

Supporting Information

Selective Photocatalytic CO₂ Reduction by Cobalt Dicyanamide

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Table S1 ATR- FTIR data of **Co-dca** sample.

| Vibration | Wavenumber (cm ⁻¹) |
|---|--------------------------------|
| $\delta(\text{N}-\text{C}\equiv\text{N})$ | 502 |
| $\gamma(\text{N}-\text{C}\equiv\text{N})$ | 526 |
| $\delta(\text{N}-\text{C}\equiv\text{N})$ | 681 |
| $\nu(\text{N}-\text{C})$ | 963 |
| $\nu(\text{N}-\text{C})$ | 1314 |
| $\nu(\text{C}\equiv\text{N})$ | 2207 |
| $\nu(\text{C}\equiv\text{N})$ | 2270 |

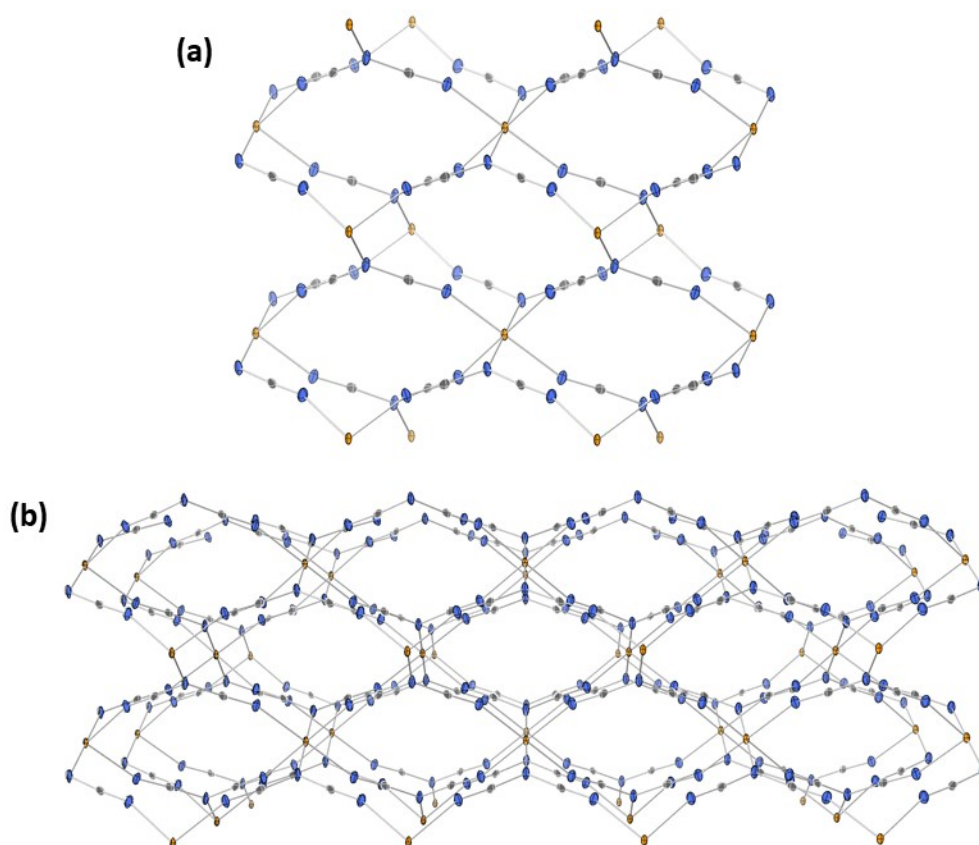


Fig. S1 (a) 3D structure, and (b) perspective view of Co(dca)_2 (Color code: Co = orange; C = gray; N = blue).

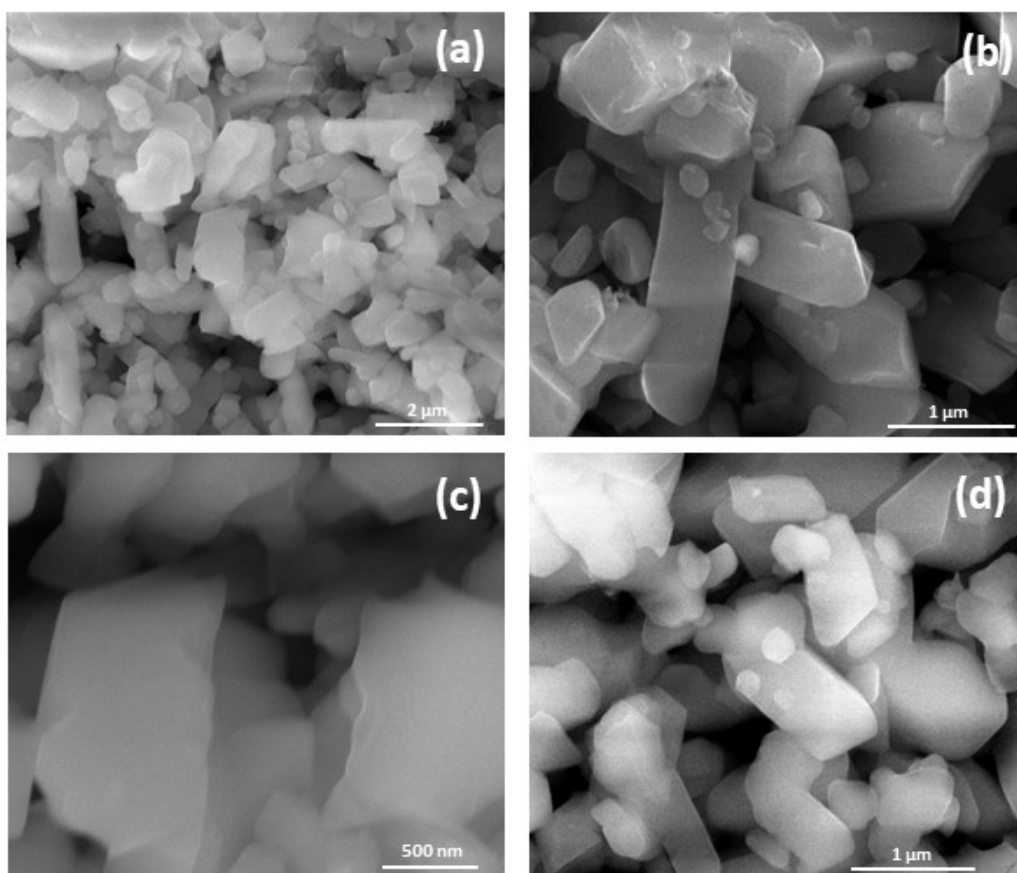


Fig. S2 (a-d) SEM images of **Co-dca**.

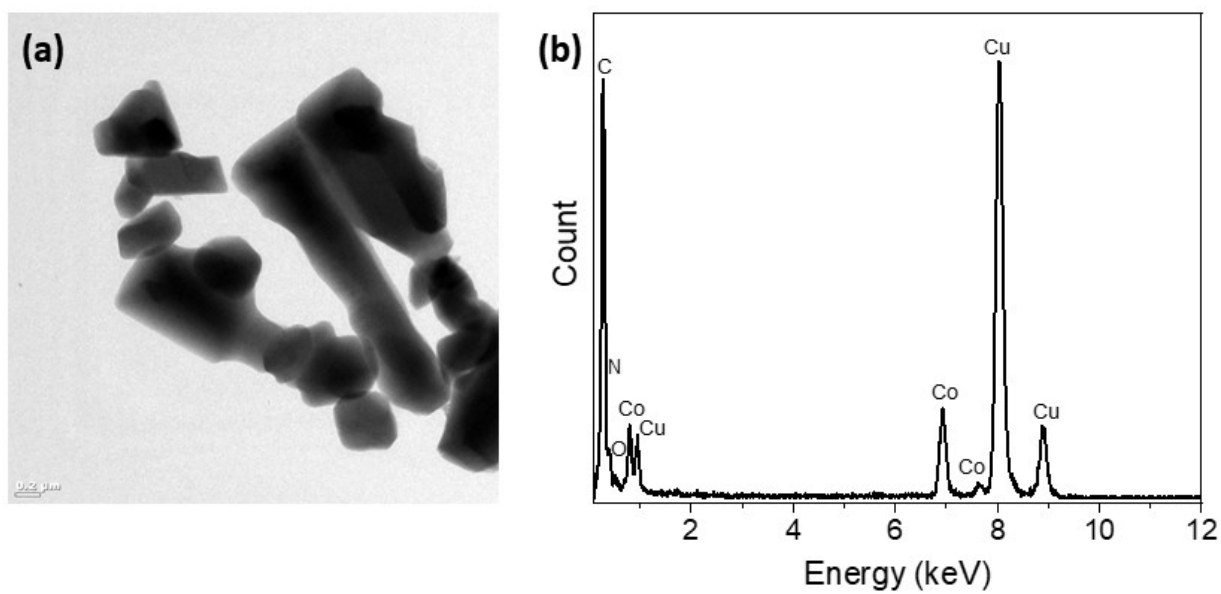


Fig. S3 (a) TEM image and (b) EDS elemental analysis of **Co-dca**. The signal for Cu is from the TEM grid.

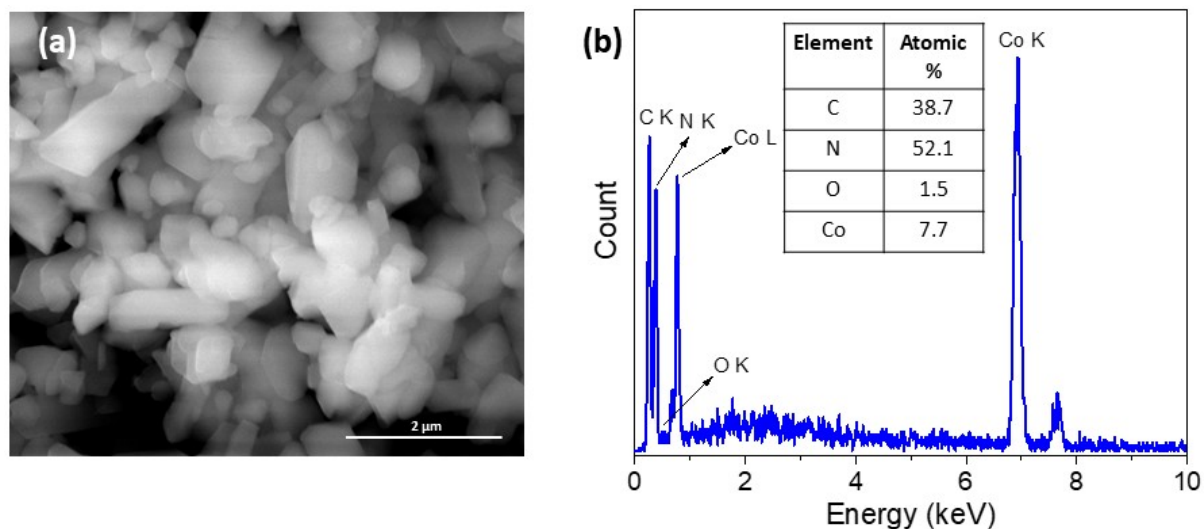


Fig. S4 (a) SEM image and (b) SEM-EDS analysis of **Co-dca**. Inset: The atomic ratio of all elements for the **Co-dca**.

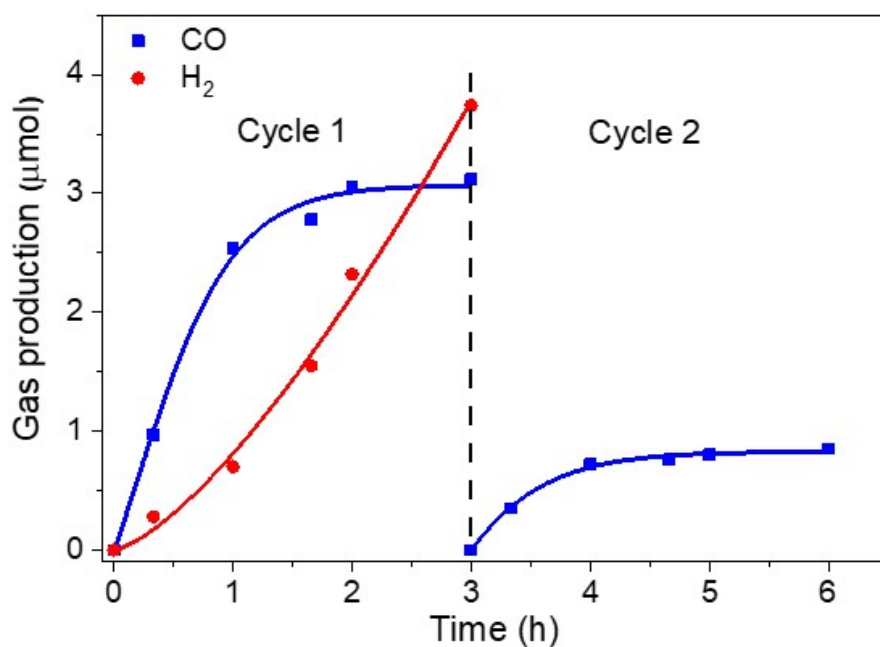


Fig. S5 (a) Yields of H₂ and CO from the CO₂ under visible light irradiation over 2 cycles. Reaction conditions: 10 mg **Co-dca**, 3.74 mg [Ru(bpy)₃]Cl₂·6H₂O (0.5 mM), 8 mL acetonitrile, 2 mL TEOA, 25 °C, 30 min purging with CO₂, under visible light irradiation ($\lambda > 420$ nm). After the first cycle, the catalyst was dispersed in a fresh solution, and 3.74 mg of Ru photosensitizer was added.

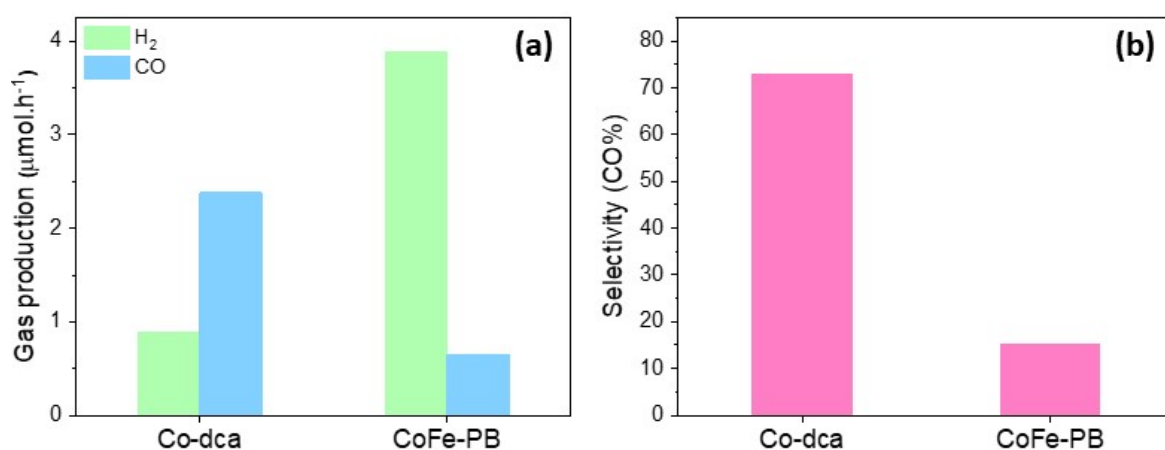


Fig. S6 Comparison of (a) the photocatalytic CO and H_2 evolution activity and (b) corresponding selectivity of photocatalytic CO_2 to CO conversion over H_2 evolution of **Co-dca** and CoFe-PB. Reaction conditions: 10 mg catalyst, 7.48 mg $[\text{Ru}(\text{bpy})_3]\text{Cl}_2\cdot 6\text{H}_2\text{O}$ (1 mM), 8 mL acetonitrile, 2 mL TEOA, 25 $^\circ\text{C}$, 30 min purging with CO_2 , under visible light irradiation ($\lambda > 420 \text{ nm}$).

Preparation of CoFe-PB: For the synthesis of CoFe-PB, $\text{K}_3[\text{Fe}(\text{CN})_6]$ (2 mmol) was dissolved in deionized water (20 mL), then an aqueous solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (3 mmol in 20 mL water) was added to the above solution at room temperature. The obtained slurry was stirred for 1 h and collected by centrifugation after rinsing with water. The obtained solid was dried at 75 $^\circ\text{C}$.

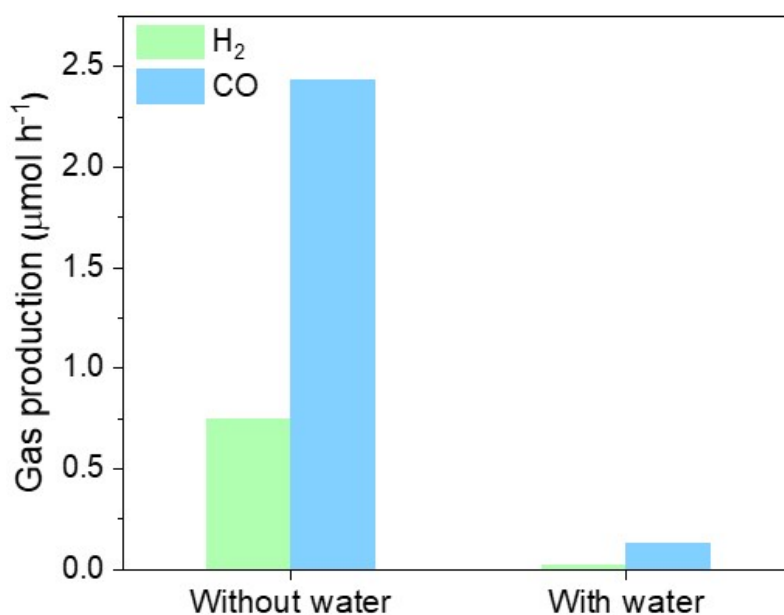


Fig. S7 Photocatalytic CO_2 reduction activity of **Co-dca** sample without water (MeCN/TEOA, 4/1, v/v) and with water (MeCN/ H_2O /TEOA, 3/1/1, v/v/v).

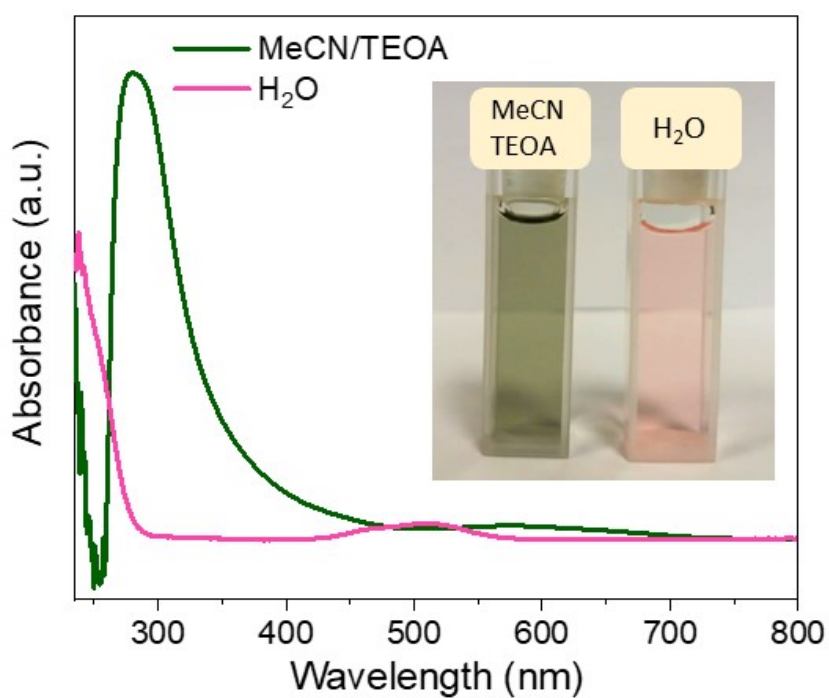


Fig. S8 The UV-Vis absorption spectra of **Co-dca** (10 mg) in MeCN/TEOA and H₂O solutions. Inset: **Co-dca** powder dissolved in MeCN/TEOA and H₂O solutions.

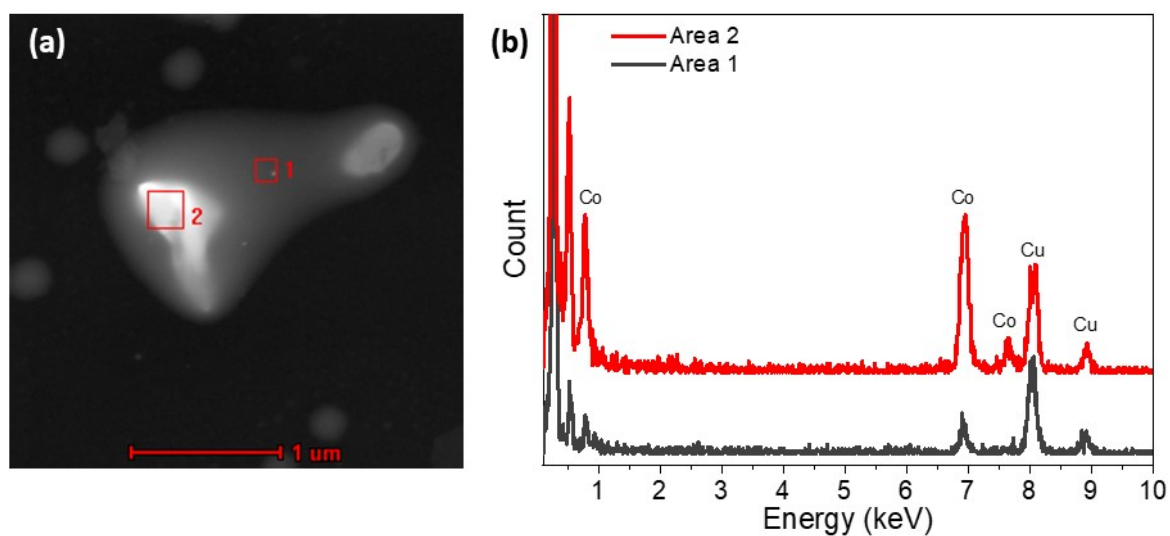


Fig. S9 (a) HAADF-STEM images of **Co-dca** for post-catalytic sample. (b) EDS elemental analysis of selected areas. The signal for Cu is from the TEM grid.

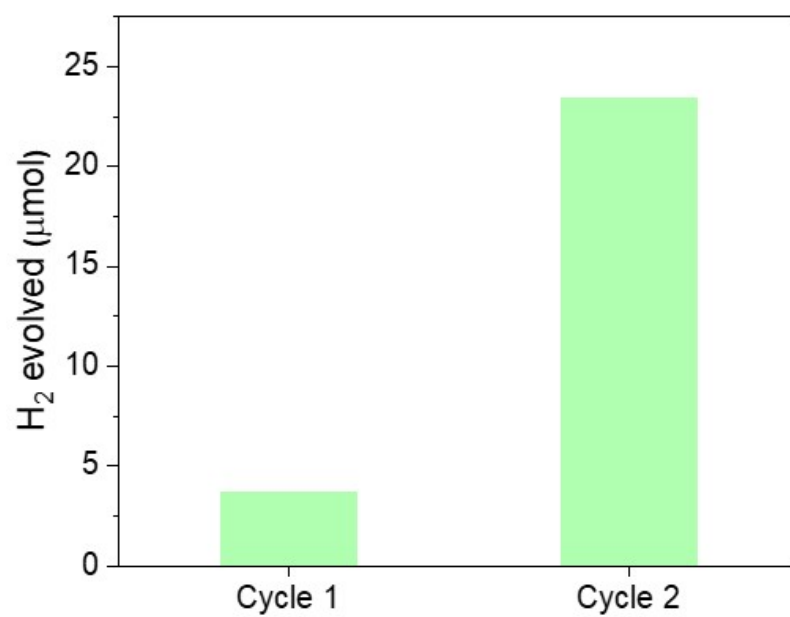


Fig. S10 The amount of H₂ evolved during the first and second cycles.