Supporting Information

Harnessing Topological Porphyrin Frameworks for Synergistic H_2O_2 Generation and Furfuryl Alcohol Oxidation

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Experimental Section

1. Materials

Tetrakis (4-Carboxyphenyl) Porphyrin (TCPP) (96%, Adamas), 1,3,5-tris (4-carboxyphenyl) benzene (BTB) (97%, Aladdin), benzoic acid (99%, Sinopharm Chemical Reagent Co., Ltd (SCRC)), acetic acid (AR, SCRC), ammonium acetate (99%, Macklin), N, N-dimethylformamide (DMF) (99%, SCRC), acetonitrile (AR, Shanghai Wokai Biological Technology Co. Ltd.), acetone (99%, SCRC), zirconium chloride (98%, Macklin), potassium iodide (99%, Macklin), potassium hydrogen phthalate (99%, sigmaaldrich). Deionized water was used for all tests and all the reagents were used as received without further purification.

2. Synthesis of PCN-134

The PCN-134 was synthesized via a solvothermal method. $ZrCl_4$ (120 mg) and BTB (50mg) were dissolved in 10 mL DMF. Then, poured it into reaction vials, which were sealed and kept at 85 ℃ for 1 h in an oven. When them were cooled to room temperature, mixed it with 10 mL DMF of TCPP (40 mg) and benzoic acid (1200 mg) dissolved. After that, the reaction vials were sealed and kept at 120℃ for 24 h in an oven. When the vials were cooled to room temperature, the power was filtered under vacuum and washed several times with DMF and acetone. Finally, the sample PCN-134 was dried at 60 ℃ in an oven under vacuum for 6 h.

3. Synthesis of PCN-224

The PCN-224 was synthesized via a solvothermal method. $ZrCl_4$ (120 mg), TCPP (40 mg) and benzoic acid (1200 mg) were dissolved in 8 mL of mixed solution of 7.5 mL DMF and 0.5 mL acetic acid, which was continuously ultrasonicated until all the solutes were totally dissolved. After that, the solution was poured into a Teflon autoclave, which was sealed and kept at 120 ℃ for 24 h in an oven. When the autoclave was cooled to room temperature, the power was filtered under vacuum and washed several times with DMF and acetone. Finally, the sample PCN-224 was dried at 60 ℃ in an oven under vacuum for 6 h.

4. Characterization

The morphology and microstructure were studied by field emission scanning electron microscopy (FE-SEM, Sigma500). 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 was performed on an ESCALAB Xi+ electron spectrometer (Thermo Fisher Scientific, US) using 300 W Al Kα radiation. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) were obtained UItima IV and Nicolet iS50. Nitrogen sorption/desorption curves were obtained using ASAP 2020 Plus 2.00. Furthermore, to evaluate the optical and electrochemical performance, we used photoluminescence (PL, FLS 1000), time-resolved photo-luminescence (TR-PL, Edinburgh-FLS-1000) spectra and an electrochemical workstation (CHI-760E) with a three-electrode system. Electron spin

resonance (ESR) was detected on Bruker EMX PLUS using DMPO as radical capture reagent.

5. Photoelectrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI760E, China) using a standard three-electrode system. Pt sheet electrode and Ag/AgCl electrode were separately used as the counter electrode and reference electrode. The working electrode was prepared by coating with thin sample film on fluorine-doped tin oxide (FTO) conductive glass. Typically, 5 mg of powder sample was dispersed in a mixed solution (250 μL ethanol and 30 μL Nafion) and sonicated for 30 min. Then the resulting suspension was dip-coated on the FTO surface and dried overnight at room temperature. Transient photocurrents, Mott-Schottky plots tests were carried out by using 0.5 mol/L Na_2SO_4 (PH=7) solution as the electrolyte. In addition, electrochemical impedance spectroscopy (EIS) measurements use potassium ferricyanide solution as the electrolyte.

6. Photocatalytic Preparation of Hydrogen Peroxide

To quantify photocatalytic H_2O_2 production, a standard heterogeneous reaction protocol was implemented. A 5 mg aliquot of the photocatalyst was suspended in 50 mL of ultrapure water containing 25 μL of furfuryl alcohol (FAL) as the sacrificial electron donor. Atmospheric control was achieved by pre-equilibration of the suspension with either nitrogen or oxygen gas for 30 minutes prior to irradiation. The heterogeneous reaction mixture was subjected to visible light illumination from a 300 W xenon lamp for 3 hours under continuous stirring, with temperature precisely

regulated at 20 °C using a thermostatic circulating water system. Periodic sampling (every 30 minutes) facilitated the monitoring of H_2O_2 evolution. The analytical determination of H_2O_2 involved a validated iodometric assay: a 0.5 mL sample was reacted with 0.5 mL of 0.4 mol/L Potassium iodide (KI) and 0.5 mL of 0.1 mol/L Potassium hydrogen phthalate (KHP) in darkness for 30 minutes. The absorbance of the liberated iodine was subsequently quantified at 351 nm using UV-DRS spectroscopy (Fig. S4a), and concentrations were derived from a linear standard calibration curve (Fig. S4b-c).

7. Photocatalytic Preparation of Furfuryl Alcohol Oxidation

The quantitative analysis of the oxidation products including furoic acid and furfural were carried out by high-performance liquid chromatograph (HPLC). 10 μL of liquid was obtained at 0, 1, 2 and 3 h and analyzed by the HPLC (LC20AD, Shimadzu, Japan) with a UV–vis detector (SPD-20A, Shimadzu, Japan) and 5 μm C18 column. The mobile phase consisted of acetonitrile (chromatographic grade purity) and 5 mM ammonium acetate aqueous solution (volume ratio is 4:6) and the flow rate was 0.8 mL/min. In addition, the detection wavelength is set at 230 nm.

8. Degradation experiment of Hydrogen Peroxide

To investigate catalyst stability and interaction within a hydrogen peroxide milieu, a 5 mg quantity of the catalyst was dispersed in 50 mL of a 1 mmol/L H_2O_2 aqueous solution. Prior to analysis, the heterogeneous suspension was thoroughly degassed under an inert nitrogen atmosphere for 30 minutes, ensuring the absence of atmospheric oxygen. Subsequently, the sealed reaction vessel was subjected to full

spectrum irradiation. Temporal changes in H_2O_2 concentration were monitored at 30-minute intervals via an appropriate analytical technique.

9. Apparent quantum Efficiency (AQE) calculation

To calculate the apparent quantum yield (AQE), different incident lights were used as the source to trigger the photocatalytic reaction. We have calculated the AQE for the reaction under monochromatic light irradiation at 400, 475 and 600 nm. The detailed calculation method has been added to the following formulae, and the AQE values have been incorporated into Fig.S9. The results demonstrate that PCN-224 achieves an AQE of 0.22% at 475 nm.

$$N = \frac{E\lambda}{hc}$$

$$AQE = \frac{2 \times the\ number\ of\ evolved\ H_2O_2}{the\ number\ of\ incident\ photons} \times 100\%$$

h: Represents the Planck constant. h≈6.626*10^{-34}J·s

λ: The wavelength representing light waves

c: Represents the speed of light in a vacuum

S1

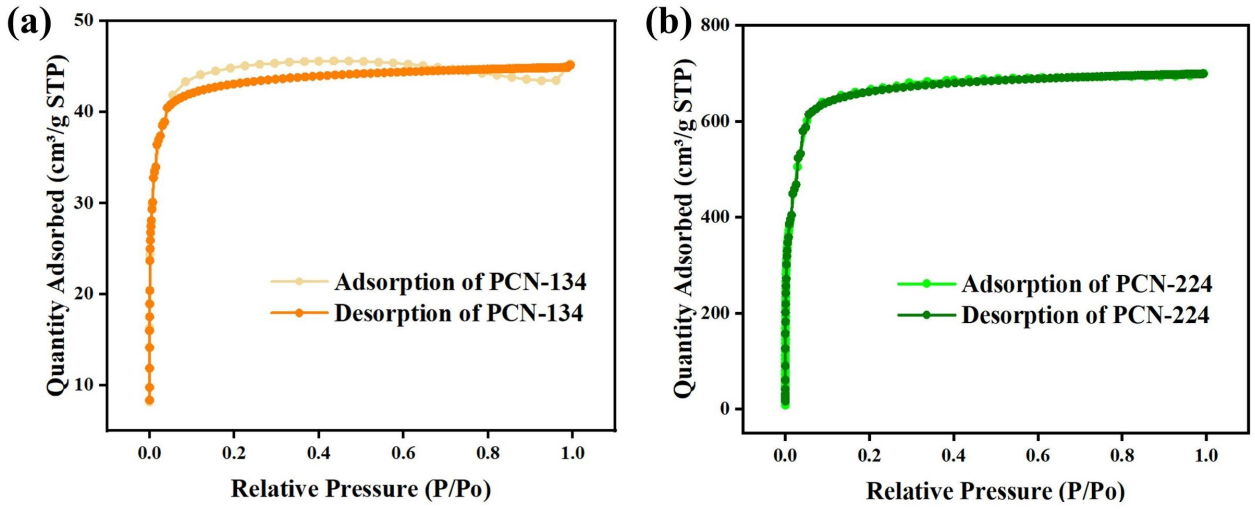

Fig. S1 Comparison of the N_2 adsorption-desorption isotherms of PCN-134 and PCN-224.

S2

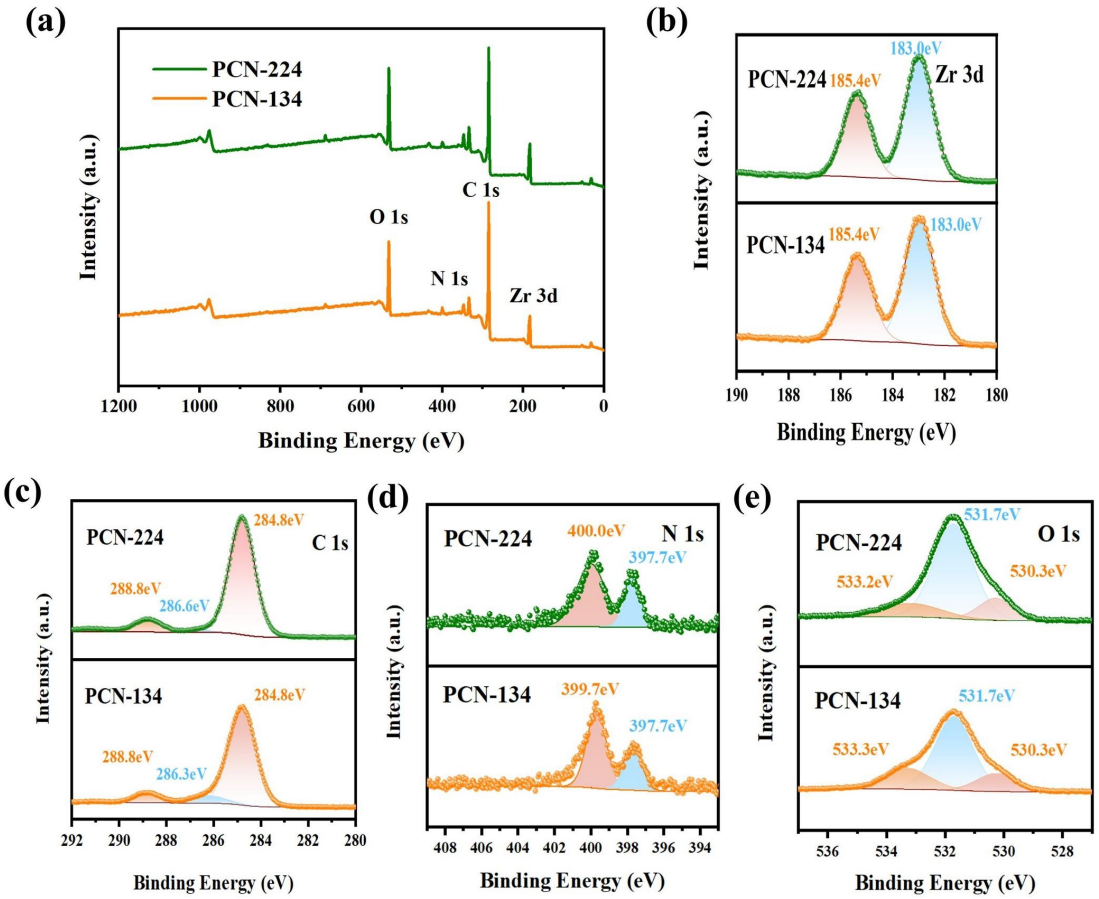

Fig. S2 Comparison of the XPS (a), XPS-Zr (b), XPS-C (c), XPS-N (d) and XPS-O (e) spectra of PCN-134 and PCN-224.

S3

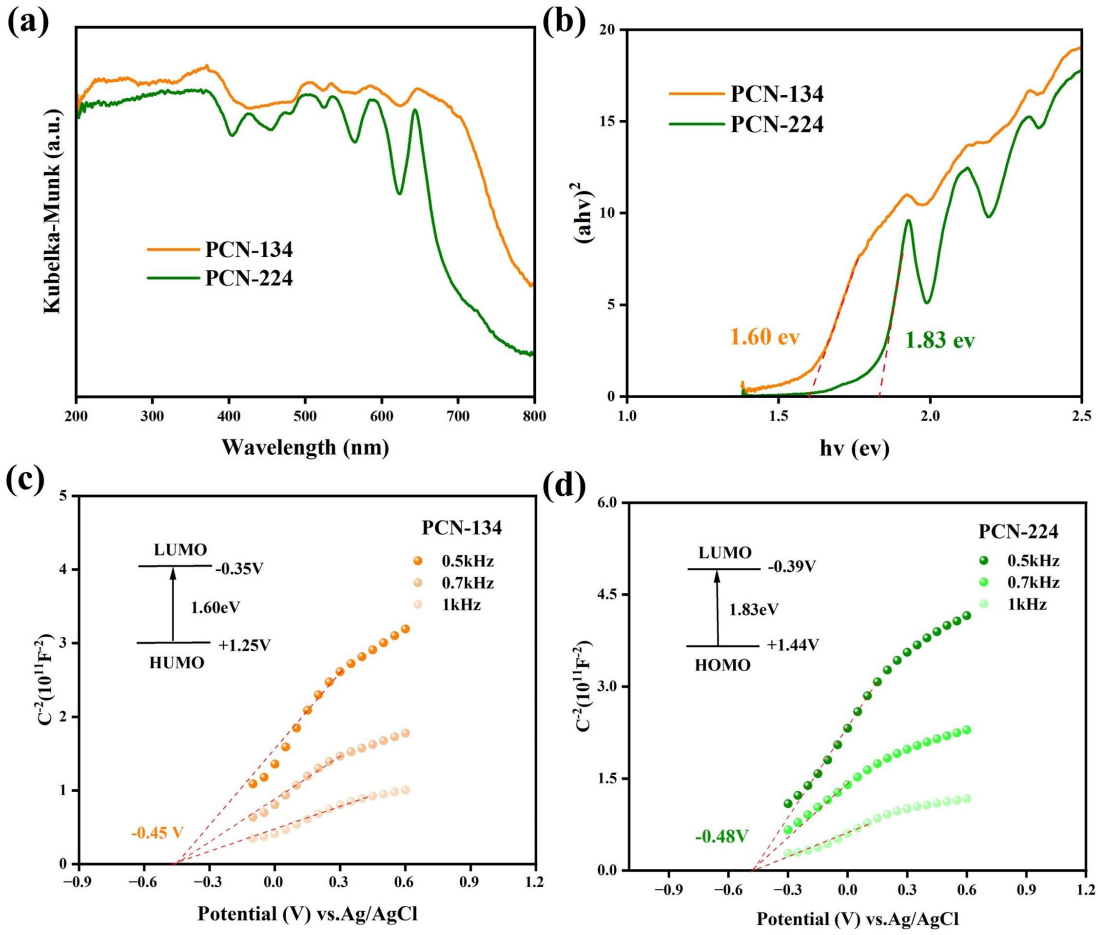

Fig. S3 (a) UV-vis absorption spectra and (b) Tauc plots of PCN-134 and PCN-224; (c-d) Mott-Schottky plots of PCN-134 and PCN-224.

S4

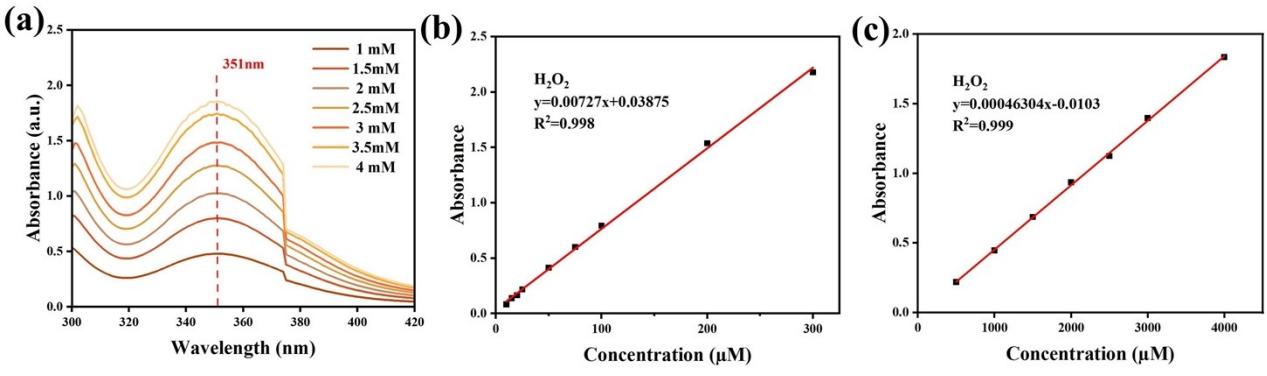

Fig. S4 (a) Absorbance curves at different H_2O_2 concentrations; (b-c) Calibration curve for quantifying photocatalytic H_2O_2 yields.

S5

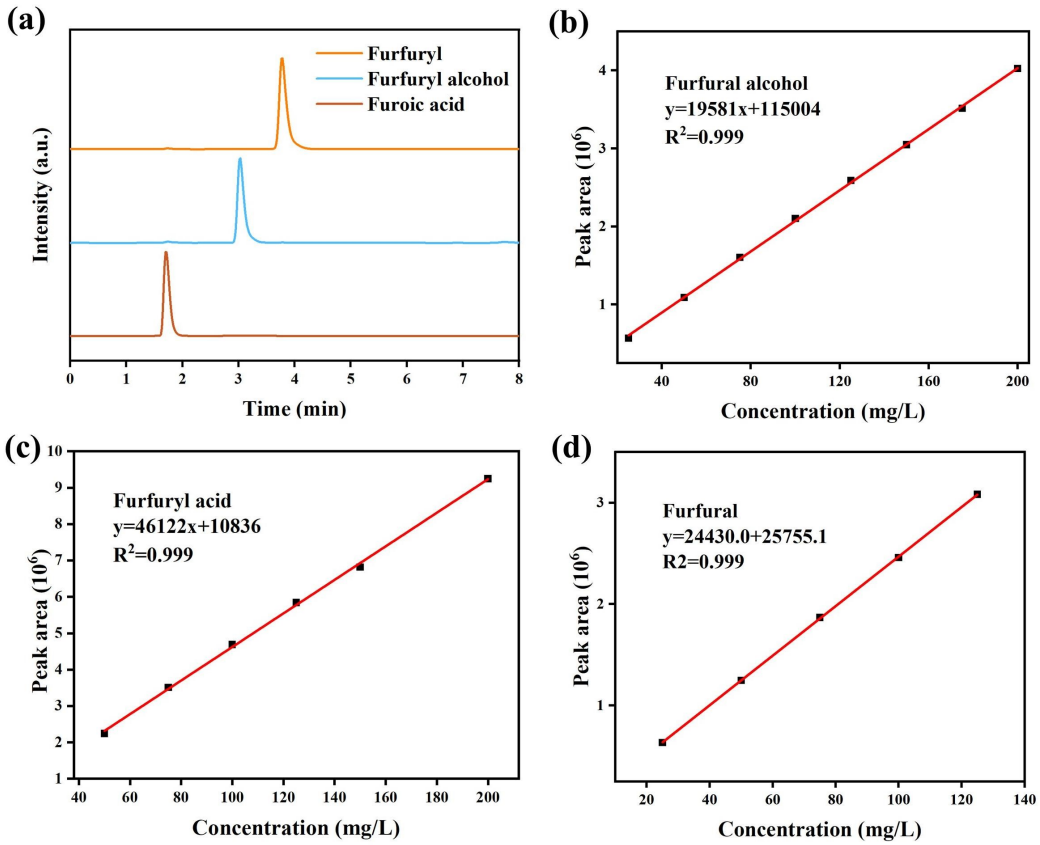

Fig. S5 (a) HPLC chromatograms of furfuryl alcohol, furfural and furoic acid at optimized reaction condition; (b) The standard curve for the calibration of furfuryl alcohol concentration; (c) The standard curve for the calibration of furfural concentration; (d) The standard curve for the calibration of furoic acid concentration.

S6

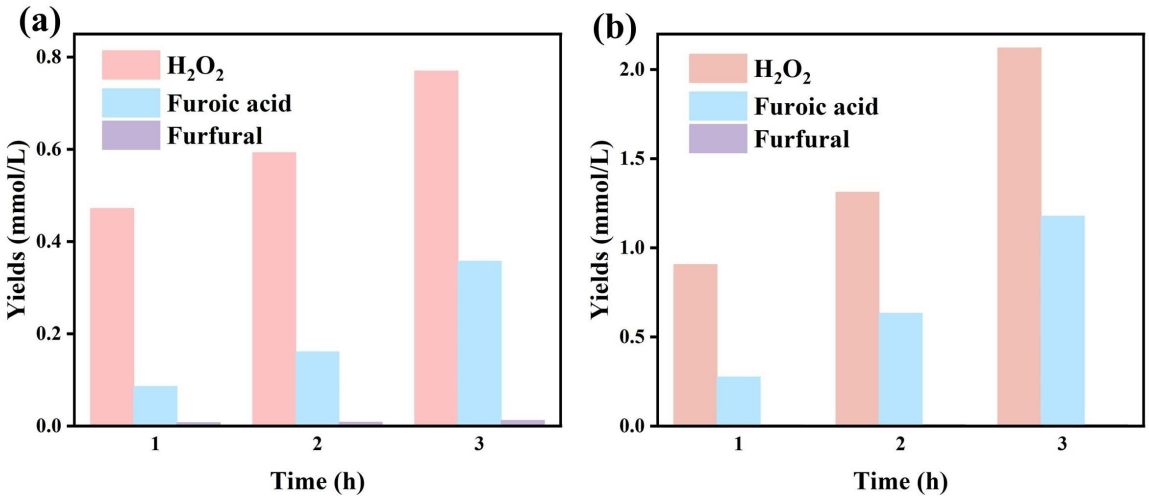

Fig. S6 Times course of H_2O_2, FF, FAC over PCN-134 and PCN-224 in 3 h.

S7

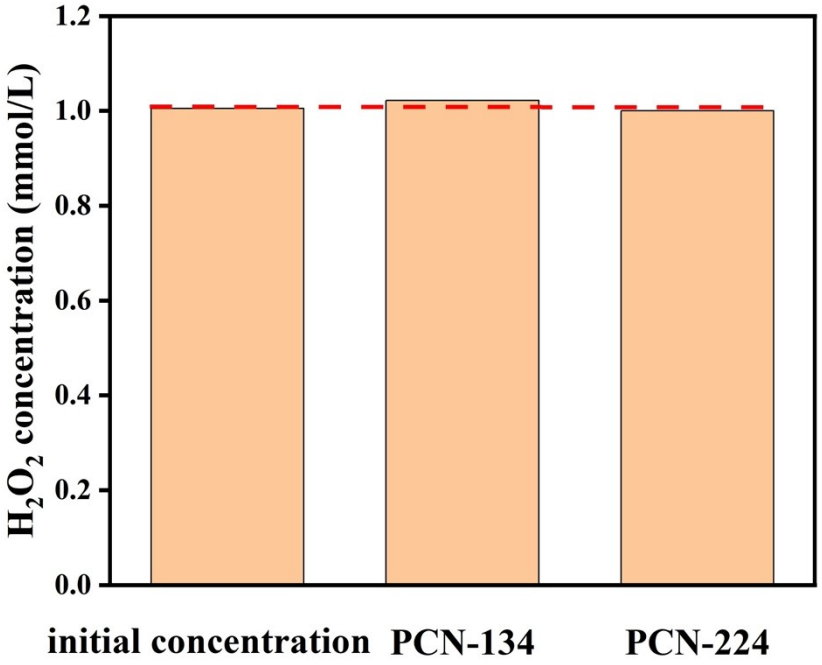

Fig. S7 The decomposition experiment of H_2O_2 under dark conditions

S8

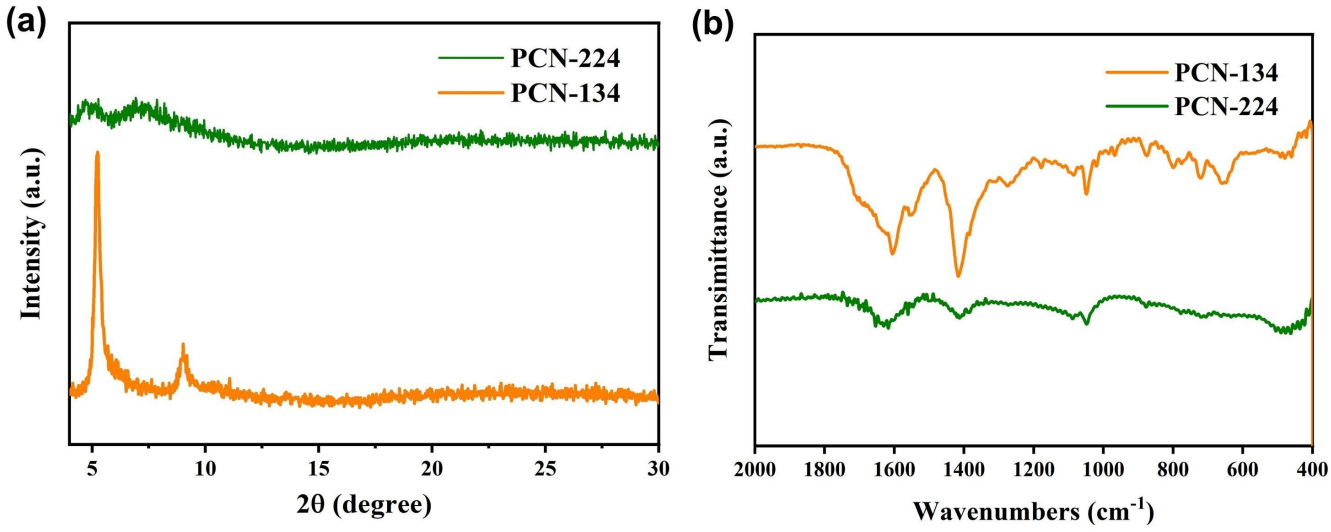

Fig. S8 (a) The XRD and FTIR spectra of PCN-134 and PCN-224 after the reaction.

S9

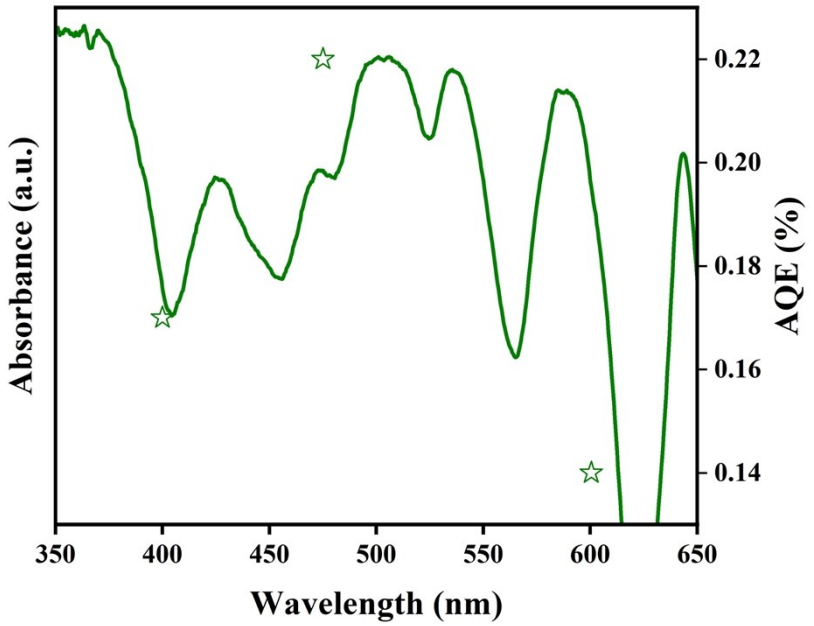

Fig. S9 UV-Vis of PCN-224 and the wavelength dependence of AQE

S10

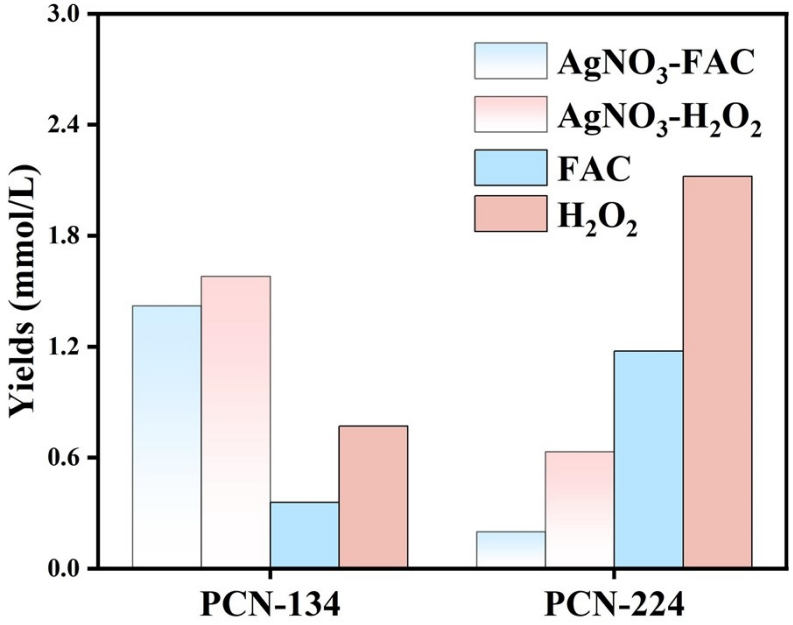

Fig. S10 Yields of H_2O_2 and Furoic acid over PCN-134 and PCN-224 after 3 h, with adding $AgNO_3$ and no scavenger.

Table S1. Calculated FAL conversion and product selectivity over PCN-134 and PCN-224.

Sample	Time(h)	Conv. (%)	Sel. of FAC (%)	Sel. of FF (%)
PCN-134	3	30	21	0.6
PCN-224	3	60	33	0.2

Table S2. Fitting parameters and average lifetimes (τ_{Ave}) over PCN-134 and PCN-224.

$$\tau_{avg}=(A_1*\tau_1^2+A_2*\tau_2^2)/(A_1*\tau_1+A_2*\tau_2)$$

Sample	τ_1	A_1	τ_2	A_2	τ_{avg}
PCN-134	0.7141	1532.6136	3.0320	115.4619	1.276
PCN-224	0.6800	1570.3964	3.0379	108.2939	1.235

Table S3. Comparing the photocatalytic performance of H_2O_2 production with other photocatalysts.

photocatalysts	Sacrificial	Solution	H_2O_2	Reference
PCN-224	30	Water	9.04mmol/g/	This work
NH_2-MIL-125-	No	Water	101μmol/g/h	1
NH_2-UiO-	EtOH	Water	243μmol/g/h	2
UiO-66-NH_2	benzyl alcohol	acetonitrile	67.2mmol/g/	3
MIL-125-PDI	No	acetonitrile	4800μmol/g/	4
EZUNH-2 MOF	IPA	Water	35.2μmol/L	5
OPAFe-Zr-mof	benzyl alcohol	Water	13.1mmol/g/	6
NH_2-MIL-125	TEOA	MeCN/H_2O	925.8μmol/h	7
Re10-MFM-67	benzyl alcohol	BzOH/Water	8.50mmolgc	8

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