

Supplementary Information for:

Post-synthetic atomically precise single-Cu^{II} sites in a thiacalix[4]arene-supported octahedral Na@Co₂₄ cluster: the Cu-Co synergistic effect for selective photocatalytic CO₂ to CO

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Experimental Section

Materials and Characterization. *p-tert*-Butylthiacalix[4]arene was synthesized by a previously reported procedure,¹ and other reagent-grade chemicals were purchased from commercial sources and used without further purification. Thermal gravimetric analysis (TGA) was performed on a TA Q600 TGA thermogravimetric analyzer. X-ray photoelectron spectroscopic (XPS) measurements were carried out on an ESCALAB 250Xi using a monochromic Al K α X-ray source (1486.6eV). UV-vis spectra were recorded on an Agilent Cary5000 Spectrometer. Fourier transform infrared (FT-IR) spectra using KBr pellets were taken on a Perkin Elmer Spectrum GX spectrometer. The electrochemical measurements were conducted on a CHI660E (Chenhua, Shanghai) electrochemical workstation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Elan DRC-e Plasma mass spectrometer) was performed to investigate the molar ratio of Co and Cu in the mixed-metal cluster.

X-ray Crystal Structure Determination. The intensity data were recorded on a Bruker D8 QUEST with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structure was solved using direct methods and refined by employing full-matrix least squares on F^2 (SHELXTX-2014).² All non-hydrogen atoms were refined anisotropically except for solvent molecules, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The diffraction data were treated by the “SQUEEZE” method as implemented in PLATON,³ which significantly improved the crystal data. CCDC numbers 2247793 (Na@Co₂₄), and 2247794 (Cu@Co₂₄) contain the supplementary crystallographic data for this paper, which are available free from the Cambridge Crystallography Data Centre (CCDC).

Determine the solvent molecules in Na@Co₂₄:

The residual electron density of Na@Co₂₄ was treated as diffuse contributions using the program *SQUEEZE*. There are a series of voids (total 12917 \AA^3) with 2756 estimated electrons occupied by solvents (DMF or CH₃OH). 67 DMF (40 e-) and 4 CH₃OH (18 e-) per unit cell were determined by analysis of electron numbers, the size, and the position of the void. As there are two formula units in one cell ($Z = 2$), DMF is approximately

37.5 (incorporating 4 DMF structurally confirmed) and CH₃OH is 2 for each formula. These solvent molecules are included in the sum formula, formula weight, calculated density, μ and $F(000)$, respectively. The *TENTATIVE* formula for Na@Co₂₄ is H₂[Co₂₄Cl₆(TC4A)₆(2,4,6-PTC)₈Na₄(H₂O)₈] (DMF)_{37.5} (CH₃OH)₂

SQUEEZE RESULTS (APPEND TO CIF)

Note: Data are Listed for all Voids in the P1 Unit Cell

i.e. Centre of Gravity, Solvent Accessible Volume,

Recovered number of Electrons in the Void and

Details about the Squeezed Material

loop_

_platon_squeeze_void_nr

_platon_squeeze_void_average_x

_platon_squeeze_void_average_y

_platon_squeeze_void_average_z

_platon_squeeze_void_volume

_platon_squeeze_void_count_electrons

_platon_squeeze_void_content

1	0.000	0.000	0.000	411	142 '' *
2	-0.001	0.502	-0.001	11917	2432 '' ★
3	0.000	0.000	0.500	89	20 '' ※
4	0.500	0.500	0.500	411	142 '' *
5	0.500	0.500	0.000	89	20 '' ※

_platon_squeeze_details

* Possibly occupied by three DMF and one CH₃OH molecules.

★ Possibly occupied by 67 DMF combined with TGA experiment.

※ Possibly occupied by one CH₃OH molecule

Determine the solvent molecules in Cu@Co₂₄:

The residual electron density of Cu@Co₂₄ was treated as diffuse contributions using the program *SQUEEZE*. There are a series of voids (total 12830.9 Å³) with 3289 estimated electrons occupied by solvents. By analysis of electron numbers, the size and position of the void, it is indicated that voids 2, 4, and 6 in-between two clusters cannot stably accommodate CHCl₃ which leads to the easy release of solvents at ambient conditions. The voids 3, 5, 8, and 9 are located in the calixarene cavities, being the efficient sites to encapsulate CHCl₃. 51 CHCl₃ (58 e-), 10 CH₃OH (18 e-), and 8 H₂O (10 e-) per unit cell were determined. As there are two formula units in one cell ($Z = 2$), CHCl₃, CH₃OH, and

H₂O are calculated to be 25.5, 5, and 4 for each formula, respectively. The presence of both chloroform and water is not inconsistent in this system, because chloroform is outside the cage, and water and methanol are inside the cage. These solvent molecules are included in the sum formula, formula weight, calculated density, μ and $F(000)$, respectively. TGA indicated the loss of solvents even at ambient conditions. The TENTATIVE formula for Cu@Co₂₄ is [Co₂₄Cl₆(TC4A)₆(2,4,6-TCP)₈Cu_{2.5}Na(H₂O)_{3.5}](CHCl₃)_{25.5}(CH₃OH)₅(H₂O)₄.

SQUEEZE RESULTS (APPEND TO CIF)

Note: Data are Listed for all Voids in the P1 Unit Cell

i.e. Centre of Gravity, Solvent Accessible Volume,

Recovered number of Electrons in the Void and

Details about the Squeezed Material

loop_

_platon_squeeze_void_nr

_platon_squeeze_void_average_x

_platon_squeeze_void_average_y

_platon_squeeze_void_average_z

_platon_squeeze_void_volume

_platon_squeeze_void_count_electrons

_platon_squeeze_void_content

1	0.000	0.000	0.000	489	152 '' *
2	-0.001	0.492	0.000	12060	2375 '' ★
3	0.000	0.000	0.326	172	57 '' §
4	0.000	0.000	0.500	572	190 '' ※
5	0.000	0.000	0.674	172	58 '' §
6	0.500	0.500	0.000	572	190 '' ※
7	0.500	0.500	0.500	489	152 '' *
8	0.500	0.500	0.174	172	58 '' §
9	0.500	0.500	0.825	172	57 '' §

_platon_squeeze_details

* Possibly occupied by four CH₃OH (18 e-) and eight H₂O (10 e-) molecules.

★ Possibly occupied by 41 CHCl₃ (58 e-) combined with the TGA experiment.

※ Possibly occupied by three CHCl₃ (58 e-) and one CH₃OH (18 e-) molecules

§ Possibly occupied by one CHCl₃ (58 e-) molecule

Synthesis of Na@Co₂₄

Purple block crystals of Na@Co₂₄ were synthesized and crystallized from a mixture of *p*-*tert*-butylthiacalix[4]arene (0.072 g, 0.1 mmol), Co(Ac)₂·4H₂O (0.1 g, 0.4 mmol), 2,4,6-H₃TCP (0.02 g, 0.076 mmol), NaCl (0.0045 g, 0.076 mmol), CH₃OH (5 mL), and DMF (5 mL) in a 23 mL Teflon-lined autoclave, which was heated from 20 °C to 130 °C, maintained at 130 °C for 3 days, and then cooled to 20 °C. The crystals were isolated by filtration and then washed with CH₃OH: DMF (1:1, v/v). Yield: *ca.* 60% with respect to H₄TC4A.

Synthesis of Cu@Co₂₄

In a typical synthesis, the crystals of Na@Co₂₄ (30 mg, *ca.* 0.005 mmol) were dissolved in 6 mL CHCl₃. Then, Cu(NO₃)₂·3H₂O (*ca.* 0.05 mmol) solution dissolved in CH₃OH was added dropwise to the above solution. After stirring for 30 min, 4 mL CH₃OH was added into the resultant solution and stirred for 10 h. After that, the brown solution was filtered into a glass vial and kept at ambient conditions. After a week, brown crystals were obtained. The crystals were washed with cold CH₃OH quickly and dried in the air. Yield: *ca.* 26.83% based on Na@Co₂₄.

Photocatalytic Activity Tests. The photocatalytic reduction of CO₂ was investigated in a 200 mL quartz reactor. A 30W LED lamp was used as the light source. To eliminate the heat effect of irradiation, circulating cold water flows through the reactor to make the reaction temperature kept on 25 °C. Before the photocatalytic reaction test, 30 mg photocatalyst (dry in a vacuum at 80 °C for 10h) was spread onto a square quartz plate with a side of 2 cm and then loaded onto the reactor. After that, the reactor was purged with Ar gas to ensure air removal. Subsequently, CO₂ (99.99%) bubbled through the water and was followed into the reactor for 1.5 h to guarantee the reactor was filled with the mixed CO₂ and H₂O vapor. The gas product was analyzed per hour by a gas chromatograph (GC-7920) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID).

Electrochemical Analysis. Photoelectrochemical (PEC) measurements were performed on an electrochemical workstation (CHI660E) in a standard three-electrode cell using a Pt wire and an Ag/AgCl electrode (saturated KCl) as the counter and reference electrodes,

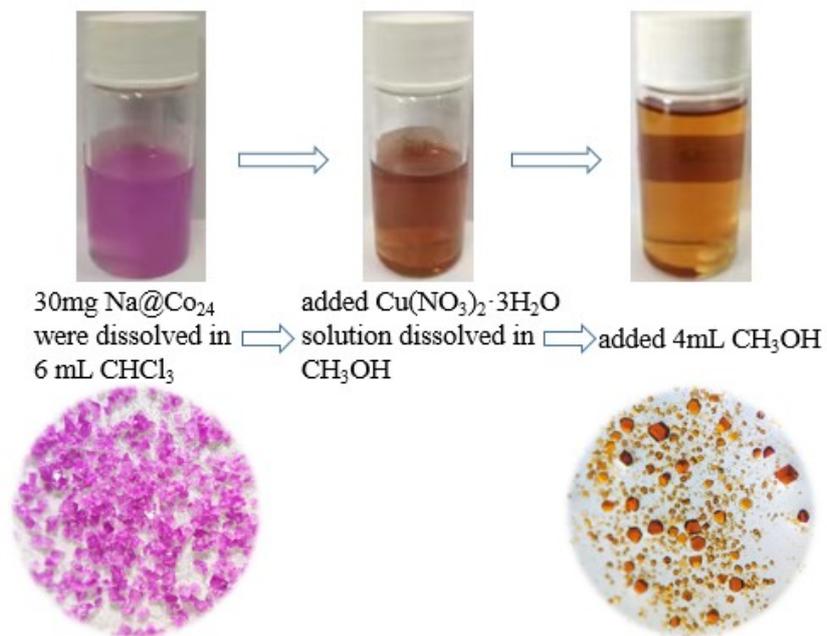
respectively. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass with its boundary being protected by Scotch tape. The as-synthesized powder (2 mg) was dispersed into 0.4 mL of C₂H₅OH under sonication for 30 min to obtain a colloidal dispersion. The dispersion was drop-casted onto the FTO glass. After natural air drying, the uncoated part of the FTO glass was isolated with epoxy resin glue. Na₂SO₄ aqueous solution (0.2M, pH = 6.8) was used as an electrode. A solar simulator was utilized as a light source for the measurements. Nyquist plots were recorded over the frequency range of 100 MHz to 100kHz at a bias of 0.2 V.

In-situ FT-IR Measurements. In-situ FT-IR measurements were carried out on PE GX Spectrum equipped with a volume and gas control system. All spectra were obtained with a resolution of 4.0 cm⁻¹ and an accumulation time of 5s. Before the measurement, a vacuum pump was used to evacuate all the gases from the reaction chamber for 20 min. Then, the background spectrum in the presence of the sample was collected. After that, CO₂ and H₂O vapor, as reaction gases, were introduced into the reaction chamber through the gas valve. Next, the FT-IR spectra were recorded as a function of time, in which a 30W spot LED light was used to illuminate the sample.

References

- 1 N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi and S. Miyano, *Tetrahedron*, 2000, **56**, 1437-1443.
- 2 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found Adv*, 2015, **71**, 3-8.
- 3 A. L. Spek, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 9-18.

Additional Scheme and Figures



Scheme S1 Schematic illustration of the synthesis of Cu@Co₂₄

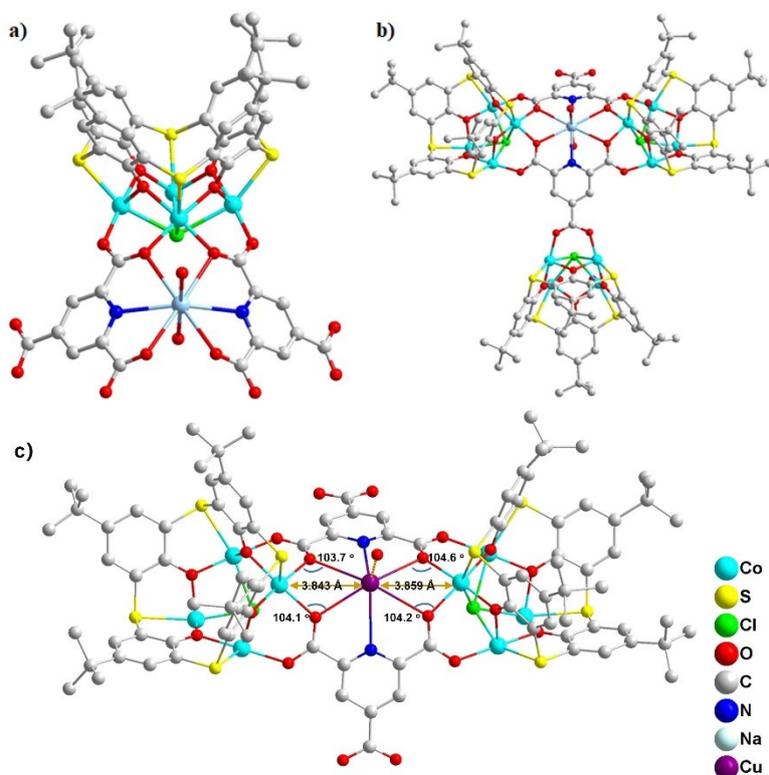


Fig. S1 (a) The coordination environments of metal ions, (b) the link mode between Co₄-TC4A PSBUs and 2,4,6-PTC, and (c) the Co...Cu length and Co-O_{carboxyl}-Cu angle in the Cu@Co₂₄ cluster.

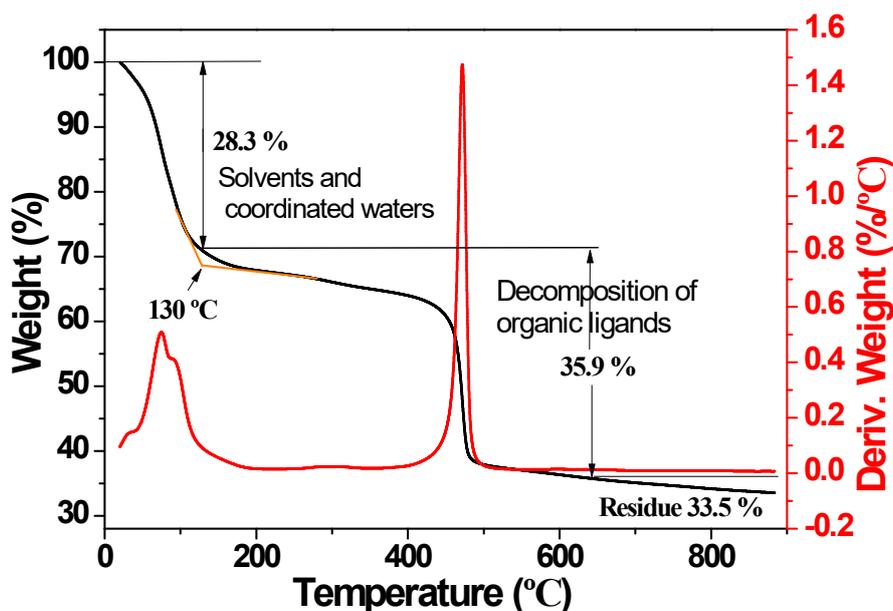


Fig. S2 The TGA curve of Na@Co₂₄ recorded in N₂ at 20 mL/min with a heating rate of 10 °C /min.

Na@Co₂₄ The sample loses about 28.3% weight from room temperature to 130 °C. This weight change is mainly attributed to volatilizing solvent molecules (including DMF, methanol, and weakly coordinated water). This assignment agreed with the one from the SQUEEZE result. The decomposition of the compound skeleton begins at about 400 °C, and the final residue fraction is 33.5%.

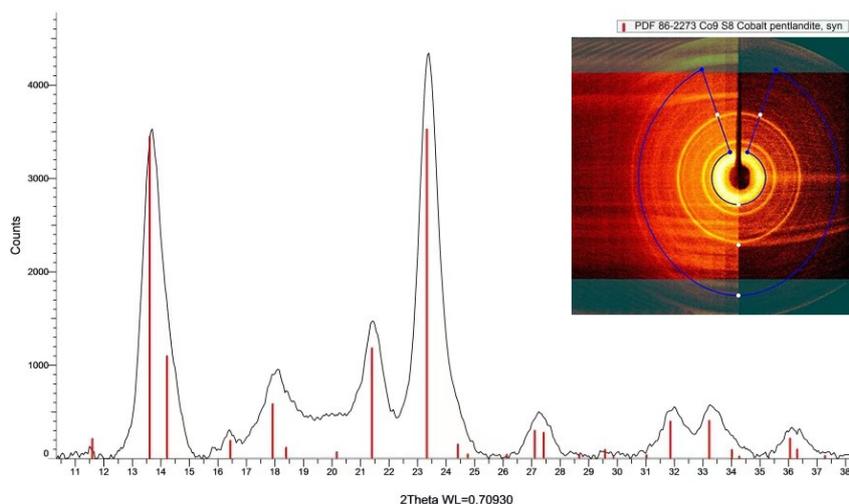


Fig. S3 The PXRD of Na@Co₂₄ after TGA (the final decomposition sample). The final decomposition product at 900 °C was found to be Co₉S₈.

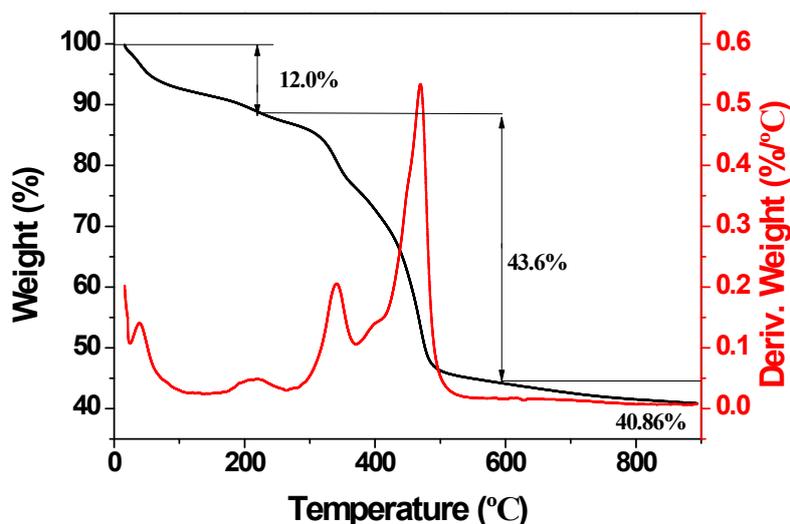


Fig. S4 The TGA curve of Cu@Co₂₄ recorded in N₂ at 20 mL/min with a heating rate of 10 °C /min.

The ratio of weight loss from room temperature to 200 °C of Cu@Co₂₄ is only about 12%, which is smaller than the ratio of weight loss of solvent molecules as a result of *SQUEEZE* determination. This indicates that Cu@Co₂₄ tends to lose solvent molecules (such as chloroform, methanol, etc) and crystallization at room temperature. Compared with Na@Co₂₄, Cu@Co₂₄ shows an obvious exothermic peak at about 340 °C, which is related to the incorporation of copper. The residue characterization also indicates the presence of copper (Fig. S5).

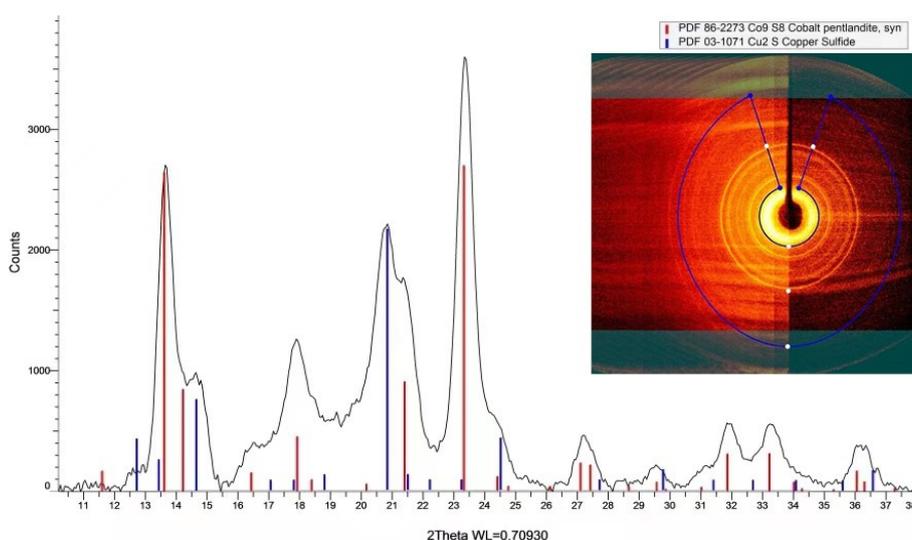


Fig. S5 The PXRD of Cu@Co₂₄ after TGA (the final decomposition sample). The final decomposition product at 900 °C was found to be a mixture of Co₉S₈ and Cu₂S.

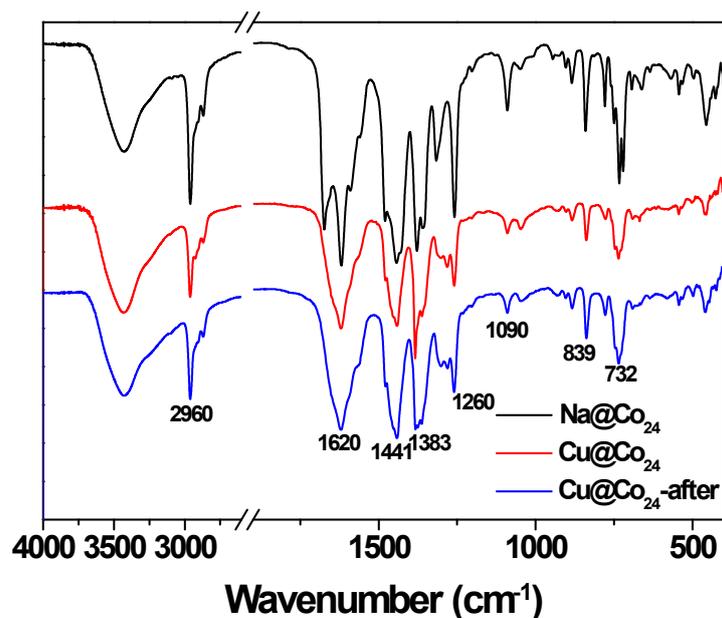


Fig. S6 FT-IR spectra of Na@Co₂₄, Cu@Co₂₄, and Cu@Co₂₄ after 4 cycles of photocatalysis. The main characteristic peaks corresponding to calixarene and carboxylate were found and kept unchanged.

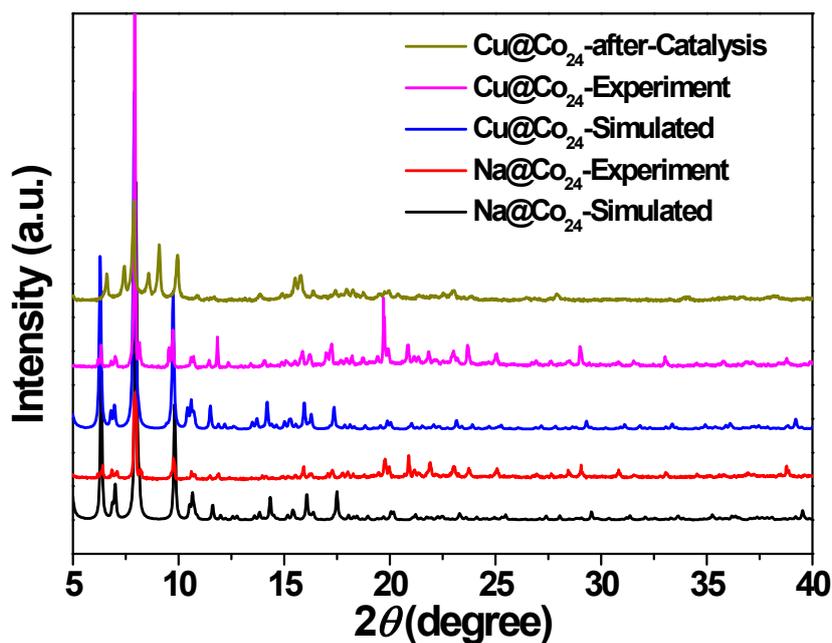


Fig. S7 PXRD patterns of Na@Co₂₄, Cu@Co₂₄, and Cu@Co₂₄ after 4 cycles of photocatalysis.

The experiment PXRD plot is well accordant with the one from single crystal determination for both Na@Co₂₄ and Cu@Co₂₄, respectively. However, Cu@Co₂₄ lose its initial crystallinity after the experiment. The structure stability of Cu@Co₂₄ after reaction can be determined by XPS and EDS.

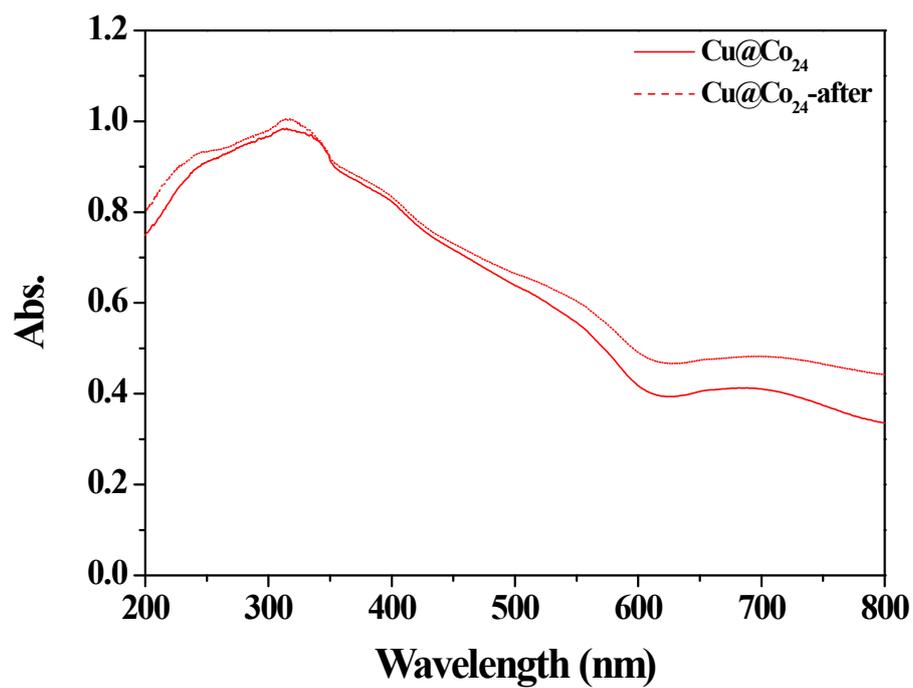
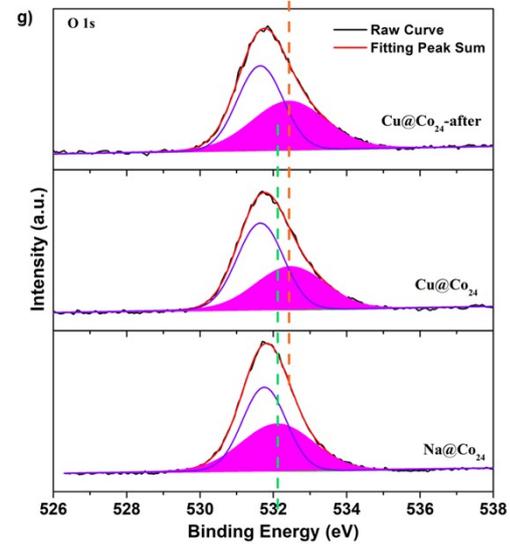
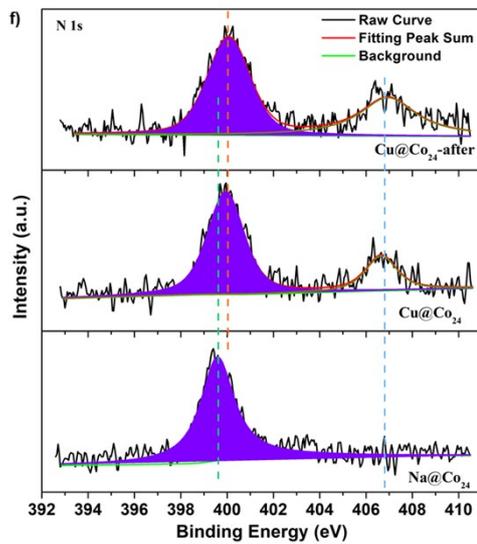
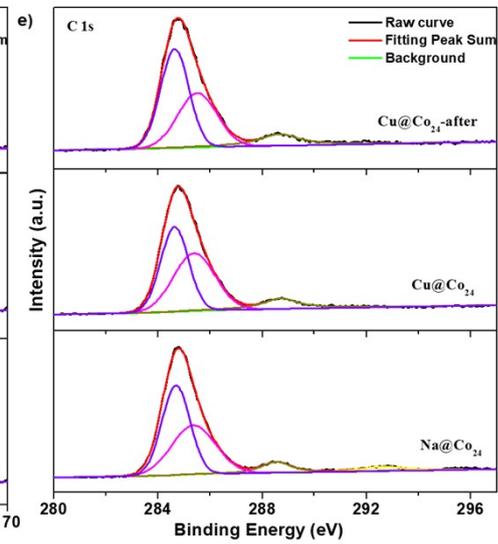
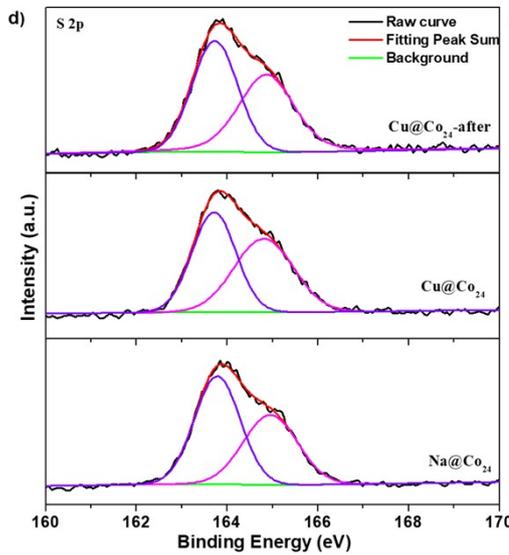
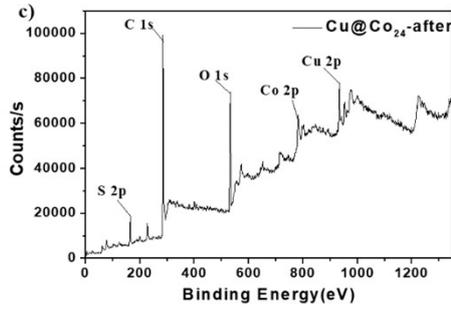
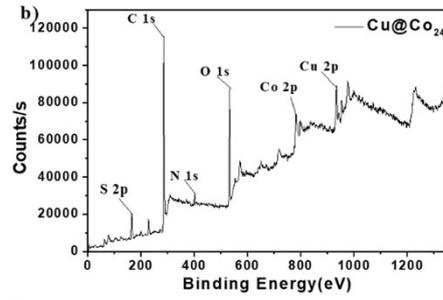
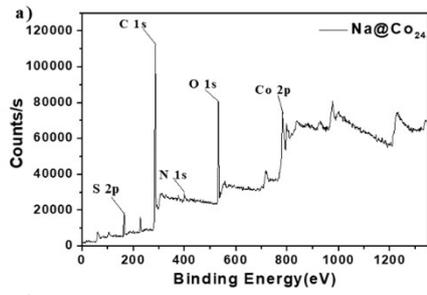


Fig. S8 Solid-state UV-vis spectra of Cu@Co₂₄ and Cu@Co₂₄ after 4 cycles of photocatalysis.



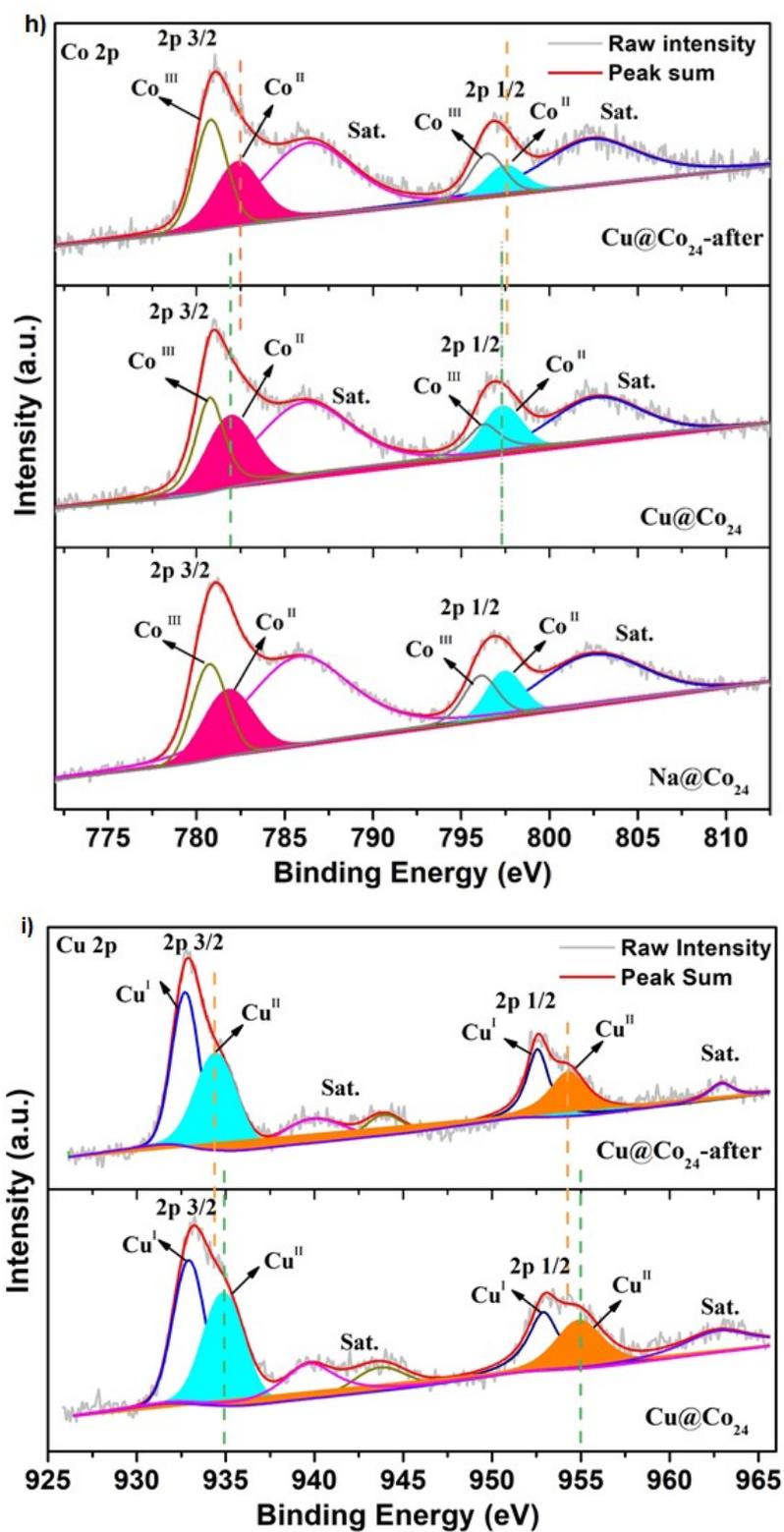


Fig. S9 XPS survey of Na@Co₂₄ (a), Cu@Co₂₄ (b), and Cu@Co₂₄ after 4 cycles of photocatalysis (c) and Corresponding high-resolution for S2p (d), C1s (e), N1s (f), and O1s (g), Co2p (h), Cu2p (i).

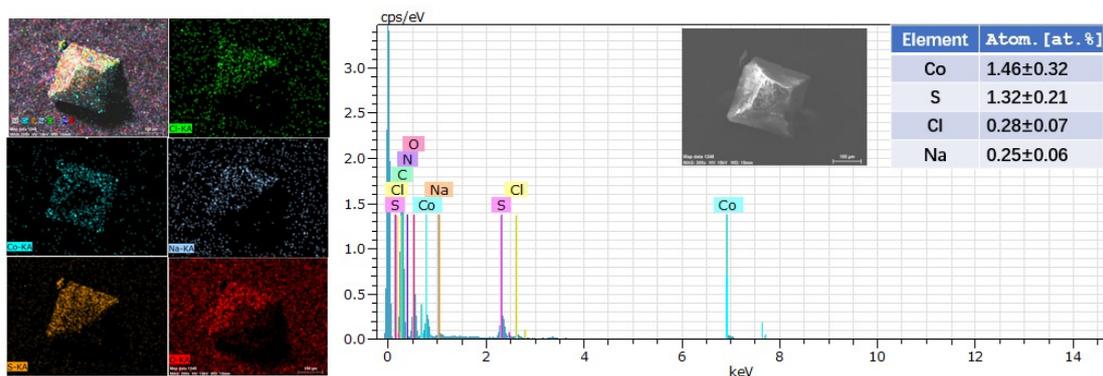


Fig. S10 The EDS pattern of Na@Co₂₄

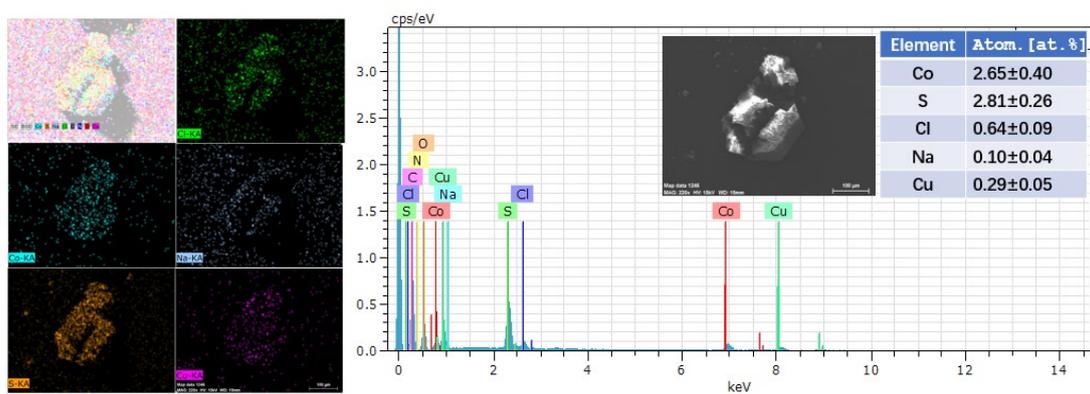


Fig. S11 The EDS pattern of Cu@Co₂₄

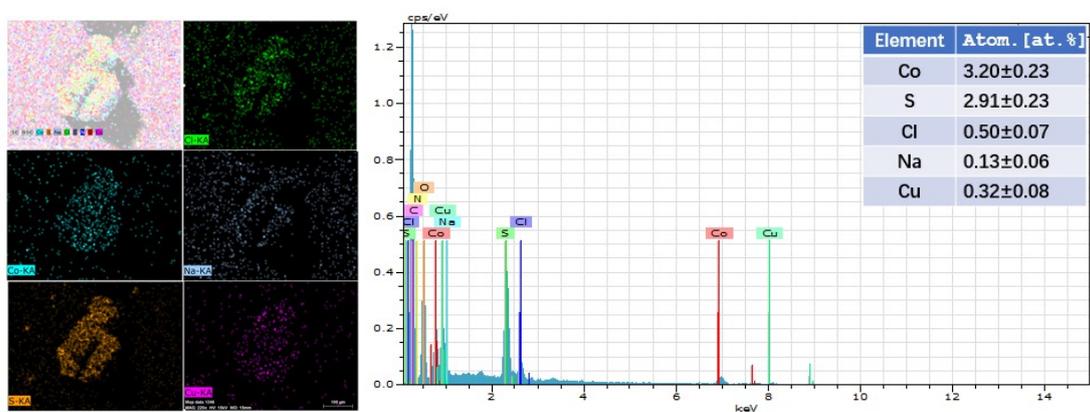


Fig. S12 The EDS pattern of Cu@Co₂₄-after 4 cycles of photocatalysis

The EDS mapping shows the elements are in the same region, and the ratios of the elements are accordant with that from SCXRD.

Tables

Table S1 Crystal data and structure refinement parameters for Na@Co₂₄ and Cu@Co₂₄

Compound	Na@Co ₂₄	Cu@Co ₂₄
Formula	C _{416.5} H _{560.5} Cl ₆ Co ₂₄ N _{45.5} Na ₄ O _{117.50} S ₂₄	C _{334.50} H ₃₃₇ Cl _{82.50} Co ₂₄ Cu _{2.50} N ₈ NaO _{84.50} S ₂₄
Mr	10572.99	11111.33
Crystal system	Tetragonal	Tetragonal
space group	<i>I</i> 4/m	<i>I</i> 4/m
<i>a</i> (Å)	25.7160(11)	25.981(3)
<i>b</i> (Å)	25.7160(11)	25.981(3)
<i>c</i> (Å)	43.4014(19)	43.544(5)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å ³)	28702(3)	29393(8)
Z	2	2
Temperature(K)	150	150
<i>D_c</i> (g/cm ³) ^c	1.223	1.255
μ (mm ⁻¹)	0.860	1.259
Total reflections collected	54017	52338
Unique data (<i>R_{int}</i>)	0.062	0.056
<i>GOF</i> on <i>F</i> ²	1.04	1.00
<i>R</i> ₁ [<i>I</i> >2sigma(<i>I</i>)] ^a	0.0836	0.0728
<i>wR</i> ₂ ^b	0.2848	0.2482

$${}^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; {}^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

Table S2 The atom ratio of the as-synthesized Cu@Co₂₄ and Cu@Co₂₄-after photocatalysis calculated from inductively coupled plasma (ICP) measurements

Complex	Co (ppm)	Cu (ppm)	Co: Cu (molar ratio)	Experimental value
Cu@Co ₂₄	824.60	86.45	9.54:1	Co ₂₄ Cu _{2.52}
Cu@CO ₂₄ -after photocatalysis	1024.36	107.15	9.56:1	Co ₂₄ Cu _{2.51}

Table S3 Comparison of the performances with some Cu-based or Co-based catalysts for photocatalytic reduction CO₂ to CO

Catalyst	Reaction condition	Sacrificial agent	Photosensitizer	CO product	CO selectivity	Gas by-product	Refs.
Cu@Co ₂₄	Gas-solid with water vapor	none	none	8.54 μmol/g/h	100%	n.d	This work
MAF-34-CoRu	Gas-solid with water vapor	none	none	5.43 μmol/g/h	89.2%	CH ₄	<i>J. Am. Chem. Soc.</i> , 2022, 144 , 8676-8682.
	Gas-solid with water vapor (Diluted CO ₂)	none	none	4.26 μmol/g/h	95.5%	CH ₄	
	CH ₃ CN/H ₂ O	none	none	11.2 μmol/g/h	100%	n.d	
CuTCPP@UiO-66/TiO ₂	Gas-solid with water vapor (CO ₂ 0.1 MPa)	none	none	31.32 μmol/g/h	n.r	CH ₄	<i>Sci Bull.</i> , 2019, 64 , 926-933.
Cu _{0.7} -ZnIn ₂ S ₄	Gas-solid with water vapor	none	none	47.2 μmol/g/h	74.8%	H ₂	<i>ACS Sustainable Chem. Eng.</i> , 2022, 10 , 11902-11912.
Cu ₂ O@Cu@UiO-66-NH ₂	Gas-solid	TEOA	none	20.9 μmol/g/h	n.r	CH ₄	<i>ACS Appl. Nano Mater.</i> , 2020, 3 , 10437-10445.
Co ₆ -MOF	CH ₃ CN-H ₂ O	TEOA	[Ru(bpy) ₃]Cl ₂	39.36 μmol (3 h)	n.r	H ₂	<i>J. Mater. Chem. A.</i> , 2017, 5 , 12498-12505.
Co(bpy) ₂ Cl ₂	CH ₃ CN-H ₂ O	TEOA,	[Ru(bpy) ₃]Cl ₂	62.3 μmol (4 h)	n.r	H ₂	<i>J. Energy. Chem.</i> , 2018, 27 , 502-506.
Co-dca	CH ₃ CN	TEOA	[Ru(bpy) ₃]Cl ₂	254 μmol/g/h	93%	H ₂	<i>Dalton Trans.</i> , 2022, 51 , 12569-12575.
[Cu ₆ [BH(im) ₃] ₈]	CH ₃ CN-H ₂ O	TEOA	[Ru(bpy) ₃]Cl ₂	3334 μmol/g/h	82.6%	H ₂	<i>Angew. Chem., Int. Ed.</i> , 2019, 58 , 11752-11756.
0.5%Cu/TiO ₂ -SiO ₂	Gas-solid with water vapor (CO ₂ 0.1 MPa)	none	none	60 μmol/g/h	n.r	CH ₄	<i>Appl Cata B- Environ.</i> , 2010, 100 , 386-392.
Co-ZIF-9/TiO ₂	Gas-solid with water vapor (CO ₂ 70 kPa)	none	none	17.58 μmol/g/h	79.3%	CO, CH ₄	<i>J. Mater. Chem. A</i> , 2016, 4 , 15126

n.r = not reported; n.d = not detected