Electronic Supplementary Information

Porphyrin-based conjugated organic polymer with dual metal sites for visible-light-driven reduction of CO_2 to CO with highly active and selective

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Physical measurements

Fourier transform infrared (FT-IR) spectra were performed as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution (m_{Sample}:m_{KBr}=1:100). Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance XRD diffractometer using Cu-Ka radiation (I = 1.54060 Å) at room temperature. Transmission electron microscopy (TEM) images were measured on a JEOL JEM-2100 electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images were obtained using a JEOL JEM-6510A scanning electron microscopy. For TEM imaging, a drop of freshly prepared sample solution was cast onto a carbon copper grid. For SEM imaging, a drop of freshly prepared sample solution was cast onto a silicon slice, and then Au (1-2 nm) was sputtered onto the grids to prevent charging effects and to improve the image clarity. X-ray photoelectron spectroscopy (XPS) was carried out on PHI 5300 ESCA System (Perkin-Elmer, USA). The excitation source is Al Kα radiation. Metal content was determined by Optima 2100DV inductively coupled plasma atomic emission spectrometry (ICP), by digesting the sample in concentrated nitric acid.

Photoelectrochemical characterization.

The photocurrent measurement were performed on three-electrode system using an electrochemical workstation. The cleaned ITO glass deposited with samples, Pt and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. The light source was a 300 W Xe lamp equipped with an ultraviolet cutoff filter (> 400 nm) and 0.5 M Na_2SO_4 aqueous solution acted

as the electrolyte.

| Entry	catalysts	SA	Main Product	Wavelength (nm)	Activity (μmol g^{-1} h^{-1})	Selectivity (%)	Ref
1	Co-POM	TEOA	CO	400 ~ 800	17	80	[1]
2	TTCOF-Zn	H$_2$0	CO	420 ~ 800	2.06	100	[2]
3	Azo-Por-Bpy-POP	H$_2$0	CO	> 400 nm	38.75	100	[3]
4	CdS-EF/FeTCPP	TEOA	CO	420 ~ 780	7.5	88	[4]
5	ZrPP-1-Co	TEOA	CO	> 420	14	96.4	[5]
6	CuTBPP-DTBP-Co	H$_2$0	CO	> 400 nm	32.5	100	**This Work**

**Table. S1** Photocatalytic activity and selectivity of CO_2 reduction in reported heterogeneous systems.
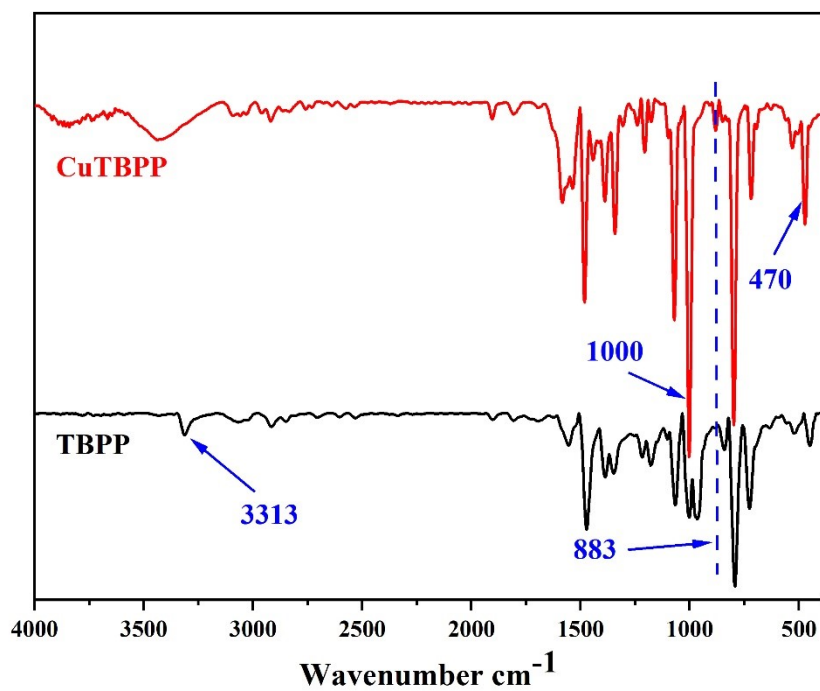
Fig. S1 IR spectra of CuTBPP and TBPP. The IR spectrum of TBPP showed that the characteristic N-H stretching vibration at 3313 cm^{-1} of TBPP disappeared after the reaction, N-Cu and C-Br stretching vibration of CuTBPP at 883 cm^{-1} and 470 cm^{-1},1000 cm^{-1} for porphyrin skeleton vibration.
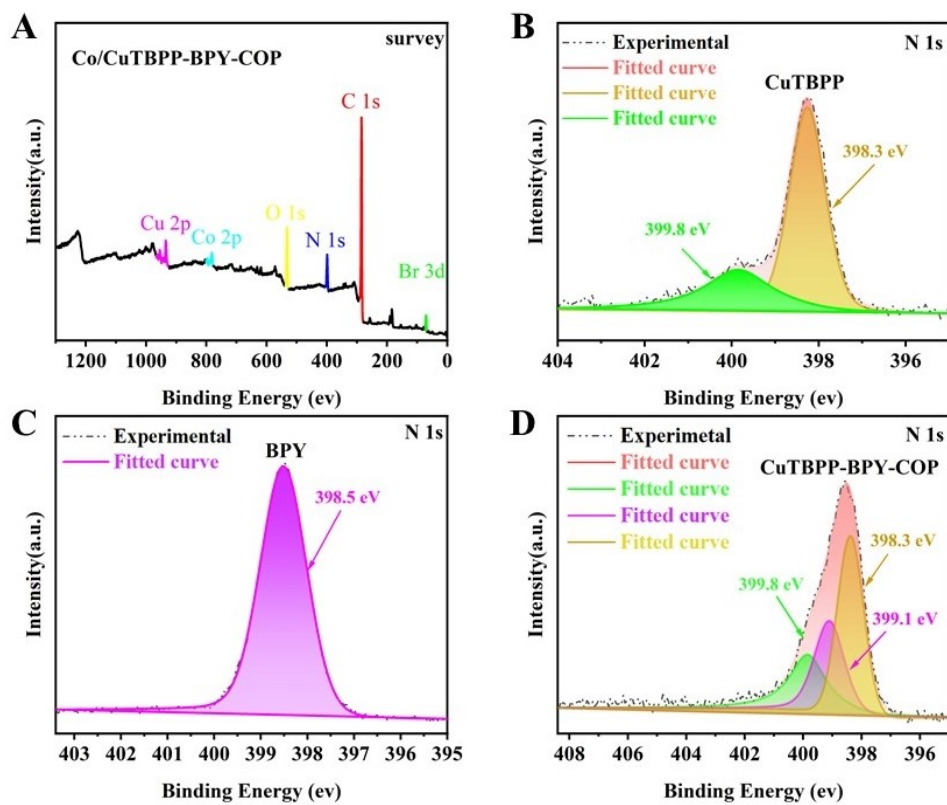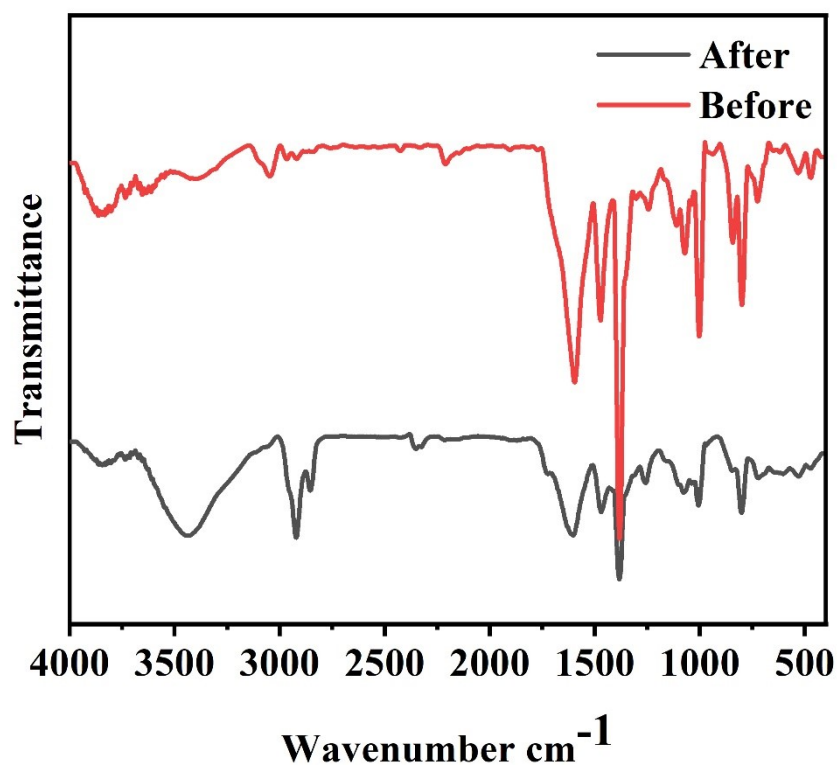
Fig. S2 (A) XPS survey spectrum of Co/CuTBPP-BPY-COP (B) N 1s XPS spectrum of CuTBPP. (C) N 1s XPS spectrum of BPY. (D) N 1s XPS spectrum of CuTBPP-BPY-COP.
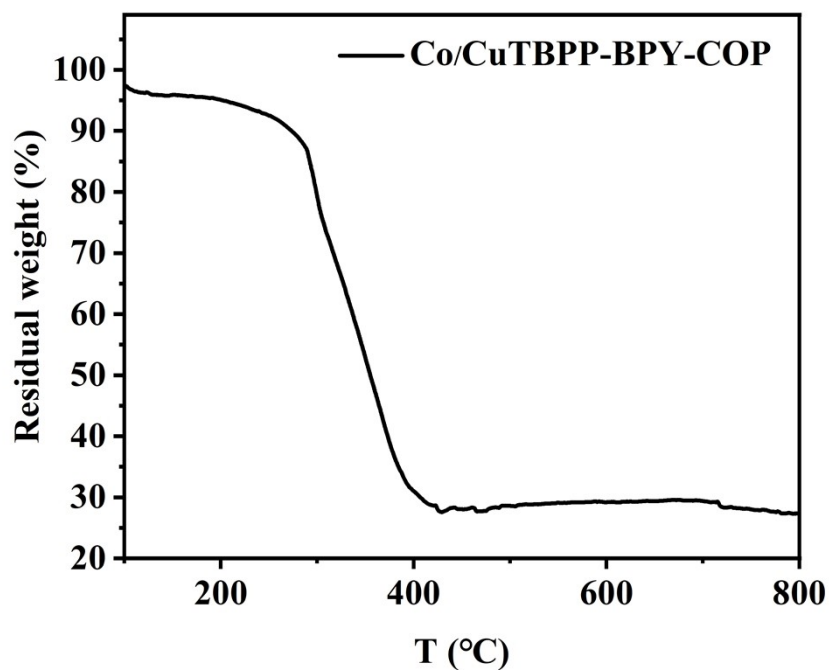
Fig. S3 Thermogravimetric analysis (TGA) data of Co/CuTBPP-BPY-COP.
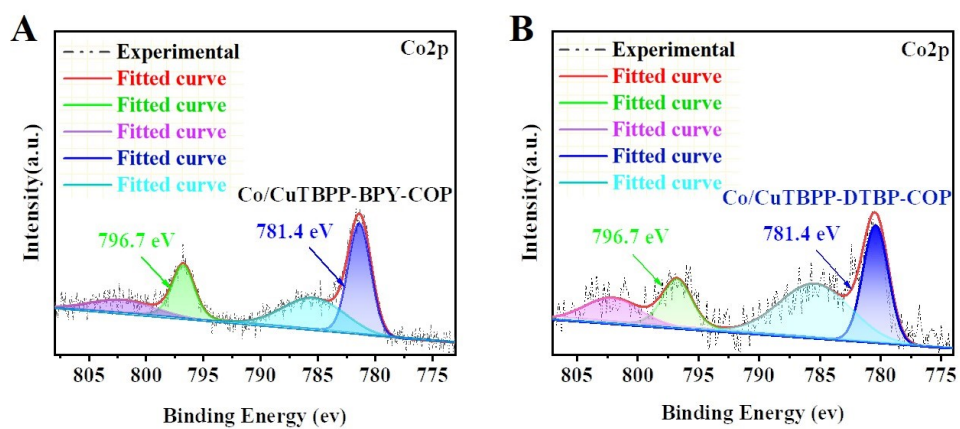
Fig. S4 XPS spectra of the Co 2p region for Co/CuTBPP-BPY-COP after (B) and before (A) photocatalysis.

Fig. S5 The FT-IR spectra of Co/CuTBPP-BPY-COP after (red) and before (black)

photocatalysis.

Sample	Co amount by ICP (wt%)	CO$_2$ reduction efficiency (μmol g^{-1})
Co/CuTBPP–BPY–COP-1	0.26	64.6
Co/CuTBPP–BPY–COP-2	0.55	78.9
Co/CuTBPP–BPY–COP	0.77	130.1

Table. S2 ICP analysis result of Co/CuTBPP–BPY–COP-1，Co/CuTBPP–BPY–

COP-2 and Co/CuTBPP–BPY–COP.

1. G. Zhao, H. Pang, G. Liu, P. Li, H. Liu, H. Zhang, L. Shi and J. Ye, *Applied Catalysis B: Environmental*, 2017, **200**, 141-149.
2. M. Lu, J. Liu, Q. Li, M. Zhang, M. Liu, J. L. Wang, D. Q. Yuan and Y. Q. Lan, *Angewandte Chemie International Edition*, 2019, **58**, 12392-12397.
3. Y. Hou, E. Zhang, J. Gao, S. Zhang, P. Liu, J.-C. Wang, Y. Zhang, C.-X. Cui and J. Jiang, *Dalton Transactions*, 2020, **49**, 7592-7597.
4. P. Li, C. Hou, X. Zhang, Y. Chen and T. He, *Applied Surface Science*, 2018, **459**, 292-299.
5. E.-X. Chen, M. Qiu, Y.-F. Zhang, Y.-S. Zhu, L.-Y. Liu, Y.-Y. Sun, X. Bu, J. Zhang and Q. Lin, *Advanced Materials*, 2018, **30**, 1704388.