

Electronic Supplementary Information (ESI) for

Construction of Polymeric Cobalt Phthalocyanine/Mesoporous Graphitic Carbon Nitride Composite for Efficient Photocatalytic CO₂ Reduction

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Experimental section

Chemicals and Materials.

Cyan diamide, 1,2,4,5-tetracyanobenzene, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), isopropanol, absolute ethanol, ammonium hydrogen fluoride (NH_4HF_2) and triethanolamine (TEOA) were commercially obtained from Sigma-Aldrich Co., Ltd. without further purification. 40 % dispersion of colloidal SiO_2 particles (LUDOX HS-40) were purchased from Aldrich Co., Ltd, and the sizes of SiO_2 particles are 12 nm. Fluorine-doped tin oxide (FTO) glasses were purchased from Dalian Heptachroma Co., Ltd. All the aqueous solutions were prepared using Milli-Q ultrapure water ($> 18 \text{ M}\Omega$).

Preparation of mpg- C_3N_4 .

Firstly, cyanamide was added into the dispersion of SiO_2 particles in water, the ratio of SiO_2 to cyanamide is 2:1. The obtained mixture was stirred at 333 K overnight to afford white powder. The solid was heated to 823 K with a heating rate of 2.3 K min^{-1} and kept this temperature over 4 h, the resulting brown-yellow powder was added to an aqueous NH_4HF_2 solution (4 M) to remove the SiO_2 template. The obtained powder was collected by centrifugation and washed with water and absolute ethanol. Finally, the mpg- C_3N_4 sample was dried at 343 K in a vacuum oven overnight.

Preparation of CoPPc@mpg- C_3N_4 .

In a typical experiment, 60 mg of mpg- C_3N_4 was dispersed in 40 mL of EtOH with the assistance of sonication, and 40 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 43 mg of DBU, and 60 mg of 1,2,4,5-tetracyanobenzene were added, and the obtained suspension was sonicated for 30 min. The suspension was then transferred to a Teflon-lined autoclave for solvothermal reaction at $180 \text{ }^\circ\text{C}$ for 8 h. After cooling to room temperature, CoPPc@mpg- C_3N_4 was collected by centrifugation and washed repeatedly with ethanol and water, and finally dried at $60 \text{ }^\circ\text{C}$ in a vacuum oven.

Instrumentations and characterizations.

Powder X-ray diffraction (PXRD) patterns of the samples were recorded on an X-ray diffractometer (Bruker D8 Advance) at 1600 W (40 kV voltage, 40 mA) power with

Cu K α radiation. The Co content of CoPPc@mpg-C₃N₄ was determined using inductively coupled plasma optical emission spectrum (ICP-OES, Agilent 725). Fourier transform infrared (FT-IR) spectra were collected on an FT-IR spectrometer (NICOLET 6700) with a frequency range of 4000~450 cm⁻¹. Raman spectra were collected from a Renishaw inVia Raman spectrometer with an incident laser of 633 nm. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field emission scanning electron microscope (20 kV). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM-2100 electron microscope equipped with an EDS detector at an accelerated voltage of 200 kV. Nitrogen adsorption-desorption isotherms were recorded at 77 K using an Accelerated Surface Area and Porosimetry 2020 (ASAP2020) adsorption apparatus. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher ESCALAB 250Xi spectrometer using C 1s (284.6 eV) as the reference line. The formed gaseous products were analyzed using a gas chromatography (GC) instrument equipped with a thermal conductivity detector (TCD) and a hydrogen flame ionization detector (FID) with a methanizer.

Photoelectrochemical (PEC) measurements.

To measure the photocurrent response, photocathodes were prepared as follows. 4 mg of sample was dispersed in 400 μ L isopropanol containing 10 μ L 5 wt% Nafion solution by sonication for 30 min. The obtained catalyst ink was dropped on the FTO conductive glass (100 μ L cm⁻¹) and allowed to dry under ambient conditions. PEC measurements were performed in a glass cell equipped with a quartz window using a three-electrode system. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Each photocathode was irradiated using a solar light simulator with a Xe lamp (100 mW cm⁻²) equipped with an air mass 1.5 global filter (AM 1.5G). Prior to each measurement, the electrolyte was purged with CO₂ for 30 min.

Photocatalytic CO₂ reduction experiments.

Typically, 5 mg of each photocatalyst was added in a 20.0 mL 9:1 MeCN/TEOA in a

quartz photoreactor (total volume 55 mL). The photoreactor was purged with CO₂ for 30 min and then sealed with a rubber septum. The photoreactor was then irradiated using a UV-filtered solar light simulator with a Xe lamp (100 mW cm⁻², AM 1.5 G, $\lambda > 400$ nm).

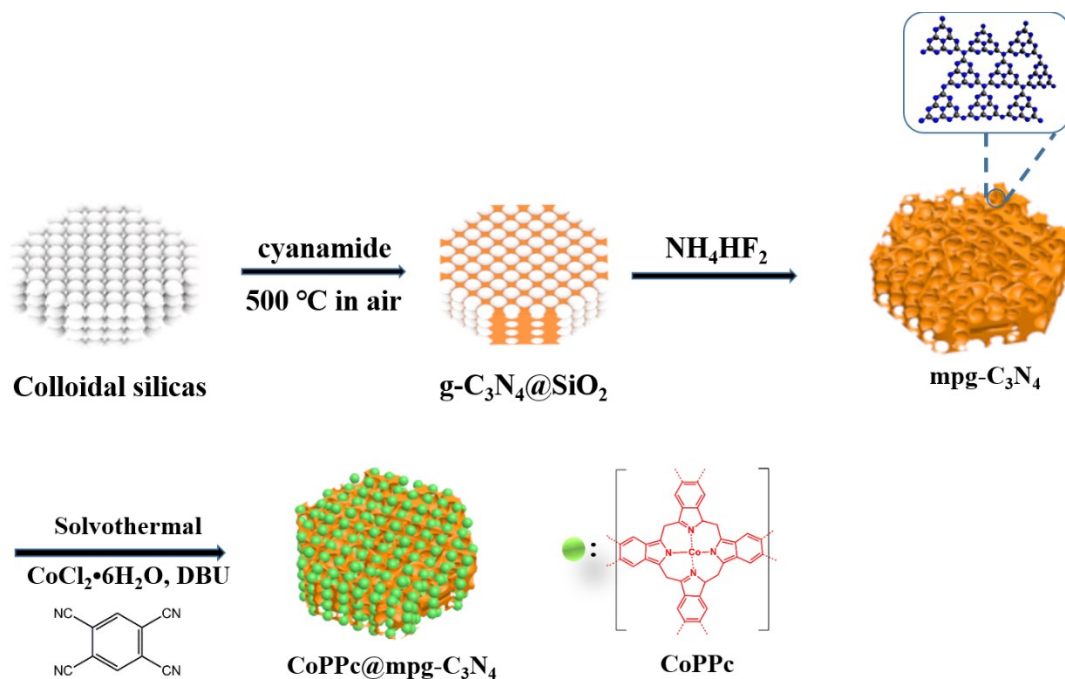


Figure S1. Schematic illustration of the in-situ polymerization of CoPPc on mpg-C₃N₄ via the solvothermal reaction.

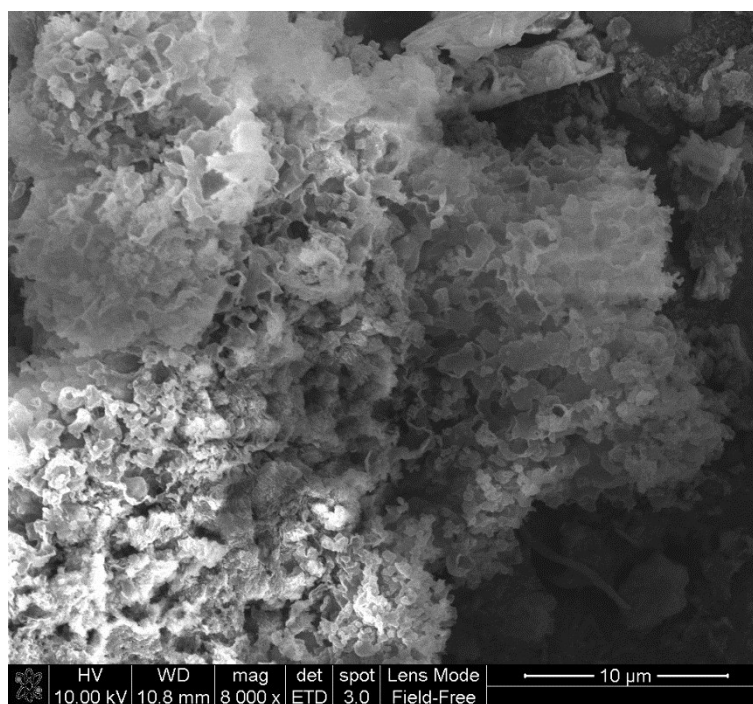


Figure S2. SEM image of mpg-C₃N₄.

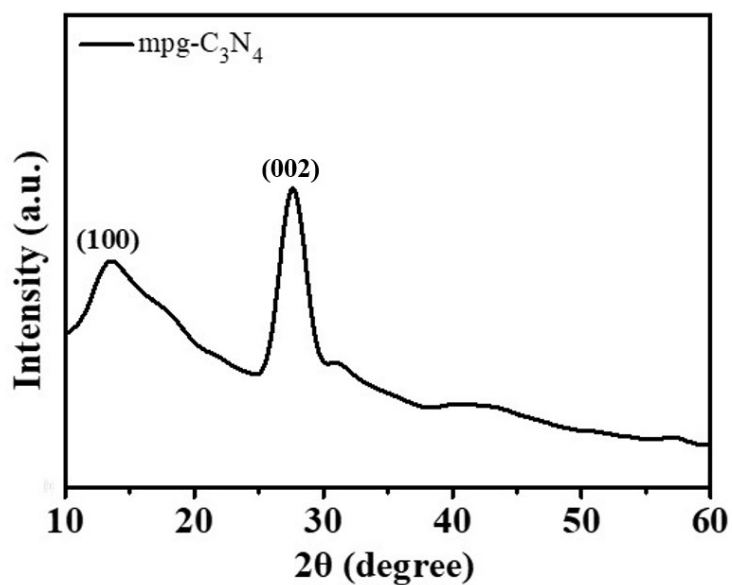


Figure S3. Powder XRD patterns of pristine mpg-C₃N₄.

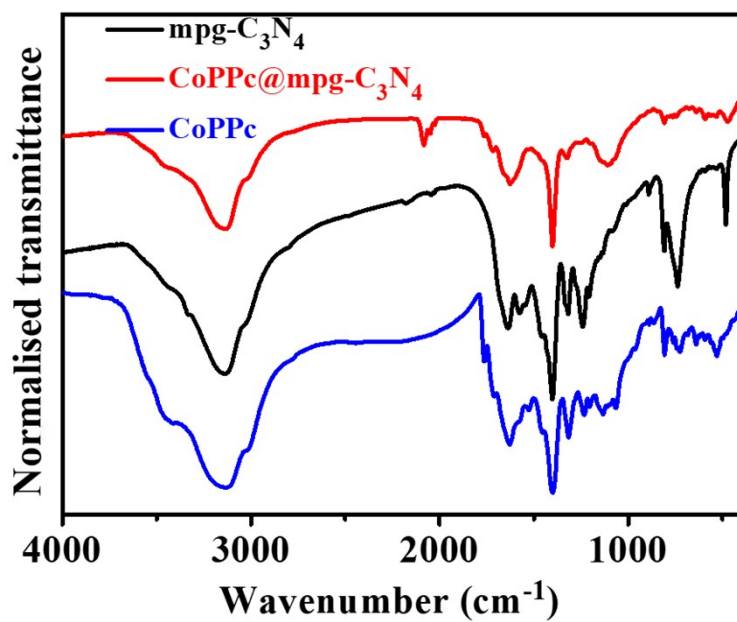


Figure S4. FT-IR spectra of mpg-C₃N₄, CoPPc, and CoPPc@mpg-C₃N₄.

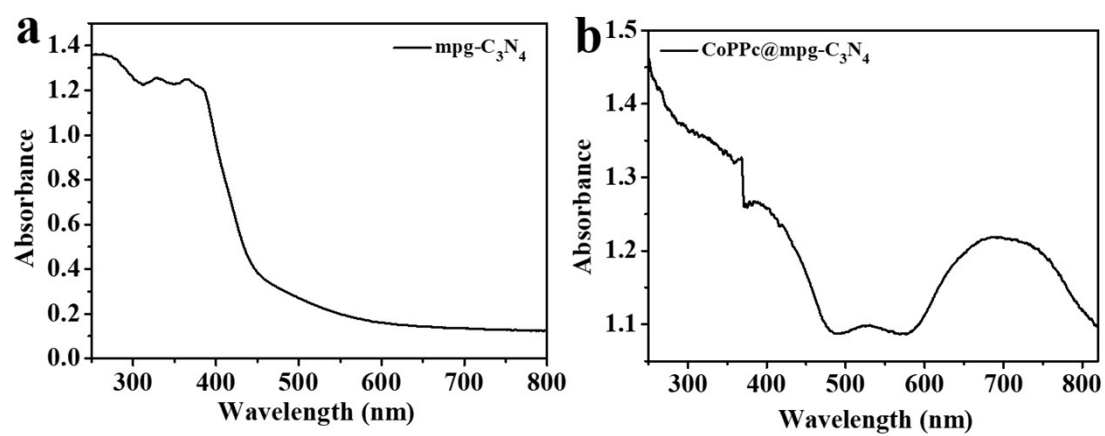


Figure S5. UV/Vis absorbance spectra recorded from a) bare mpg-C₃N₄ and b) CoPPc@mpg-C₃N₄.

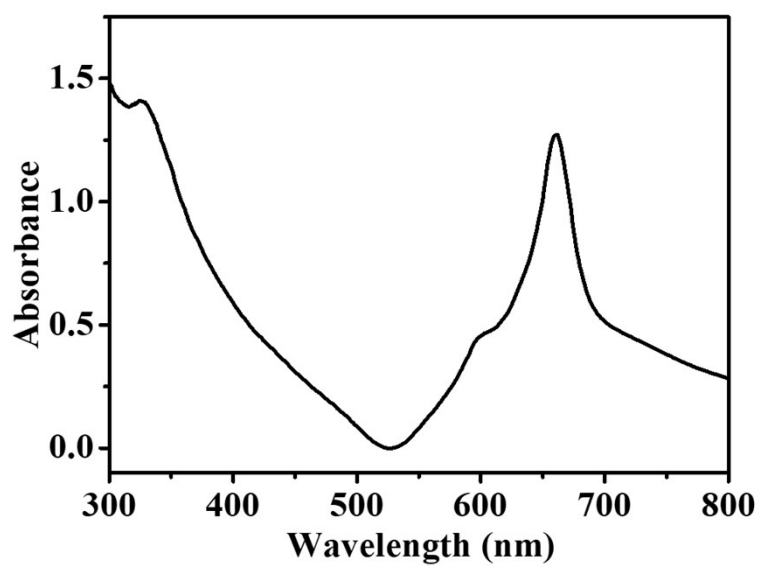


Figure S6. UV/Vis absorbance spectrum recorded from CoPc monomer in DMF.

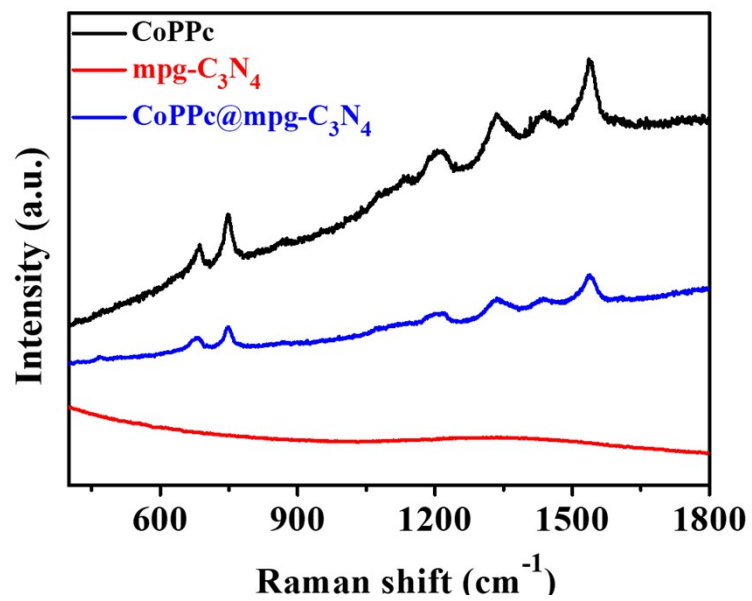


Figure S7. Raman spectra of CoPPc, mpg-C₃N₄, and CoPPc@mpg-C₃N₄.

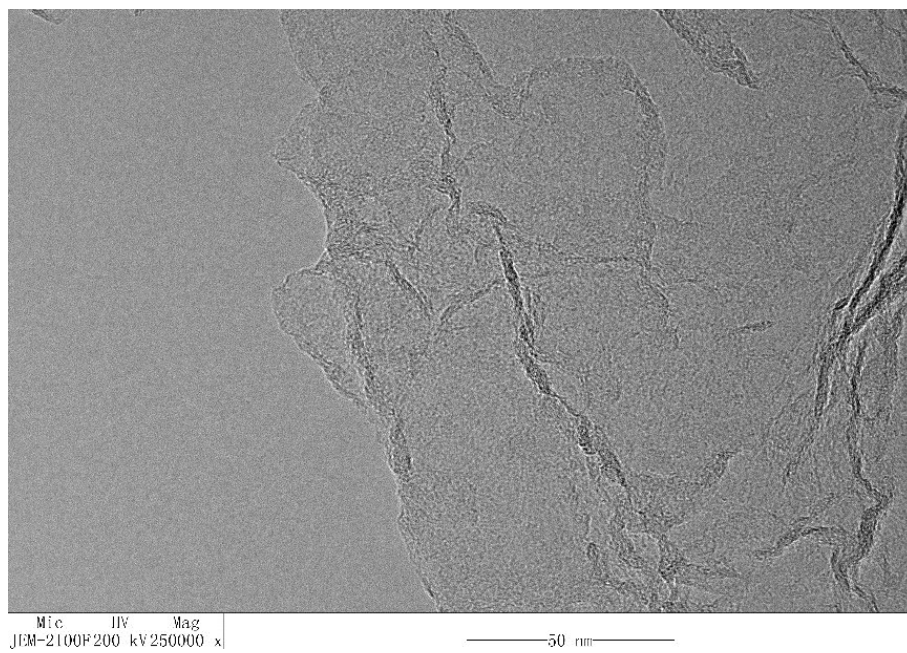


Figure S8. TEM image of bare mpg-C₃N₄.

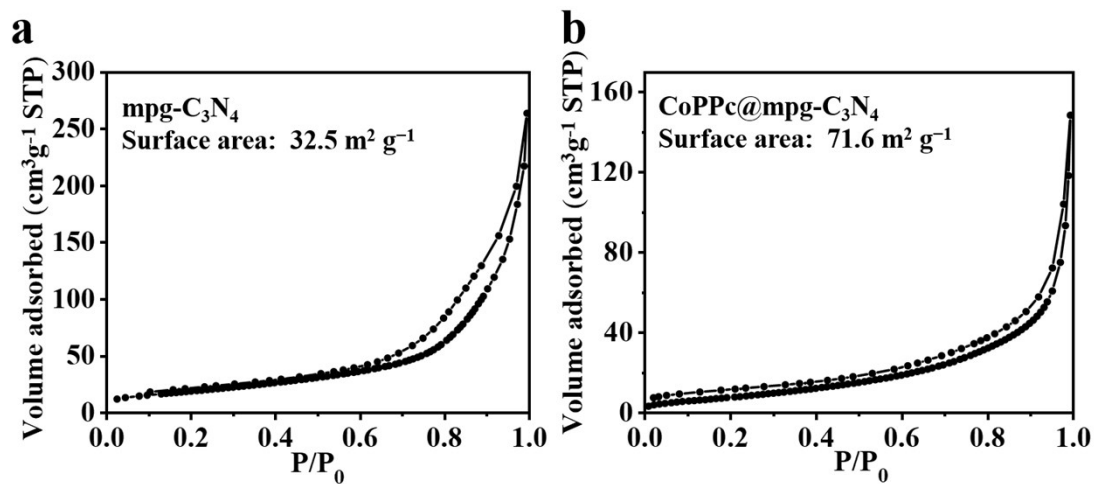


Figure S9. N₂ adsorption/desorption isotherms of a) mpg-C₃N₄ and b) CoPPc@mpg-C₃N₄.

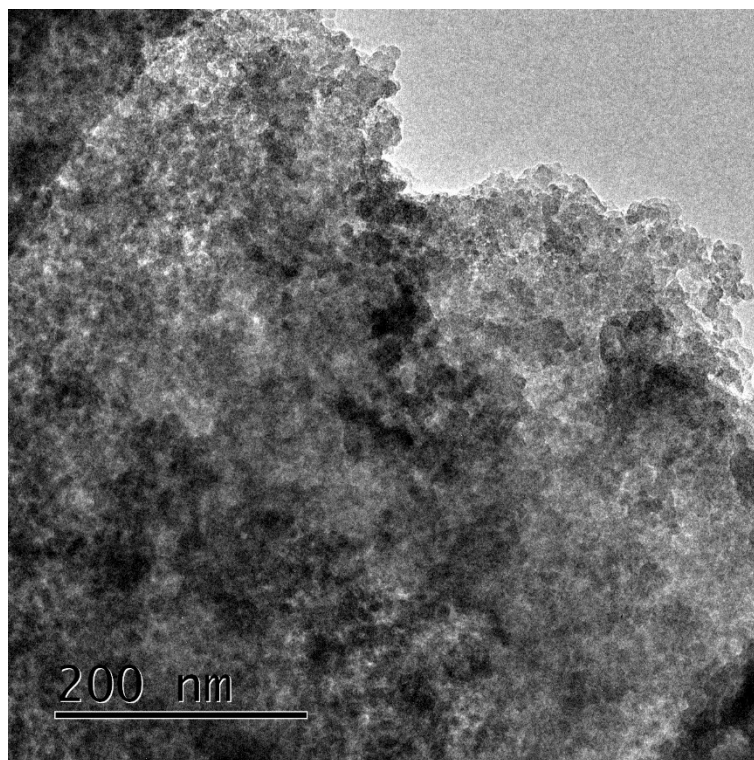


Figure S10. TEM image of CoPPc₇₃₀@mpg-C₃N₄.

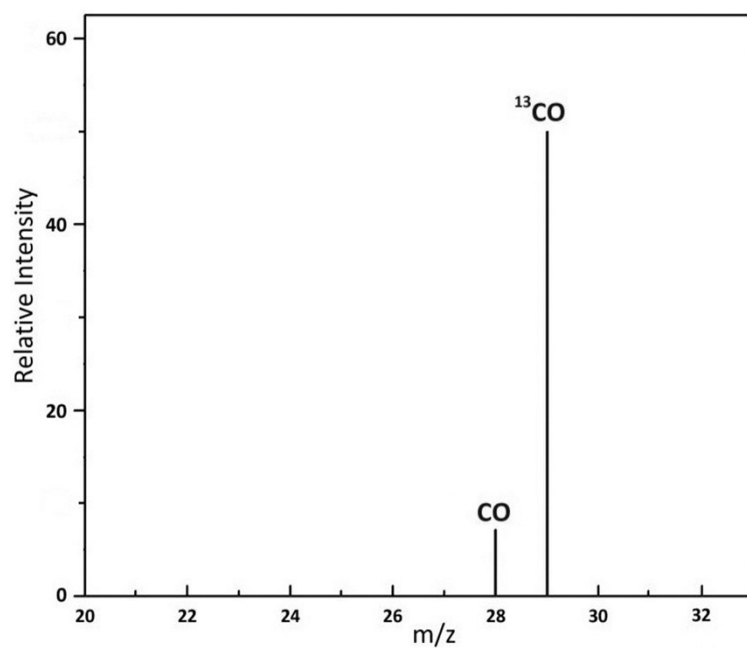


Figure S11. The mass spectrum of the CO GC peak obtained after long-term photocatalysis under ¹³CO₂ atmosphere.

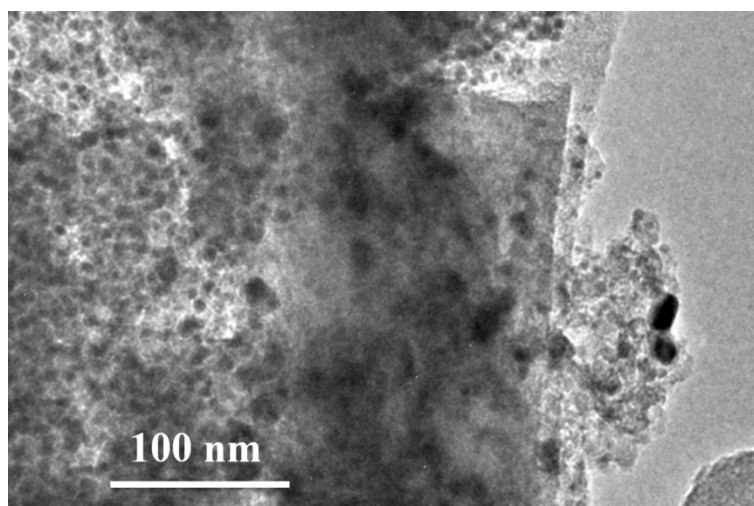


Figure S12. TEM image of CoPPc@mpg-C₃N₄ recorded after long-term photocatalysis.

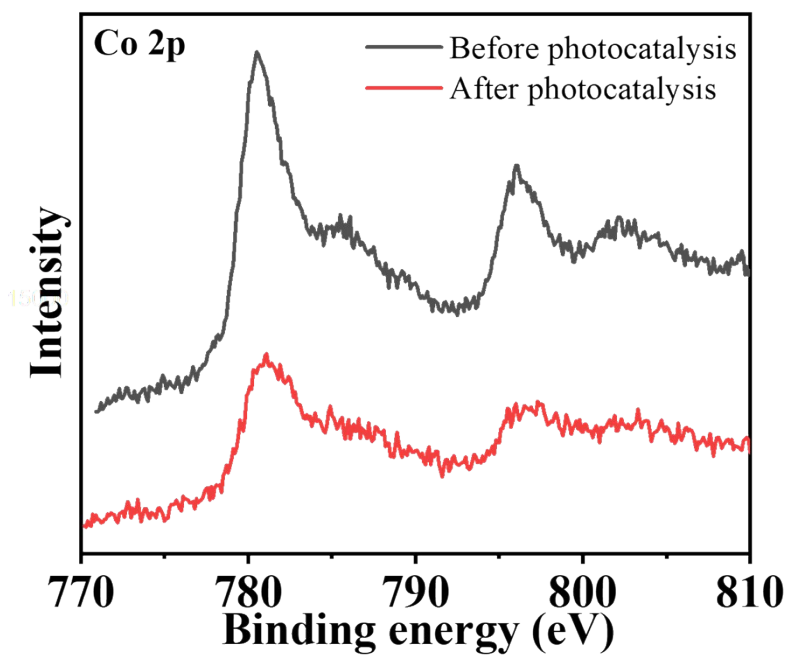


Figure S13. Co 2p core-level XPS spectra of CoPPc@mpg-C₃N₄ before and after photocatalysis.

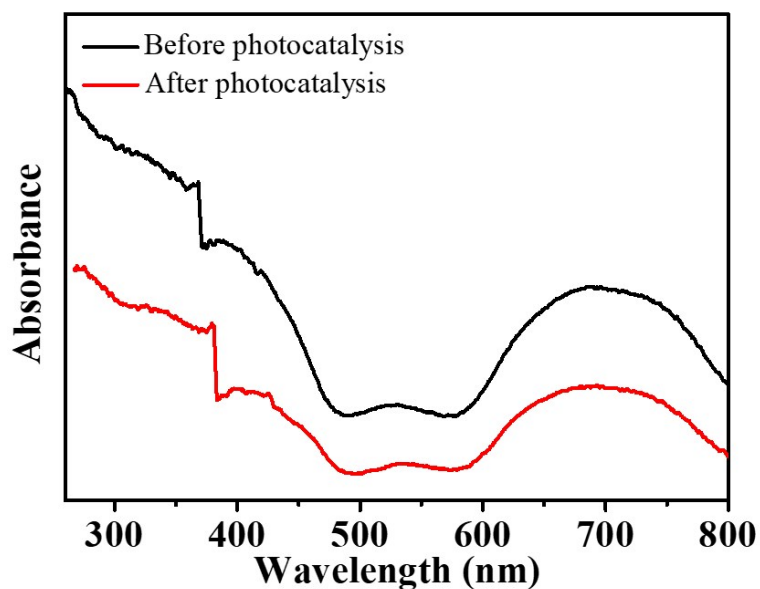


Figure S14. UV/Vis absorbance spectra of CoPPc@mpg-C₃N₄ before and after photocatalysis.

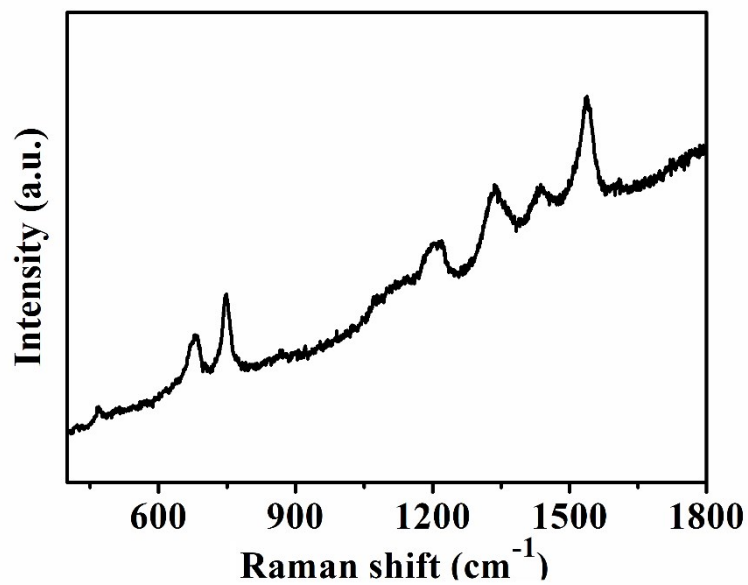


Figure S15. Raman spectrum of CoPPc@mpg-C₃N₄ after long-term photocatalysis.

Table S1. The preparation of CoPPc@mpg-C₃N₄ with various CoPPc loading by changing the ratio of starting materials.

Photocatalyst	Starting materials (mg)			Co content ($\mu\text{mol Co g}^{-1}$)
	mpg- C ₃ N ₄	CoCl ₂ ·6H ₂ O	1,2,4,5- tetracyanobenzene	
CoPPc ₂₂₁ @mpg- C ₃ N ₄	60	30	45	221
CoPPc ₃₅₆ @mpg- C ₃ N ₄	60	40	60	356
CoPPc ₅₀₉ @mpg- C ₃ N ₄	60	50	75	509

CoPPc ₆₁₁ @mpg- C ₃ N ₄	60	60	90	611
CoPPc ₇₃₀ @mpg- C ₃ N ₄	60	80	120	730

Table S2. Visible-light-driven CO₂ reduction under different reaction conditions.

entry	catalyst	product (μmol)	
		H ₂	CO
1 ^a	mpg-C ₃ N ₄	3.7	0
2 ^a	CoPPc	0	0
3 ^b	CoPPc ₃₅₆ @mpg- C ₃ N ₄	0	0
4 ^c	CoPPc ₃₅₆ @mpg- C ₃ N ₄	5.8	0
5 ^d	CoPPc ₃₅₆ @mpg- C ₃ N ₄	0	0
6 ^e	CoPPc ₃₅₆ @mpg- C ₃ N ₄	1.4	2.8

^aReaction conditions: 5 mg of catalyst in a CO₂-saturated MeCN solution containing 10% TEOA. Light source: UV-filtered Xe lamp (100 mW cm⁻², λ > 400 nm). Reaction time: 8 h. ^bThe reaction was conducted in a CO₂-saturated MeCN solution without TEOA. ^cUnder an argon atmosphere. ^dIn the dark. ^eIrradiation of the photoreactor under visible light equipped with optical filter (λ > 455 nm).

Table S3. Comparison of CoPPc@mpg-C₃N₄ with other g-C₃N₄ based organic/inorganic photocatalysts.

Photocatalyst	Product (CO)	TON _{CO}	Ref.
g-C ₃ N ₄ - C _{0.05} /FeTCPP	28.3 mmol g ⁻¹ (6 h)	24.9	S1
g-C ₃ N ₄ /FeTCPP	6.52 mmol g ⁻¹ (6 h)	5.7	S2

CoPc@P-g-C ₃ N ₄	295 μmol g ⁻¹ (24 h)	not mentioned	S3
mpg-CN _x CoPPc	1000 μmol g ⁻¹ (48 h)	84	S4
CoPPc@mpg-C ₃ N ₄	74.4 ± 0.5 mmol g ⁻¹ (120 h)	209	This work

References

- S1. X. Zhang, L. Lin, Q. Dan, J. Yang, Y. Weng, Z. Wang, Z. Sun, Y. Chen and T. He, *Appl. Catal. B-Environ.*, 2020, **265**, 118595.
- S2. L. Lin, C. Hou, X. Zhang, Y. Wang, Y. Chen and T. He, *Appl. Catal. B-Environ.*, 2018, **221**, 312–319.
- S3. G. Liu, Y. Wang, Y. Zhou, J. Cao, M. Yuan and H. Lv, *J. Colloid Interf. Sci.*, 2021, **594**, 658–668.
- S4. S. Roy and E. Reisner, *Angew. Chem.*, 2019, **131**, 12308–12312.