Electronic Supplementary Information

A CO₂ photo-reduction heterogeneous cobalt-based cocatalyst by *in-situ* electrostatic adsorption–deposition

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1 Experimental

1.1 Acid treatment of Pal

The palygorskite (Pal) used in this work was obtained from Xuyi, Jiangsu province of China, and was treated with 5% hydrochloric acid with constant stirring for 24 h to remove carbonate cements. Then, it was washed with distilled water until neutralization, and dried in a muffle furnace at 100 \degree to constant weight.

1.2 Preparation of the Co/Pal samples

The Co/Pal catalysts were prepared and the standard processes are as follows: 1.46 mmol CoCl₂·6H₂O and 1.0 g acid activated Pal were dispersed into ethanol with constant stirring until natural withering. Then the gray powder was dried and calcined at a certain temperature for 4 h and then washed, dried and fully grinded. Two different Co/Pal catalysts were prepared as mentioned method by varying the calcination temperature and recorded as Co/Pal-300 and Co/Pal-600. As a comparison, similar to Co/Pal-300, the Co/Pal-300-s was obtained via changing calcination time to one hour.

1.3 Characterization of the samples

X-ray diffraction (XRD) data were collected using a Bruker D8 Advance X-ray diffractometer (Cu K1 irradiation, λ =1.5406Å). A Vario MICRO was used to conduct the elemental analysis of samples. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were manipulated on iCAP 7400. The morphology of the samples was investigated using a Hitachi New Generation SU8010 field emission scanning electron microscope (SEM). Transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectrum, selected area electron diffraction (SAED) and the corresponding elemental analysis of the samples were obtained on a FEI Tencai 20 microscope. The nitrogen adsorption-desorption isotherms were collected at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyzer. CO₂ sorption tests were conducted

on a Micromeritics ASAP 2020 at 273 K. The temperature programmed desorption of CO_2 (TPD-CO₂) tests were carried out on a ChemBET Pulsar TPR/TPD analyzer (Quantachrome Instruments U.S.). Zeta potential of the samples was measured on a Malvern Zetasizer Nano ZS. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCA Lab250 spectrometer which consists of a monochromatic Al K α as the X-ray source. All the binding energies were calibrated by the C1s peak at 284.6 eV. UV-Vis diffuse reflectance spectra (DRS) were collected using a Varian Cary 500 UV-Vis-NIR spectrometer. The room temperature photoluminescence (PL) characterizations were carried out on an EdinburghFI/FSTCSPC 920 spectrophotometer.

1.4 Photocatalytic Test

In a typical photocatalytic CO₂ reduction reaction, photosensitizer $[Ru(bpy)_3]Cl_2•6H_2O$ (bpy=2'2-bipyridine) (9 mg), co-catalyst (1 mg), solvent (5 mL, acetonitrile/H₂O = 4:1), and triethanolamine (TEOA) (1 mL) were added into a gas-closed quartz glass reactor (80 mL in volume). The reaction system was filled with high purity CO₂ gas (1 atm). A 300 W Xe lamp was used as the light source with the incident light controlled by a 420 nm long-pass cutoff filter, and the irradiation window of the reactor was ca. 6 cm². Cooling water was employed to keep the reaction temperature at 25 °C. During photocatalysis, the reaction system was energetically stirred. After reaction, the generated gaseous products (CO and H₂) were sampled and quantified by the GC.

1.5 Measurements

Products of CO₂ photoreduction were analyzed by an Agilent 7890A gas chromatograph (GC; thermal conductivity detector, TCD; TD-01 packed column; oven temperature, 50 °C; inlet temperature, 120 °C; detector temperature, 200 °C). Ar was used as the carrier gas (13 ml min⁻¹). The CO gas produced from ¹³CO₂ isotope experiments was examined by a gas chromatograph–mass spectrometer (GC-MS, SHIMADZU QP2020). The equipped column in GC-MS analysis was SH-Rtx-Wax (SHIMADZU, 30 m × 0.25 m × 0.25 µm, serial number: 1435420). The temperatures of the inlet and oven were 200 and 30 °C, respectively. Helium (He) was used as a carrier gas (0.6 mL min⁻¹).



Fig. S1 XRD patterns of the samples (a) Pal, (b) Co/Pal-300 and (c) Co/Pal-600

Table S1. The elemental quantitative analysis of Pal and Co/Pal samples

Samples	Mg (wt.%)	Al (wt.%)	Fe (wt.%)	Co (wt.%)
Pal	2.89	1.87	1.27	-
Co/Pal-300	2.81	1.73	1.41	6.86
Co/Pal-600	3.54	3.15	2.07	4.78



Fig. S2 Morphology analysis for Pal and Co/Pal samples. (a) TEM of Pal, (b) TEM of Co/Pal-300-s, (c)

TEM, (d) EDX pattern and (e) HAADF-STEM and EDX mapping images of Co/Pal-600.



Fig. S3 N_2 adsorption-desorption analysis at 77K



Fig. S4 CO₂ adsorption isotherm at 273K

Table S2 A comparison of porosity properties of hierarchically micro- and mesoporous Co/Pal cocatalysts

Cocatalyst	$S_{BET} [m^2 g^{-1}]^a$	$S_{micro} \left[m^2 g^{-1}\right]^b$	$\mathbf{S}_{\mathrm{micro}}^{}/\mathbf{S}_{\mathrm{meso}}^{}^{}$ b	$V_{meso} [cm {}^3g^{-1}]^c$	$V_s [cm^3 g^{-1}]^d$	Mesopore diameter
Pal	115	16.3	0.164	0.183	0.179	6.22
Co/Pal-300	97.8	22.3	0.295	0.244	0.155	6.33
Co/Pal-600	38.9	0.31	0.008	0.203	0.109	11.19

[a] S_{BET} is the BET surface area. [b] S_{micro} is the t-plot micropore surface area calculated from the N_2 adsorption–desorption isotherm. S_{meso} is the mesopore surface area estimated by subtracting S_{micro} from S_{BET} . [c] V_{meso} is the mesopore volume obtained from the BJH cumulative specific adsorption volume of pores of 1.70 to 300.00 nm in diameter. [d] V_s is the single point adsorption total pore volume of pores less than 40.3122 nm diameter at P/P_o = 0.95. [e] The mesopore diameter is BJH adsorption average pore diameter (4 V/A).



Fig. S5 TPD-CO₂ profiles of (a) Pal, (b) Co/Pal-300 and (c) Co/Pal-600



Fig. S6 Zeta potential plots of the Pal and Co/Pal samples

Entry	Samples	CO [µmol]	H ₂ [µmol]	CO+H ₂ [µmol]	CO Selectivity (%)
1^{b}	-	nd ^e	nd	-	-
2^{c}	-	nd	nd	-	-
3 ^d	-	nd	nd	-	-
4^{f}	-	1.50	0.45	1.95	76.9
5	Pal	1.19	0.41	1.60	74.3
6	Pal-L	1.63	0.58	2.21	73.7
7 ^g	CoO _x	3.42	1.33	4.75	72.0
8	Co/Pal-300	33.4	13.7	47.1	74.7
9	Co/Pal-300-s	36.8	15.7	52.5	70.1
10	Co/Pal-600	12.3	4.33	16.63	73.9
11 ^h	Co/Pal-300	nd	3.06	-	-

Table S3 The research of reaction conditions^a

[a] Reaction conditions: $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (9 mg), Cocatalyst (1.0 mg), solvent (5 mL, acetonitrile/H₂O=4:1), TEOA (1 mL), CO₂ (1 atm), $\lambda \ge 420$ nm, 30 ° C, 1 h. [b] In the dark. [c] Without $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$. [d] Without TEOA. [e] Not detectable. [f] Without Cocatalyst. [g] CoO_x was obtained from the direct calcination of CoCl₂ • 6H₂O. [h] Ar (1 atm)



Fig. S7 Mass spectra (m/z = 29) analysis of the carbon source of the generated CO in the photochemical reduction of 13 CO₂.



Fig. S8 CO and H₂ generated from the CO₂ photoreduction, production plots for photosensitizer



Fig. S9 CO and H₂ generated from the CO₂ photoreduction, production plots for cocatalyst





Fig. S11 Plausible mechanism for photo-reduction CO₂-to-CO based on Ru(bpy)₃Cl₂ and Co/Pal-300