Supplementary Information (SI) for ChemComm.

Supporting information

Rational Design of N-Heterocyclic COF-Based Photocatalysts: Synergistic Metal-Ligand Coordination for Efficient H_2O_2 Production

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1. Experimental Procedures

1.1 Materials

The reagents 2,4,6-triformylphloroglucinol (Tp, 97%) and p-phenylenediamine (Pd, 99%) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Pyridazine-3,6-diamine (Dz, 98%), 1,4-dioxane (99%), and 1,3,5-trimethylbenzene (97%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Analytical-reagent (AR) grade glacial acetic acid (HAc), GR grade phosphoric acid (H_3PO_4), AR grade sulfuric acid (H_2SO_4), and AR grade hydrochloric acid (HCl) were sourced from Sinopharm Chemical Reagent Co., Ltd., as were the chemically pure (CP) grade potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6]$), potassium ferrocyanide trihydrate ($K_4[Fe(CN)_6]\cdot 3H_2O$), AR grade Cadmium chloride ($CdCl_2\cdot 2.5H_2O$), AR grade potassium chloride (KCl), AR grade iron(II) sulfate heptahydrate ($FeSO_4\cdot 7H_2O$), AR grade sodium sulfate (Na_2SO_4), AR grade silver nitrate ($AgNO_3$), AR grade absolute ethanol (CH_3CH_2OH), AR grade acetone (CH_3COCH_3), AR grade tetrahydrofuran (THF), and AR grade 30% aqueous hydrogen peroxide (H_2O_2). All reagents were used as received without further purification.

1.2 Synthesis of COF and Cd-COF

The covalent organic framework (COF) was synthesized via a modified solvothermal method. Specifically, 1,3,5-triformylphloroglucinol (Tp, 0.9 mmol, 190 mg) and pyridazine-3,6-diamine (Dz, 1.35 mmol) were added to a 20 mL Teflon-lined stainless steel autoclave. Mesitylene (3 mL), 1,4-dioxane (3 mL), and 3 M acetic acid (1 mL) were introduced as solvents and catalysts, respectively. The mixture was subjected to ultrasonication for 20 min to ensure homogenous dispersion prior to sealing and heating at 120 °C for 72 h. The resulting brown precipitate was isolated via filtration, washed repeatedly (five times) with acetone, and dried under vacuum at 60 °C for 12 h, yielding the COF as a brown powder. The COF was synthesized using an analogous procedure, substituting p-phenylenediamine for pyridazine-3,6-diamine. In addition, Cd-COF photocatalytic materials were prepared by adding different moles of $CdCl_2 \cdot 2.5H_2O$ according to the above synthesis method

1.3 Photosynthesis of H_2O_2

Photocatalytic activity was evaluated using a 300 W CEL-HXF300-(T3) xenon arc lamp (Beijing China Education Au-Light Technology Co., Ltd.) fitted with a UV cutoff filter ($\lambda \geq 420$ nm). Suspensions were prepared by dispersing 15 mg of photocatalyst in 125 mL of ultrapure water within a sealed glass reactor equipped with a rubber septum. Prior to irradiation, the reactor contents were purged with O_2 for 20 min to ensure oxygen saturation. For experiments conducted under ambient atmospheric conditions, the O_2 purge was replaced with an air purge. Hydrogen peroxide concentration was determined via a colorimetric method utilizing the Fe^{2+}-activated oxidation of N,N-diethyl-p-phenylenediamine (DPD) to a chromophoric radical cation. Specifically, 0.8 mL aliquots were withdrawn at designated intervals, filtered through a 0.22 μm membrane to remove the catalyst, and subsequently mixed with a predetermined volume of DPD solution containing 5 mM H_2SO_4. The absorbance of the resulting solution at 551 nm was measured using a Unico UV-2800A UV-Vis spectrophotometer against a calibration curve generated from solutions of known H_2O_2 concentration ($y = 1.01546x+0.03223$, $R^2 = 0.992$). The concentration of generated H_2O_2 was determined using the established calibration curve.

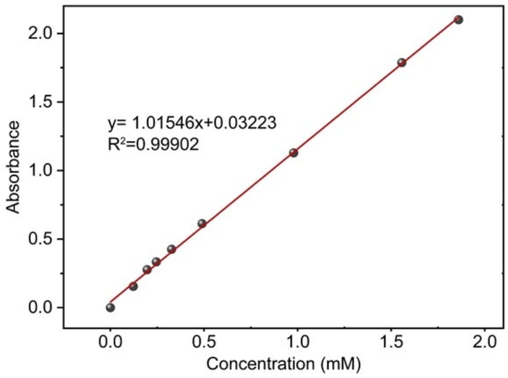

Fig. S1 Standard curve of H_2O_2

1.4 Characterization

The morphology and microstructure were studied by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F). The UV-visible absorption spectrum (UV–vis) was measured using a Shimadzu UV-2600 spectrometer, and $BaSO_4$ was selected as the reference sample. The phase and chemical composition were investigated by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C), X-ray diffraction (XRD, D/MAX2500PC) with Cu Kα (λ=1.5406 Å) at 40 kV and 150 mA, and Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50). Nitrogen sorption/desorption curves were obtained using Quantachrome NOVA 3000e. Furthermore, to evaluate the optical and electrochemical performance, we used photoluminescence (PL, FLS 980), an electrochemical workstation (CHI-760E) with a three-electrode syste.

2. Figures

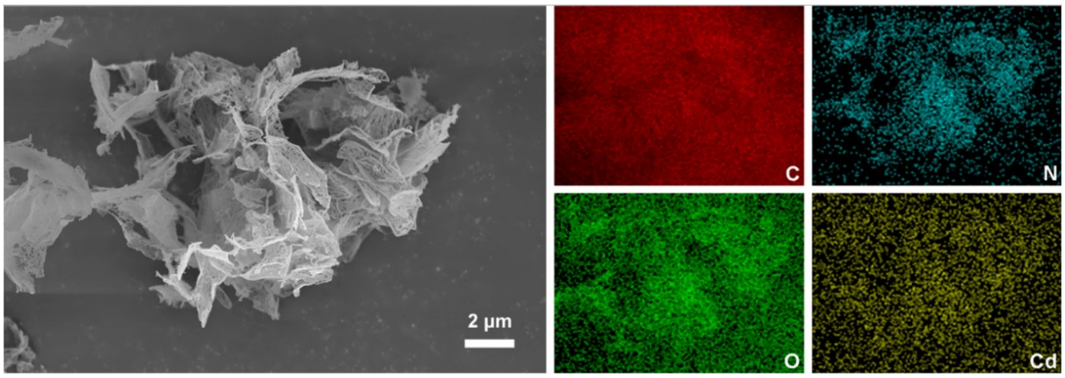

Fig. S2 EDS of Cd-COF

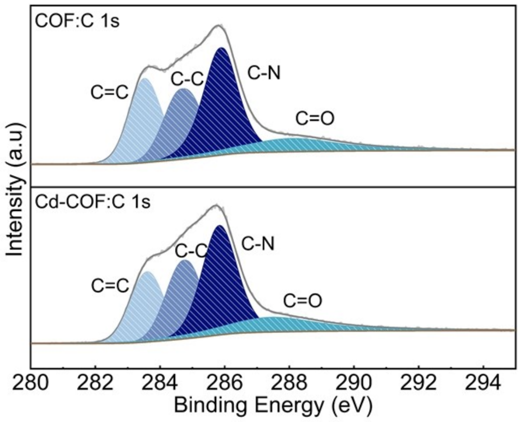

Fig. S3 XPS spectra of COF and Cd-COF

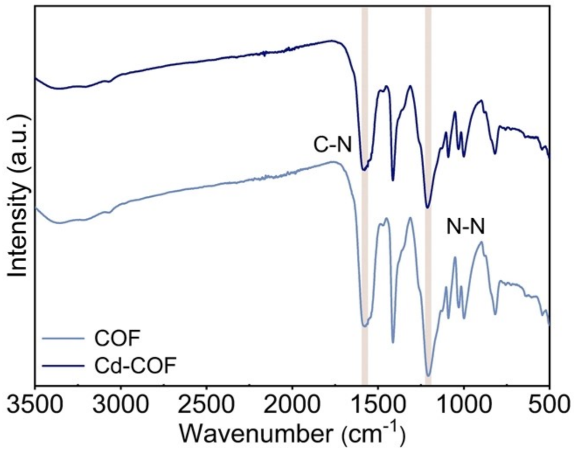

Fig. S4 FTIR spectra of COF and Cd-COF

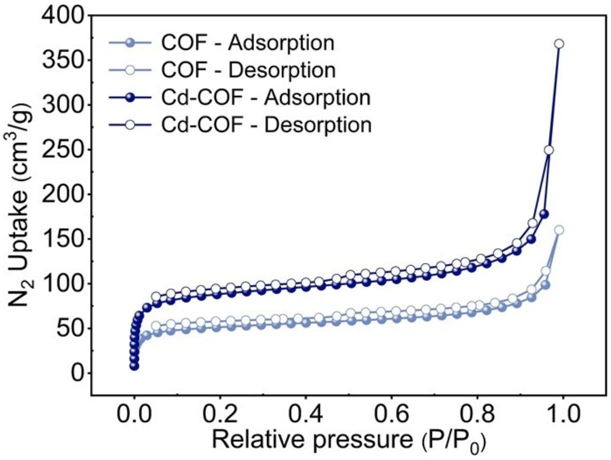

Fig. S5 N_2 sorption isotherms at 77 K of COF and Cd-COF

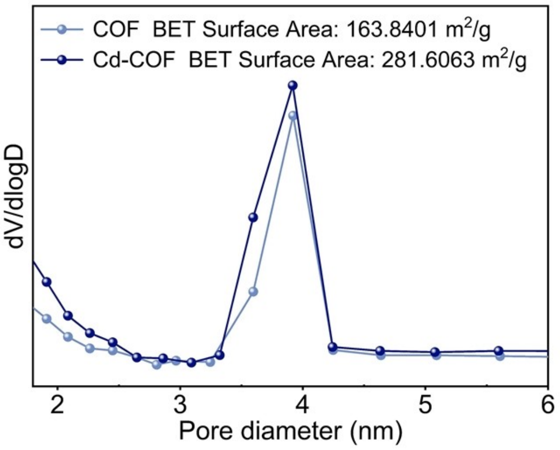

Fig. S6 Pore diameter of COF and Cd-COF

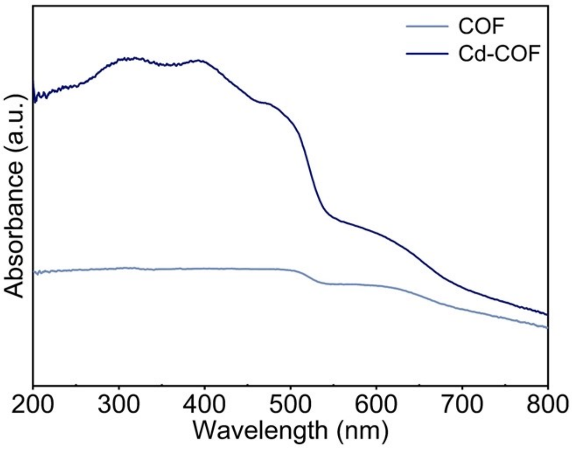

Fig. S7 UV−vis absorption spectra of COF and Cd-COF

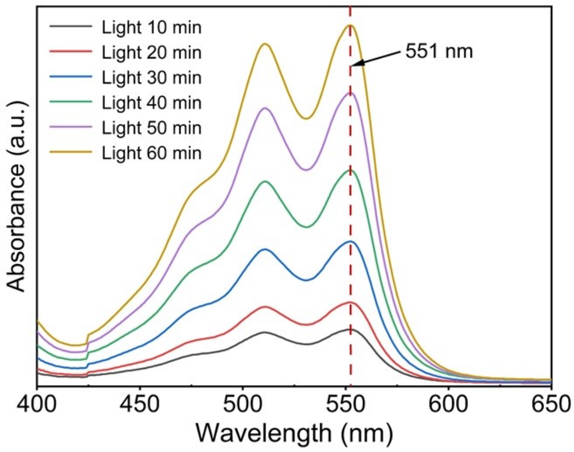

Fig. S8 The UV absorption spectrum of photocatalytic production of H_2O_2 for Cd-COF

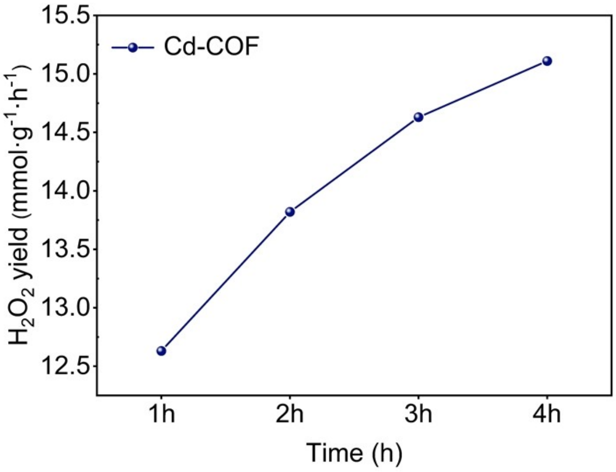

Fig. S9 Long-term photocatalytic activity of Cd-COF

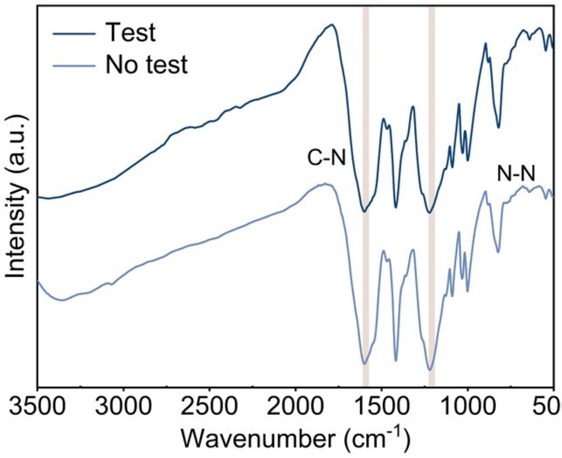

Fig. S10 FTIR of Cd-COF before and after catalytic reaction

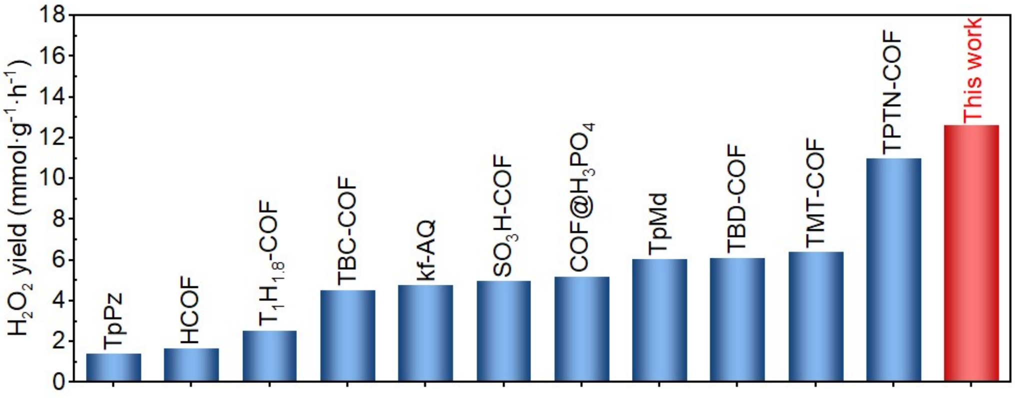

Fig. S11 Comparison with other COF for H_2O_2 production

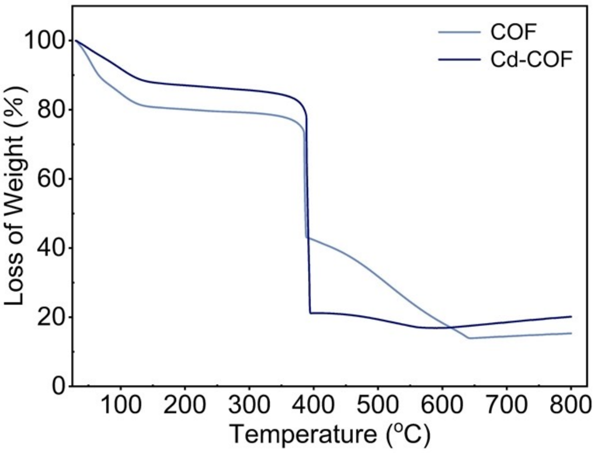

Fig. S12 TG of COF and Cd-COF

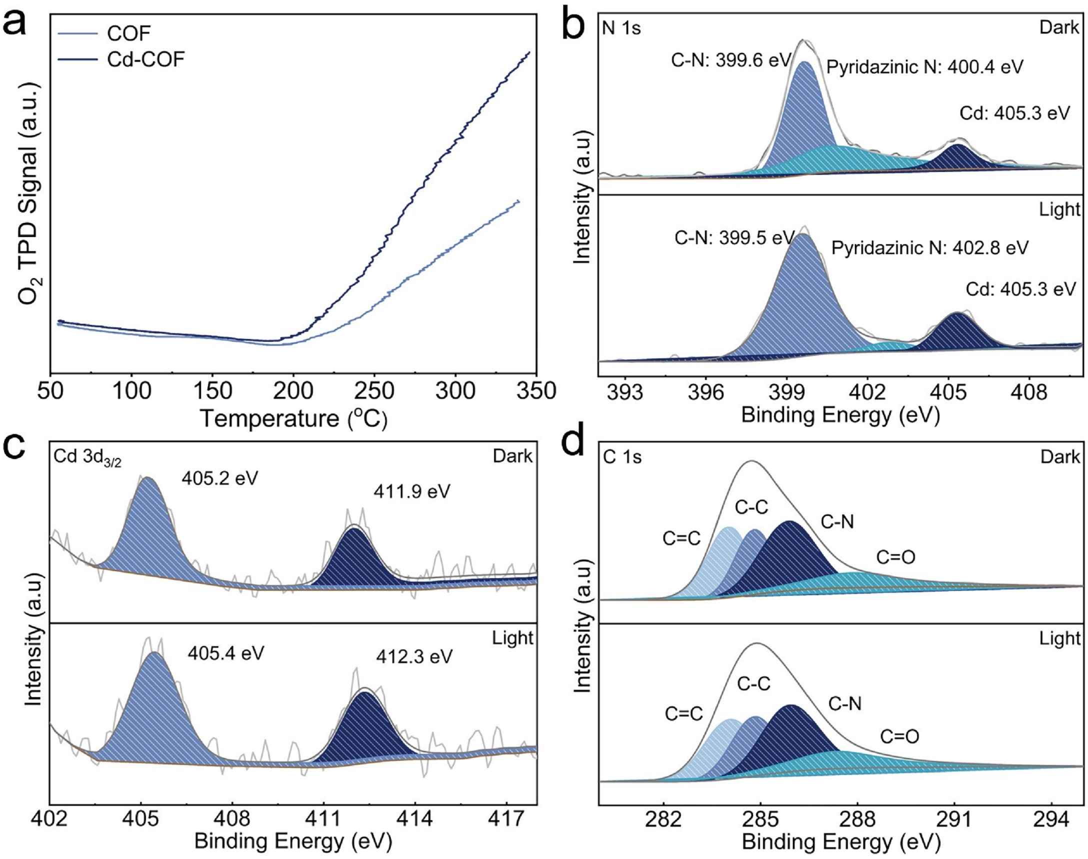

Fig. S13 (a) O_2-TPD of COF and Cd-COF; ISI-XPS spectra of (b) N 1s; (c) Cd 3d; (d) C 1s.