the sample supported on a copper

grid. X-ray photoelectron spectroscopy (XPS) characterization was carried out on a PHI Quantum 2000 XPS system with a monochromatic Al K α source and a charge neutralizer. The X-ray photoelectron spectra of all of the elements were referenced to the C 1s peak arising from adventitious carbon (its binding energy was set at 284.6 eV). Specific surface area were computed from the results of N₂ physisorption at 77 K (Micromeritics ASAP 2020) by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. UV-vis diffuse reflectance spectra (DRS) spectra were obtained on a Varian Cary 500 UV-vis-NIR spectrophotometer. BaSO₄ was used as a reflectance standard. The absorbance spectrum of the Ru-dye solution was recorded by a Varian Cary 50 UV-vis spectrophotometer. Inductively coupled plasma mass spectrometry (ICP-MS, XSeries II Thermo Scientific) was used to analyse the supernatant of the reaction mixture.

Mott-Schottky measurement was performed on a Zenuium electrochemical workstation (Zahner Co.). The measurement was performed in a conventional three electrodes cell using Pt plate and Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The working electrode was prepared on an FTO glass: 3 mg of the powder ZnCo₂O₄ sample was mixed with 1.0 mL of ethanol with sonication for 30 min to get slurry. Then, 20 μ L of the slurry was spreading onto FTO glass whose side part was previously protected by Scotch tape, and then the electrode was air dried for 24h. For Mott-Schottky experiment, the potential ranged from - 0.4 to 0.1 V (vs. Ag/AgCl), and the frequency were 0.5, 1.0, and 1.5 kHz. Prior to all measurements, the electrolyte (0.2 M Na₂SO₄ aqueous solution) was purged with nitrogen.

Gas chromatographic analysis was conducted using an Agilent 7820A gas

chromatography equipped with a thermal conductivity detector (TCD) and a TD-01 packed column, using Ar as the carrier gas. The oven temperature was held constant at 50 °C. Inlet and detector temperature were set at 120 °C and 200 °C, respectively. HP 5973 GC-MS was used to analyse the products of the $^{13}\text{CO}_2$ isotopic experiment.

Photocatalytic performance

The photocatalytic performance of ZnCo_2O_4 was evaluated by CO_2 reduction reactions under mild reaction conditions. Typically, the catalytic reactions were performed in an 80 ml reactor at 30 °C controlled by cooling water and 1 atm CO_2 partial pressure. The reaction system contained $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (bpy = 2,2'-bipyridine, 10 μmol), ZnCo_2O_4 (4 μmol), solvent (5 ml, acetonitrile: H_2O = 3: 2), TEOA (1 ml), stirred with a magnetic stirrer, and irradiated by a Xe lamp with a 400 nm cutoff filter. After reactions, the produced gases were analyzed and quantified by gas chromatograph.

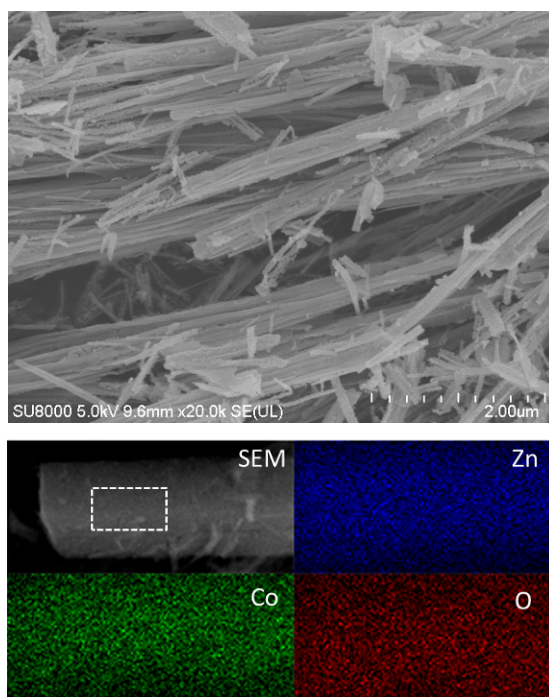


Fig. S1 Low-magnification SEM image and EDX elemental mappings of Zn, Co, and O for the ZnCo₂O₄ nanorods.

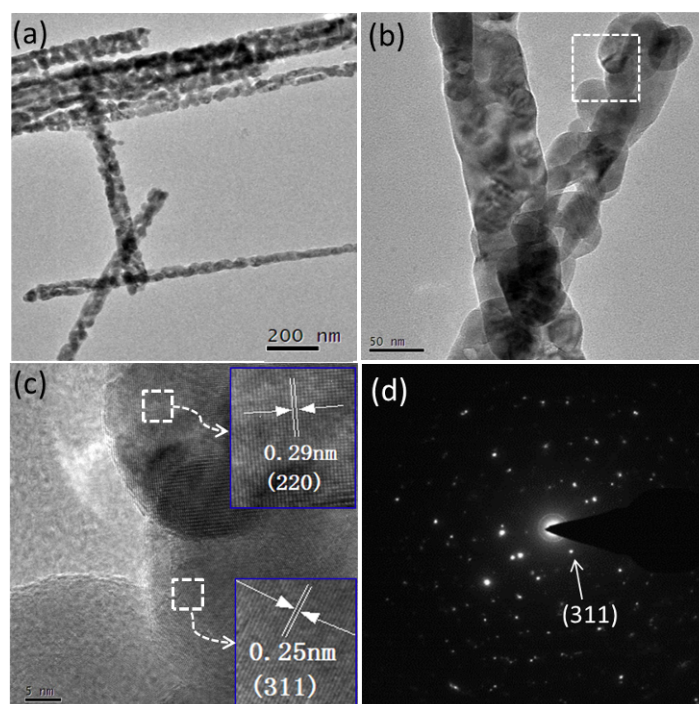


Fig. S2 (a, b) Low-magnification and (c) high-resolution TEM (HRTEM) images of the synthesized ZnCo_2O_4 nanorods. (d) The corresponding SAED pattern.

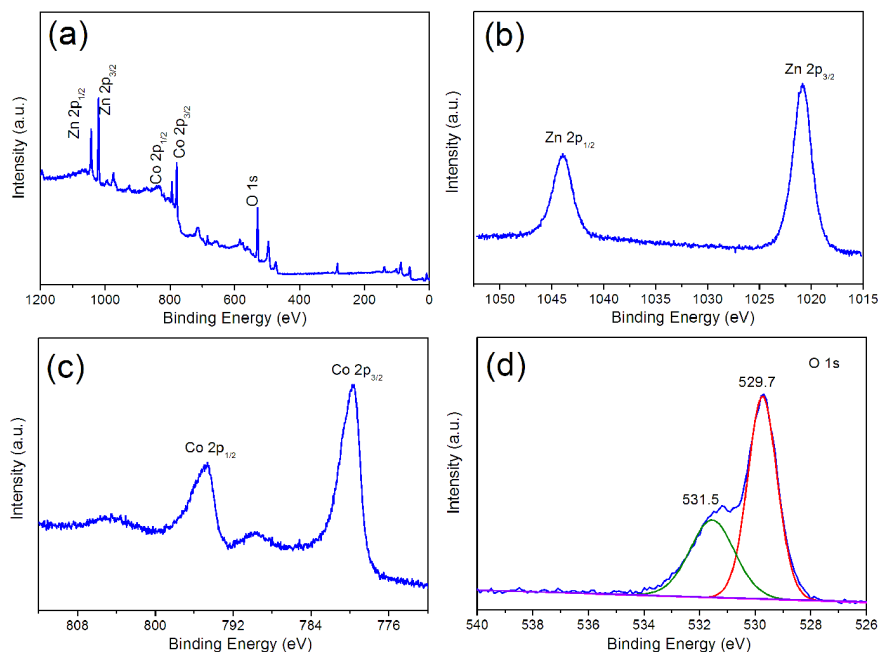


Fig. S3 XPS spectra of the ZnCo_2O_4 nanorods: (a) survey spectrum and high-resolution spectra of (b) Zn 2p, (c) Co 2p and (d) O 1s.

The survey spectrum (Fig. S3a) gives the signals of Zn, Co, and O elements, in agreement with the results of EDX analysis. In the high-resolution Zn 2p spectrum (Fig. S3b), two peaks with the binding energy values of 1044.0 and 1020.8 eV (assigned to Zn $2p_{1/2}$ and Zn $2p_{3/2}$, respectively) are observed, indicating the Zn(II) oxidation state of ZnCo_2O_4 .¹ In the spectrum of Co 2p (Fig. S3c), the two major signals at 794.6 and 779.7 eV can be correspondingly attributed to Co $2p_{1/2}$ and Co $2p_{3/2}$, with a spin-orbit splitting of ca. 15.0 eV. Additionally, there are two shake-up satellite peaks at ~804.5 and ~789.6 eV. The energy gap between the Co 2p main peak and the satellite peak is about 9.9 eV. In general speaking, if the energy gap is 9-10 eV, the Co cation holds a valence of 3+.^{2,3} The two signals at 531.5 and 529.7 eV in the O 1s spectrum (Fig. S3d) are ascribed to the lattice oxygen in the spinel ZnCo_2O_4 and the oxygen of hydroxide ions.⁴

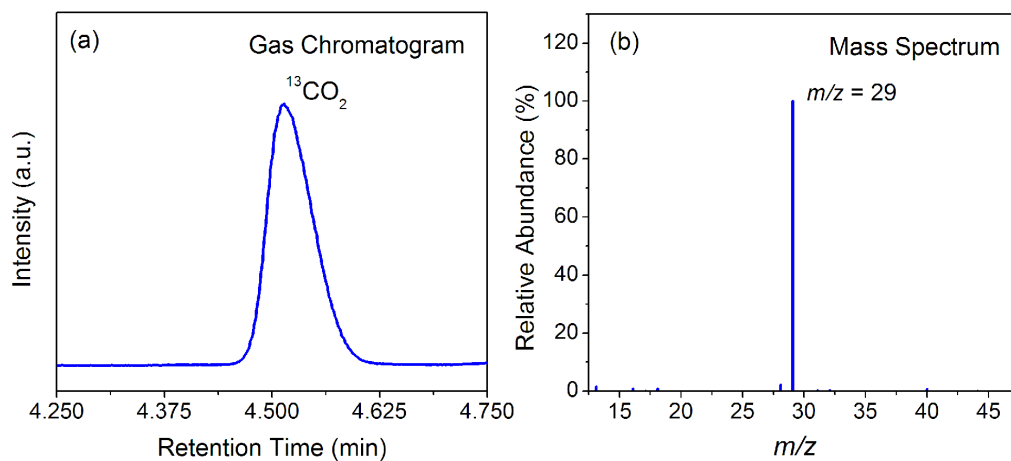


Fig. S4 (a) Gas chromatogram and (b) mass spectrum of GC-MS analysis for the produced CO from the isotopic experiment using $^{13}\text{CO}_2$. The peak in the gas chromatogram at retention time of 4.51 min (Fig. S4a), and the signal with m/z value of 29 in the mass spectrum (Fig. S4b) are assigned to ^{13}CO .

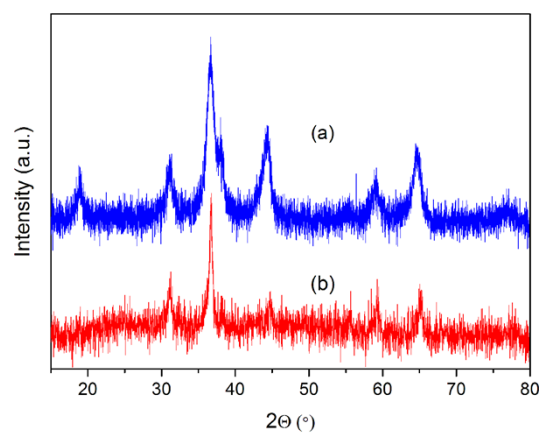


Fig. S5 XRD patterns of the ZnCo₂O₄ nanorods: (a) fresh sample and (s) used sample after the stability test for ten repeated operations.

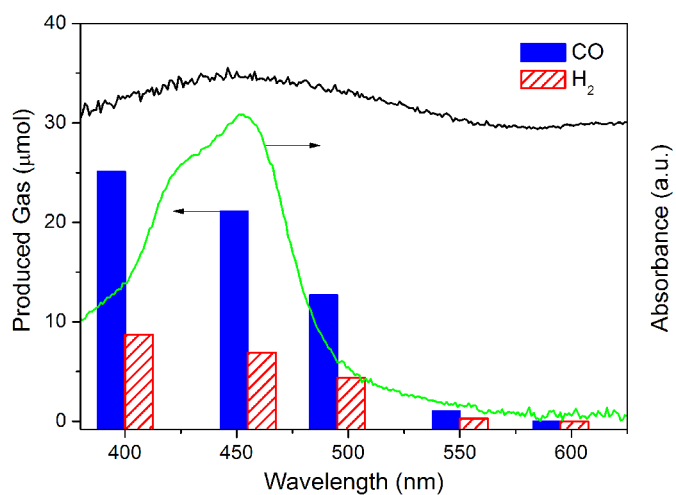


Fig. S6 Wavelength-dependent CO/H₂ evolution from the ZnCo₂O₄ catalysed CO₂ photoreduction system. The lines are the UV-Vis absorbance spectra of the Ru-dye (green) and ZnCo₂O₄ (black). The wavelength of the incident light was controlled by applying some appropriate long-pass cut-off filters.

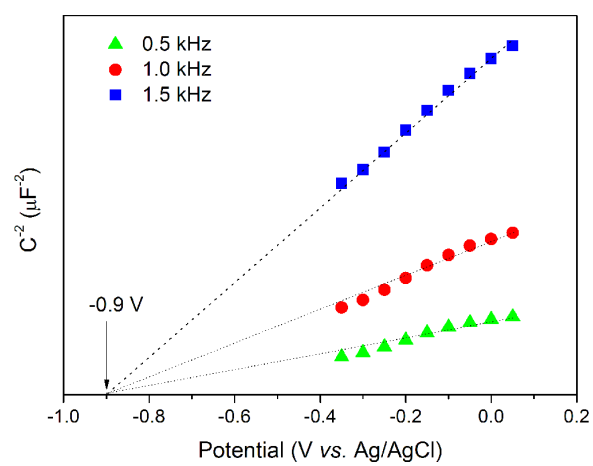


Fig. S7 Mott-Schottky plots of the ZnCo_2O_4 sample.

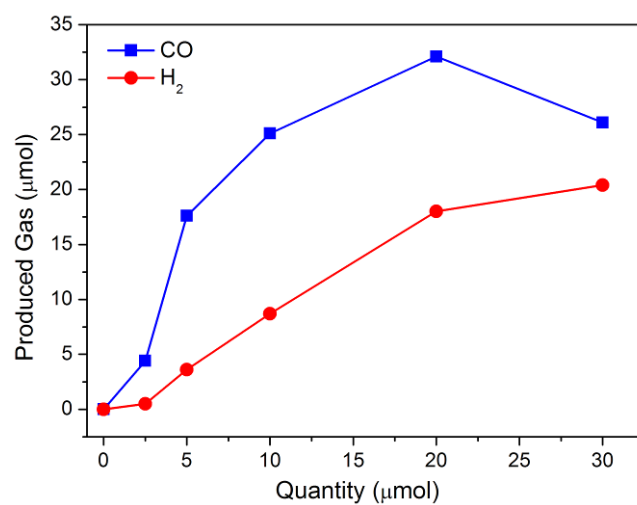


Fig. S8 Productions of CO and H₂ produced from the photocatalytic system as a function of the Ru complex quantity added in the reaction system.

Table S1 Studies on the catalytic activity of the reaction system under various conditions.^a

Entry	CO (μmol)	H ₂ (μmol)	CO+H ₂ (μmol)	Sel. _{CO} ^b (%)
1	25.1	8.7	33.8	74.3
2 ^c	n.d. ^d	n.d.	/	/
3 ^e	n.d.	n.d.	/	/
4 ^f	n.d.	n.d.	/	/
5 ^g	1.2	0.6	1.8	66.7
6 ^h	15.9	5.6	21.5	73.9
7 ⁱ	20.2	7.2	27.4	73.7
8 ^j	n.d.	1.0	1.0	0
9 ^k	1.5	0.9	2.4	62.5

^a Reaction conditions: [Ru(bpy)₃]Cl₂·6H₂O (10 μmol), ZnCo₂O₄ (4 μmol), solvent (5 ml, acetonitrile: H₂O = 3: 2), TEOA (1 ml), 30 °C, 1 atm CO₂, λ ≥ 400 nm, 1 h. ^b Sel._{CO} = mol (CO)/mol (CO + H₂). ^c In the dark. ^d Not detectable. ^e Without [Ru(bpy)₃]Cl₂·6H₂O. ^f Without TEOA. ^g Without ZnCo₂O₄. ^h Using Co²⁺ to replace ZnCo₂O₄. ⁱ Using Co₃O₄ to replace ZnCo₂O₄. ^j Using Ar to replace CO₂. ^k Using the supernatant after photocatalytic reaction.

References

- 1 H. Long, T. Shi, S. Jiang, S. Xi, R. Chen, S. Liu, G. Liao, Z. Tang, *J. Mater. Chem. A*, 2014, **2**, 3741.
- 2 J. Bai, X. Li, G. Liu, Y. Qian, S. Xiong, *Adv. Funct. Mater.*, 2014, **24**, 3012.
- 3 W. Wei, W. Chen, D. G. Ivey, *Chem. Mater.*, 2008, **20**, 1941.
- 4 T. F. Huang, S. G. Mohamed, C. C. Shen, Y. Q. Tsai, W. S. Chang, R. S. Liu, *Nanoscale*, 2013, **5**, 12115.