Supplementary Information

Reduced Polyoxometalate-Encapsulated Organo Cobalt modified phosphate Framework for improving photocatalytic reduction CO_2

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Section 1. Crystal Structure

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Section 4. Crystal data

Table S2 Sectional crystal data and structure refinements for **Co-PO_4-PW_{12}.**

Section 1. Crystal Structure

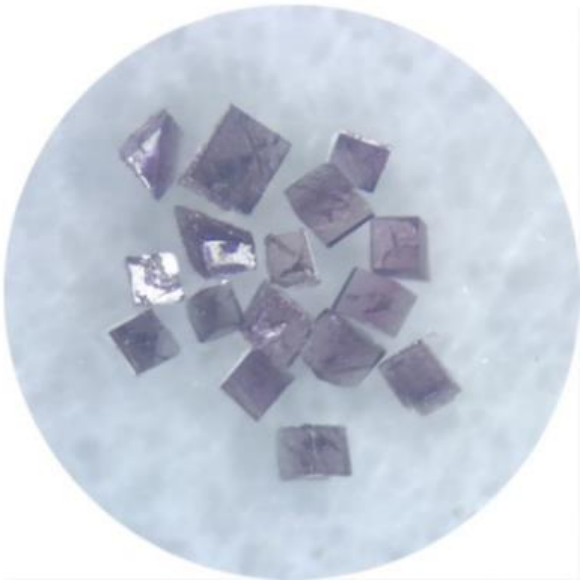

Fig. S1 The crystal image of **Co-PO_4-PW_{12}** under optical microscope.

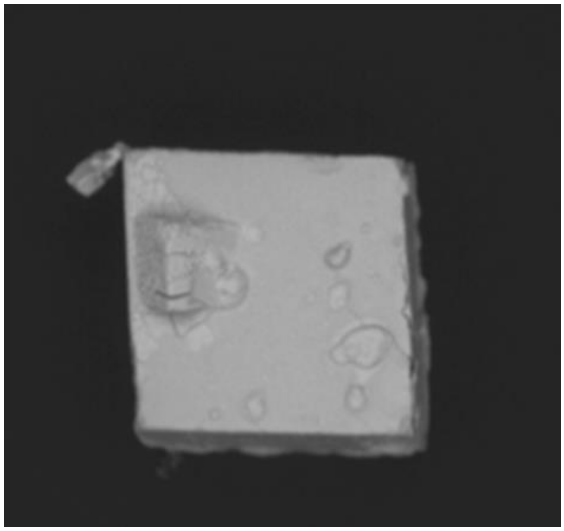

Fig. S2 SEM image of **Co-PO_4-PW_{12}**.

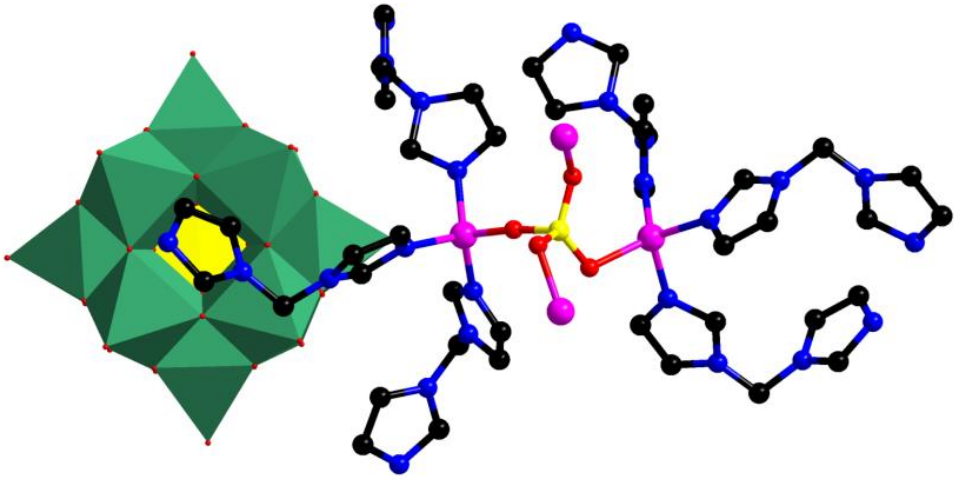

Fig. S3 Stick and polyhedral representation of basic unit for **Co-PO_4-PW_{12}**.

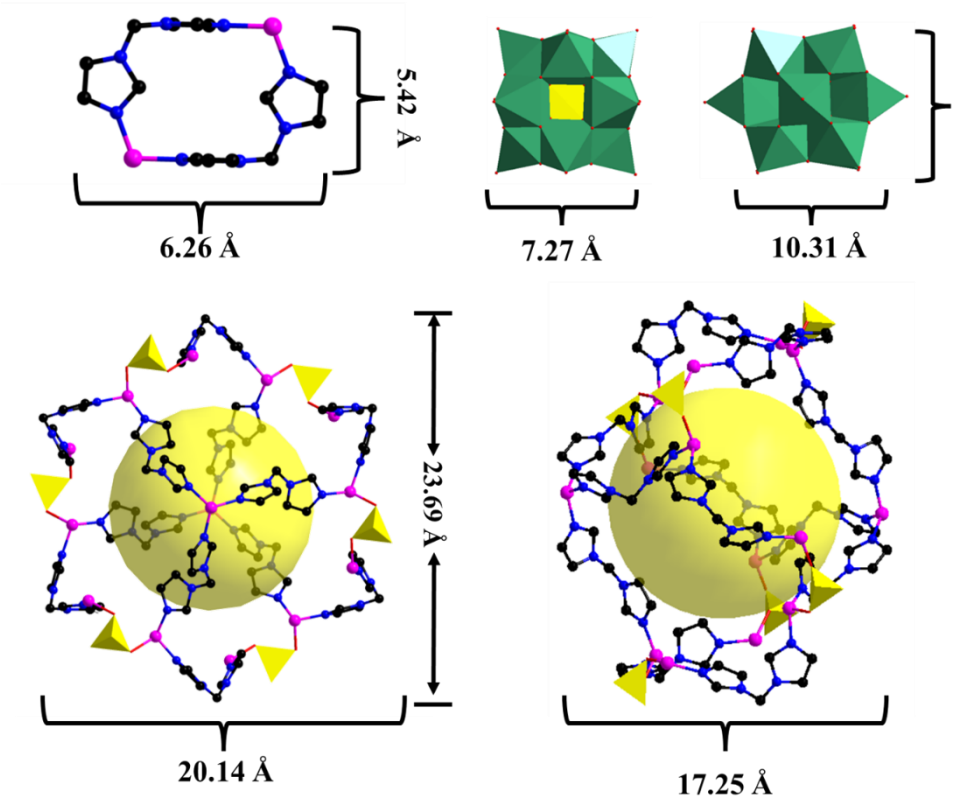

Fig. S4 Size perspective of the assembled structure for **Co-PO_4-PW_{12}**.

Section 2. Characterizations

$CoCl_2 \cdot 6H_2O$ (AR, ≥ 99.0%) and Na_2HPO_4 (AR, ≥ 99.0%) were bought from Sinopharm Chemical Reagent Co., Ltd. [Ru(2,2'-bipyridine)$_3$]$Cl_2 \cdot 6H_2O$ (98.0 %) was bought from Aladdin. Triethanolamine (AR, ≥78.0 %) and acetonitrile (AR, ≥ 99.8%) were purchased from Shanghai Ling Feng chemical agent Ltd. Nafion solution (5 wt %) was purchased from Sigma-Aldrich. Carbon dioxide (CO_2, 99.999%) gas was supplied by Jiangsu Tianhong Chemical Co.,Ltd, the $^{13}CO_2$ (99%) was purchased from Guangzhou Puyuan Gas Co., Ltd.

2.1 Materials and Physical property studies.

Powder X-ray diffraction (PXRD) data of **Co-PO_4-PW_{12}** was carried out on Smartlab TM 9KW diffractometer using Cu Kα radiation (λ = 1.54056 nm), and the range was 5 to 50°. FT-IR spectrums were performed on Nicolet 470 FTIR spectrometer with KBr pellets in the 400-4000 cm^{-1} range. Thermogravimetric (TG) curve was completed on STA449F3 thermogravimetric analyzer in N_2 atmosphere with a heating rate of 10 °C/min. The UV-vis diffuse reflectance spectra were investigated via SHIMADZU UV-2600 spectrophotometer,

and the wavelength was in range of 200-800 nm. The SEM were identified by using a Hitachi TM 3000 scanning electron microscope at an accelerating voltage of 20 kV. Elemental analyses (C, N and H) were determined by a Perkin-Elmer 2400 elemental analyzer.

2.2 Preparation of $[Co_4(PO_4)(C_7H_8N_4)_6](PW_{10}W^V_2O_{40})$

1,1′-Methylenebis(1H-imidazole) (Bim) was synthetized according to the known literature method.[1]

The following substances were dissolved in 8 mL of deionized water: $CoCl_2 \cdot 6H_2O$ (0.05 g, 0.21 mmol), $H_3PW_{12}O_{40} \cdot 18H_2O$ (0.10 g, 0.03 mmol), $C_7H_8N_4$ (Bim ligand) (0.05 g, 0.34 mmol), and Na_2HPO_4 (0.02 g, 0.14 mmol). The slurry was vigorously stirred at 25°C for 30 minutes, and then the pH was raised to 3.5 by adding 1 M hydrochloric acid, followed by 7 days of heating to 140°C. In order to gain purple polyhedral-like crystals, the autoclave was cleaned with deionized water after being cooled to room temperature. Yield: 15.64% (based on $H_3PW_{12}O_{40} \cdot 18H_2O$). Elemental analysis: experimental values: C: 12.60%, H: 1.21%, N: 8.23%; Theoretical values: C: 12.3%, H: 1.17%, N: 8.20%.

[1] X. Wang, M. M. Zhang, X. L. Hao, Y. H. Wang, Y. Wei, F. S. Liang, L. J. Xu, Y. G. Li, *Cryst. Growth Des.*, 2013, **13**, 3454-3462.

PXRD

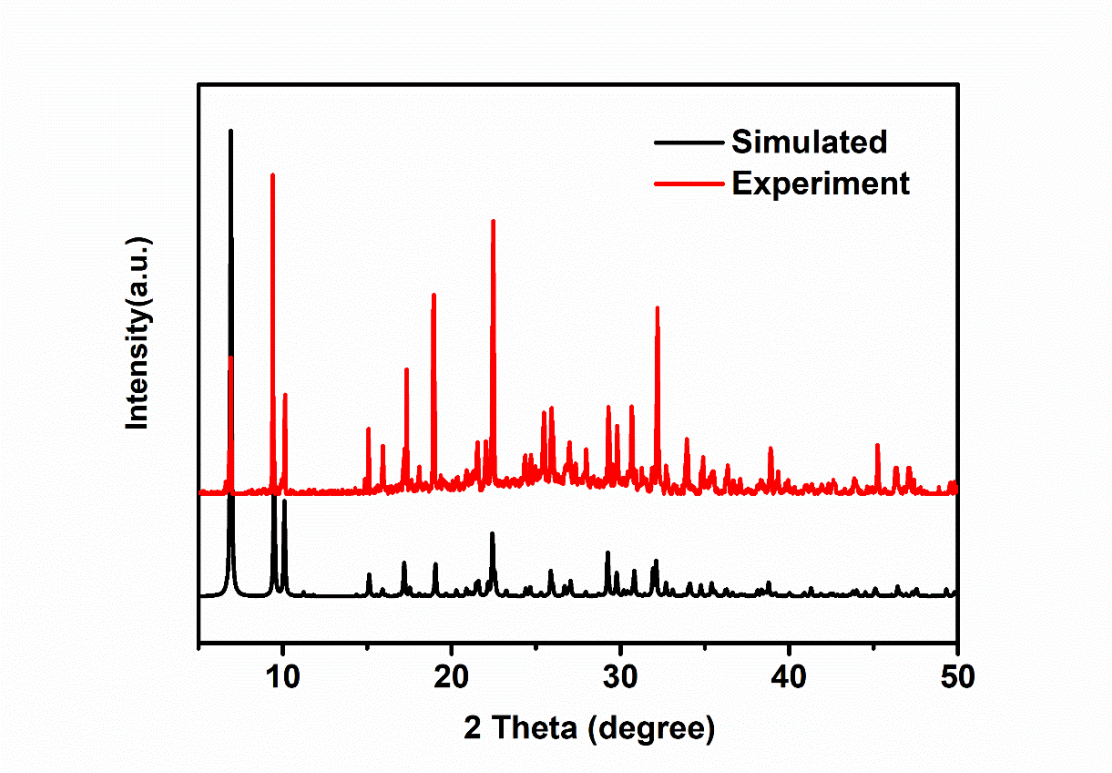

Fig. S5 The PXRD pattern of **Co-PO_4-PW_{12}**.

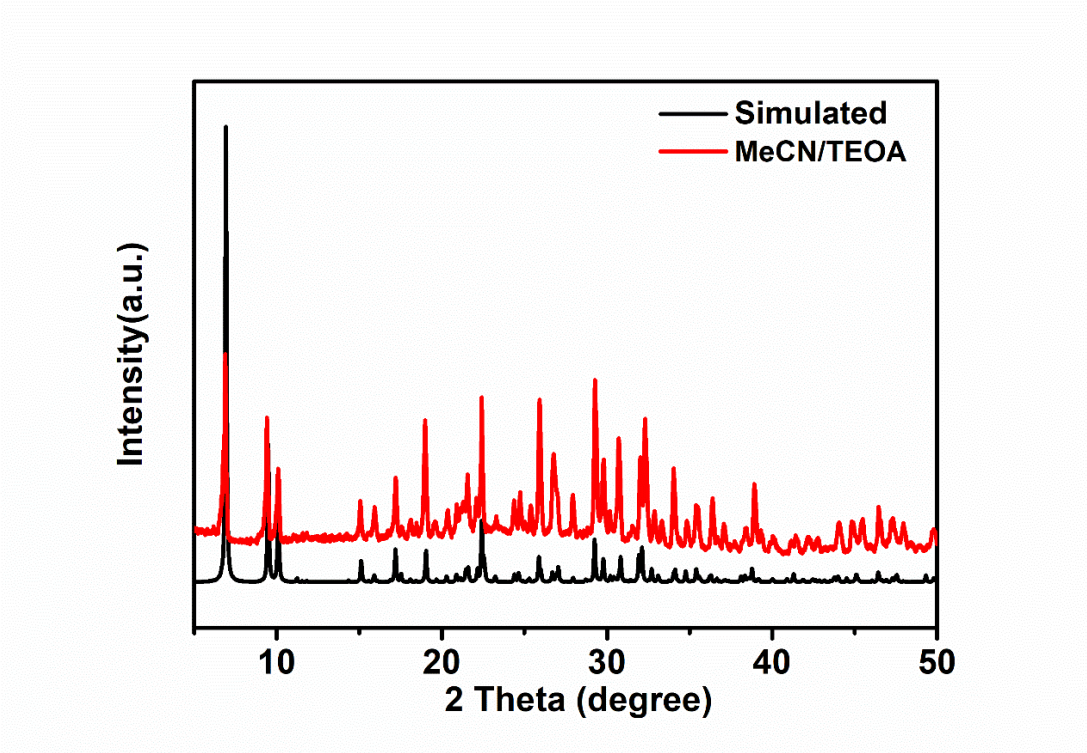

Fig. S6 PXRD patterns of 10 mg **Co-PO_4-PW_{12}** under the conditions of the specified photocatalytic reaction solution (MeCN: TEOA = 4:1 v/v, 50 mL) by soaking the samples for 24 h compared with the simulated curve.

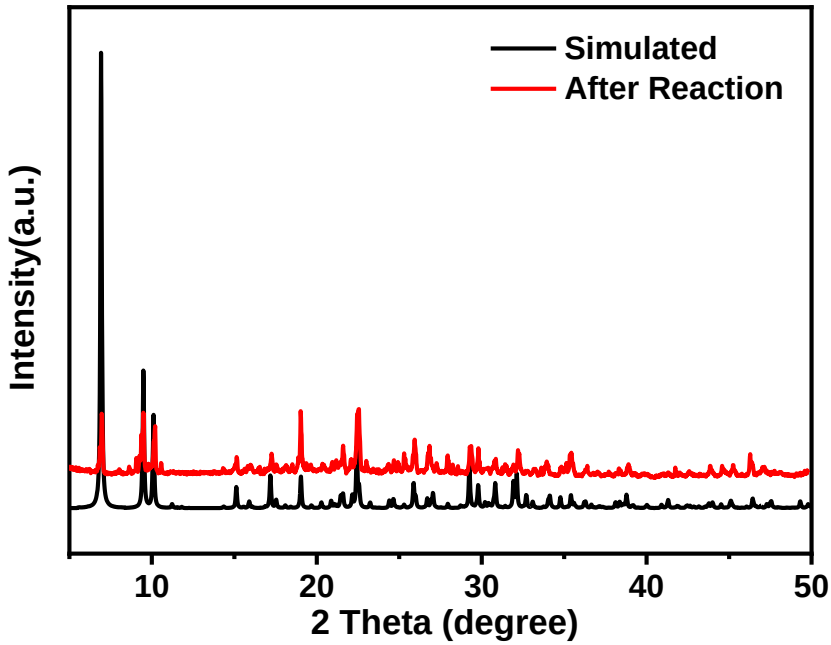

Fig. S7 PXRD of **Co-PO_4-PW_{12}** after reaction

FT-IR

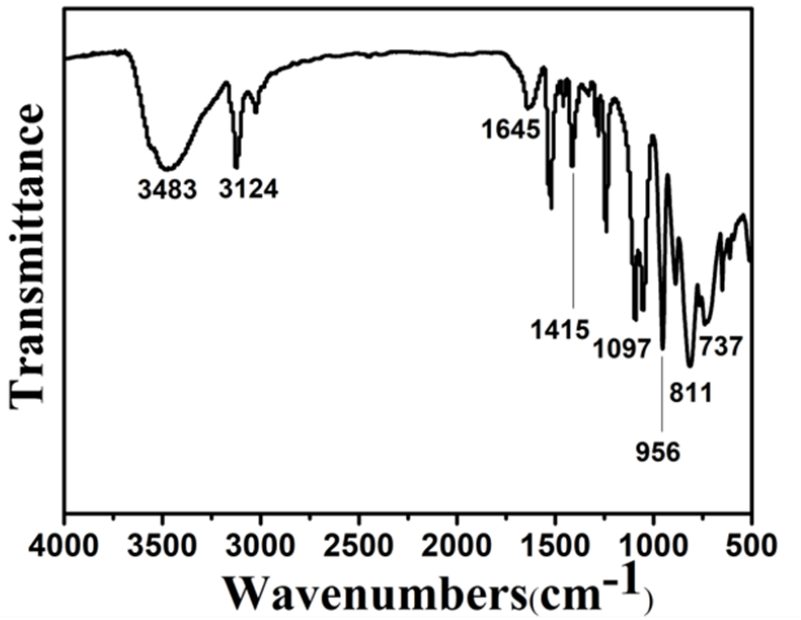

Fig. S8 The FT-IR pattern of **Co-PO$_4$-PW$_{12}$**.

TG

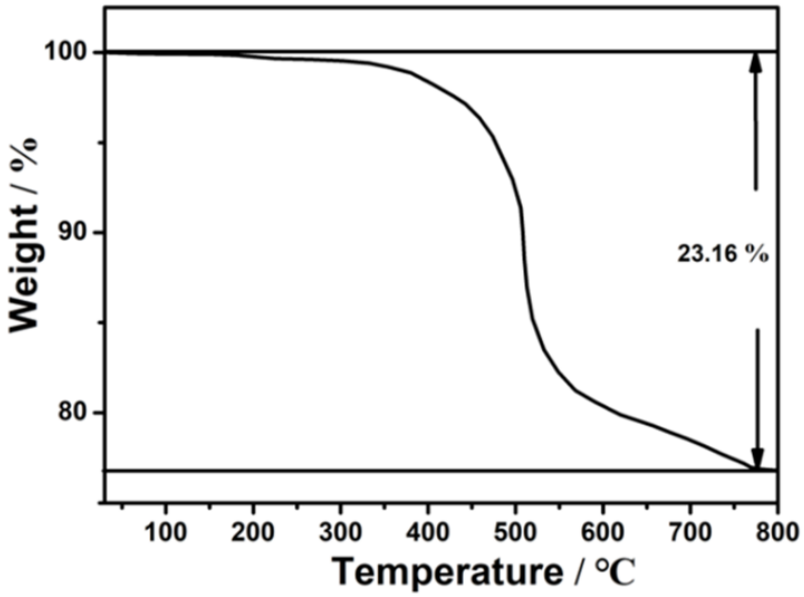

Fig. S9 The TG curve of **Co-PO$_4$-PW$_{12}$**.

XPS

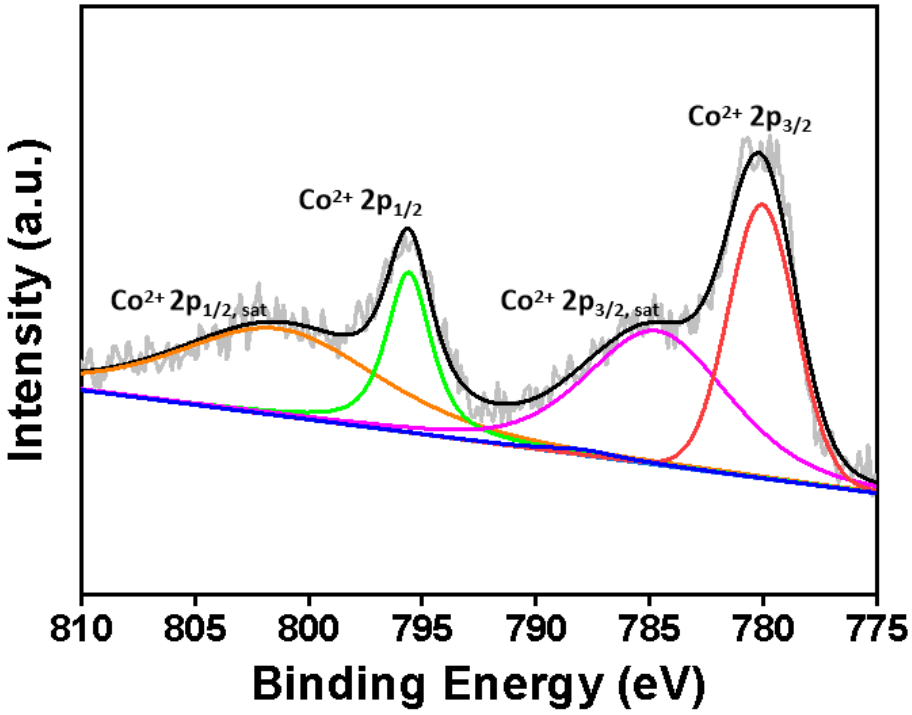

Fig. S10 The XPS spectrum of Co2p peaks for **Co-PO_4-PW_{12}**.

Section 3. The Procedure of the CO_2 Photoreduction

3.1 Electrochemical measurements.

The Mott–Schottky spots were carried out at ambient environment via using the electrochemical workstation (CHI 760e) in a standard three-electrode system: The carbon cloth (CC, 1 cm×1 cm) modified with catalyst samples, carbon rod and Ag/AgCl were used as the working electrode, counter electrode and the reference electrode, respectively. The catalyst of 5 mg was grinded to powder and then dispersed in 1 mL of 0.5% Nafion solvent by ultrasonication to form a homogeneous ink. Subsequently, 200 μL of the ink were deposited onto the carbon cloth, and dried in room temperature for Mott-Schottky spots measurements. The Mott-Schottky plots were measured over an alternating current (AC) frequency of 1000 Hz, 1500 Hz and 2000 Hz, and three electrodes were immersed in the 0.2 M Na_2SO_4 aqueous solution.

3.2 Photocatalytic CO_2 reduction experiments.

The photocatalytic performance of **Co-PO_4-PW_{12}** was evaluated by applying it to the photocatalytic reduction of CO_2 (CEL-PAEM-D8, AULTT, China). The experiments were carried out in a 100 mL Pyrex flask. A 300 W xenon arc lamp (CEL-PF300-T8, AULTT, China) (photocurrent: 15A) was employed as a visible-light source through a UV-cutoff filter with a

wavelength greater than 420 nm, which was installed 10 cm away from the reaction solution. In the system of CO_2 photocatalytic reduction, we put photocatalyst into a mixed solvent of triethanolamine (TEOA, as a sacrificial base) and acetonitrile (1:4 v/v, 50 mL), and used $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (11.3 mg) as photosensitizer. The products were analyzed by performing gas chromatography (GC7920-TF2Z, AULTT, China). The amount of CO and CH_4 was detected by FID, and the H_2 was analyzed by TCD.

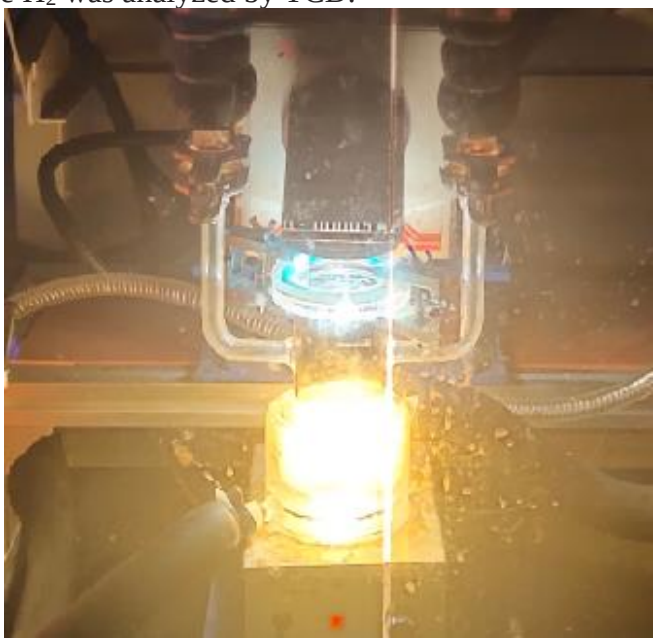

Fig. S11 The photograph of the CO_2 photoreduction devices.

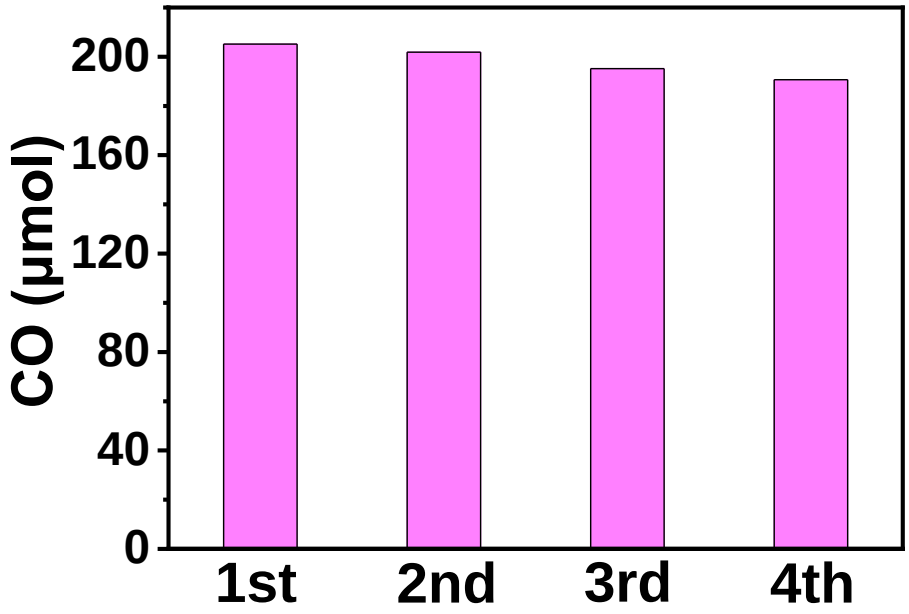

Fig. S12 The recycling experiment.

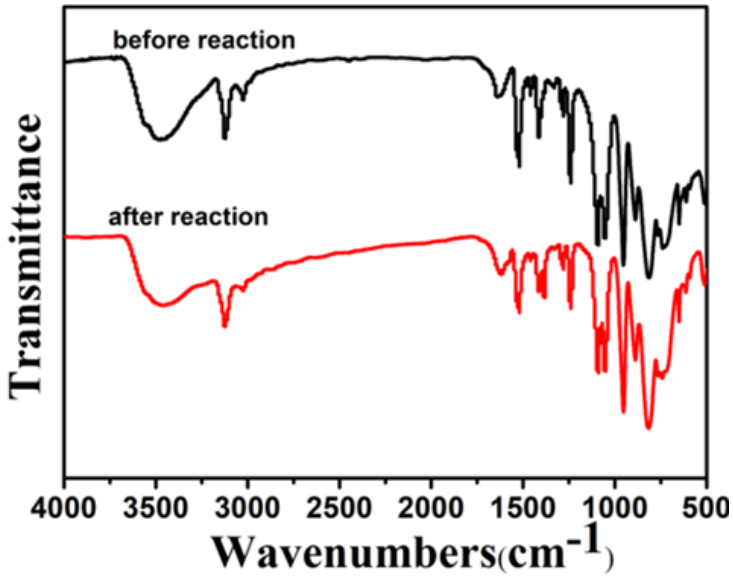

Fig. S13 The FT-IR pattern before and after the reaction.

Table S1. The comparison for the partially reported materials in CO_2 photoreduction system.

Photocatalysts	Reaction time (h)	product	Yield (μmol g^{-1})	References
$[Co_4(PO_4)(C_7H_8N_4)_6](PW_{10}W^V_2O_{40})$	5	CO	68,380	This work
1-DMF	8	CO	448	*Dalton Trans.*, **2019**, 48, 8678-8692.
Co-UiO-67	4	CO	13,170	*ACS Appl. Mater. Interfaces*, **2020**, 12, 24059-24065.
$H_{26.5}K_{2.5}Na(H_2O)_{16}[Ni_6(OH)(BO_3)_2(dien)_2(B\text{-}\alpha\text{-}SiW_{10}O_{37})_2]_2\cdot 24H_2O$	1	CO	6988	*Inorg. Chem. Front.*, **2021**, 8, 1303-1311.
$[K(H_2O)_2Fe^{II}_{0.33}Co_{0.67}(H_2O)_2(DAPSC)]_2\{[Fe^{II}_{0.33}Co_{0.67}(H_2O)(DAPSC)]_2[Fe^{II}_{0.33}Co_{0.67}(H_2O)_4]_2[Na_2Fe^{III}_4P_4W_{32}O_{120}]\}\cdot 21.5H_2O$	8	CO	55,080	*Dalton Trans.*, **2023**, 52, 9465.
$Cu_3(BTC)_2$@TiO_2	4	CH_4	11	*Adv. Mater.*, **2014**; 26: 4783–4788.

TiO_2-Mg-CPO-27	10	CH_4 CO	40.9 23.5	*Appl.Catal. B Environ.,* **2016**; 183: 47-52.
MOF-525	6	CH_4 CO	37 384	*Angew. Chem. Int. Ed.*, **2016**; 55: 14310 – 14314.
MOF-525-Zn	6	CH_4 CO	70 670	
MOF-525-Co	6	CH_4 CO	221 1204	
ZrPP-1-Co	15	CH_4 CO	8 210	*Adv. Mater.*, **2017**, 1704388.
TiO_2-Co-ZIF-9	10	CO CH_4 H_2	88 20 26	*J. Mater. Chem. A* **2016**; 4: 15126.
CNNS-UiO-66(Zr)	6	CO	17.4	*Adv. Funct. Mater.* **2015**; 25: 5360.
g-C_3N_4-Co-ZIF-9	2	CO H_2	990 157.2	*Phys. Chem. Chem. Phys.* **2014**; 16, 14656.
[Ru(bpy)$_3$] Cl_2-Co-ZIF-9	0.5	CO H_2	20.9 15.0	*Angew. Chem., Int. Ed.* **2014**; 53, 1034.
[Ru(bpy)$_3$] Cl_2-Zn-ZIF-8	0.5	CO H_2	1.0 1.2	
[Ru(bpy)$_3$] Cl_2-Co-ZIF-67	0.5	CO H_2	29600 14800	*Phys. Chem. Chem. Phys.* **2014**; 16, 14656.
[Ru(bpy)$_3$]Cl_2-MOF-253-Ru(5,5′-dcbpy) $(CO)_2Cl_2$	8	CO H_2 $HCOO^-$	548 382.4 1646.4	*Chem. Commun.* **2015**; 51, 2645.

Table S2 Sectional crystal data and structure refinements for **Co-PO_4-PW_{12}.**

Formula	$C_{42}H_{48}Co_4N_{24}O_{44}P_2W_{12}$
Formula weight	4096.90
T (K)	296 (2)
Crystal system	Trigonal
Space group	*R*-3
a (Å)	17.545(2)
b (Å)	17.545(2)

c (Å)	23.684(4)
β (°)	90
V (Å^3)	6313.6(17)
Z	3
D_c (mg m^{-3})	3.233
μ (mm^{-1})	17.223
F (000)	5538
θ range (°)	1.592-27.330
Crystal size (mm^3)	0.20 × 0.13 × 0.10
Limiting indices	$-22 \le h \le 22$, $-21 \le k \le 22$, $-30 \le l \le 28$
Reflections collected	16640
R(int)	0.1418
Data / parameters	3006/293
GOF on F^2	1.069
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	$R_1 = 0.0517$, $wR_2 = 0.1358$
R_1, wR_2 (All data)	$R_1 = 0.0706$, $wR_2 = 0.1519$

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.