

Supporting Information

Hydrophilic o-phenanthroline-based covalent organic polymer with reversible tautomeric structure for boosting photocatalytic hydrogen peroxide production

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Experimental Section

1.1 Chemicals and reagents

Terephthalaldehyde (TPA), 1,3,5-triformylbenzene (TFB), 1,3,5-triformylphloroglucinol (TP) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology. 5,6-diamino-1,10-phenanthroline (DAP) was purchased from Shanghai Bidepharm. Ethanol (AR), isopropanol (AR), Mesitylene (CP), 1,4-dioxane (AR), glacial acetic acid (AR), tertiary butanol (AR), tetrahydrofuran (AR), acetone

(AR), concentrated sulfuric acid (98 wt%), silver nitrate (AR), p-benzoquinone (AR) were purchased from Sinopharm. Potassium titanium oxalate (98 wt%) and Nafion solution (5%) were purchased from Shanghai Aladdin. Deionized water was purified by Jiangnan University.

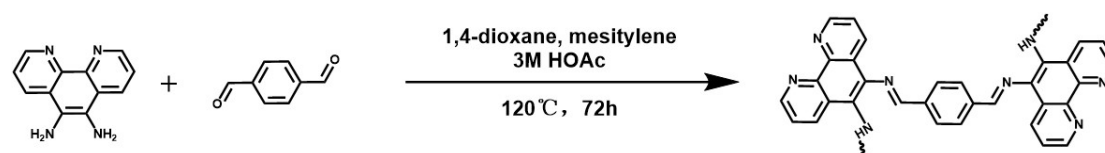
1.2 Characterization methods

The crystal structures of the samples were tested by the X-ray diffractometer (D8, Bruker, Germany) with 2θ from 2° to 30° . The structure and composition of the obtained samples were analyzed by Fourier transform infrared (FT-IR) spectroscopy (Nicolet iS50). The water contact angle of the photocatalysts was measured by the optical contact angle meter (OCA 40, LAUDA Scientific, Germany). Solid-state ^{13}C NMR spectra of the samples was obtained by the solid state nuclear magnetic resonance (Bruker Avance Neo 400WB, Germany). The morphology and elemental mappings of materials were investigated by scanning electron microscopy (SEM, S-4800, Japan) with an EDS detector, and the electron gun is a cold field emitting electron source and the accelerating voltage is 3 kV. The specific surface area of the samples was determined using the Micromeritics ASAP 2460 at 77 K. Thermogravimetric analysis (TGA) was conducted on the TGA/1100SF at the rate of $10^\circ\text{C}/\text{min}$ from 100°C to 800°C . The X-ray photoelectron spectroscopy (XPS) was carried out on AXIS Supra of Kratos Analytical Inc. using monochromatized Al $K\alpha$ radiation ($h\nu = 1486.6\text{ eV}$, 225 W) as X-ray source with a base pressure of 10^{-9} torr. The sampling parameters are set as: the operating voltage of 12 kV, the beam spot of $400\ \mu\text{m}$, the filament power supply of 6 mA, the electron emission angle of 60° , the instrumental figure of merit of 4.2 eV,

and using the binding energy of C1s 284.80 eV as the calibration standard. The photoluminescence (PL) spectra of the materials were recorded by the FS5 fluorescence spectrophotometer with an excitation wavelength of 420 nm. The photogenerated carrier lifetimes of samples were tested using a Lifespec II spectrophotometer. The absorption of visible light was studied using the UV-visible absorption spectrometer (UV-3600 plus) with BaSO₄ as the reference. Electron paramagnetic resonance (EPR) spectra were acquired with a Bruker EMXplus-6/1.

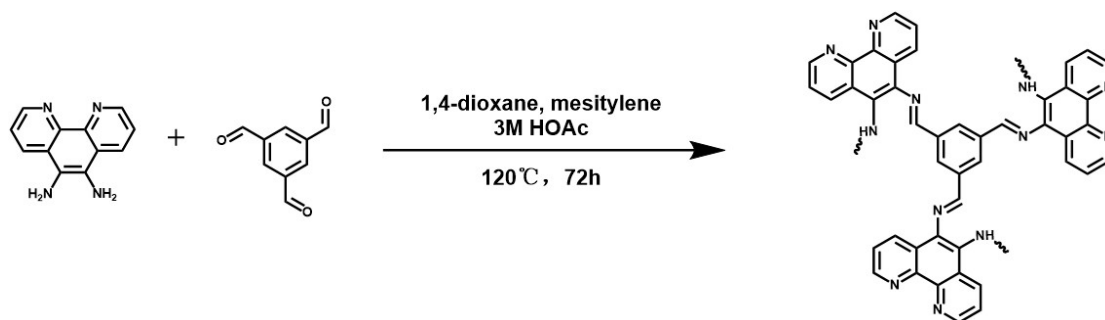
1.3 The synthesis of COFs

Synthesis of TPA-DAP



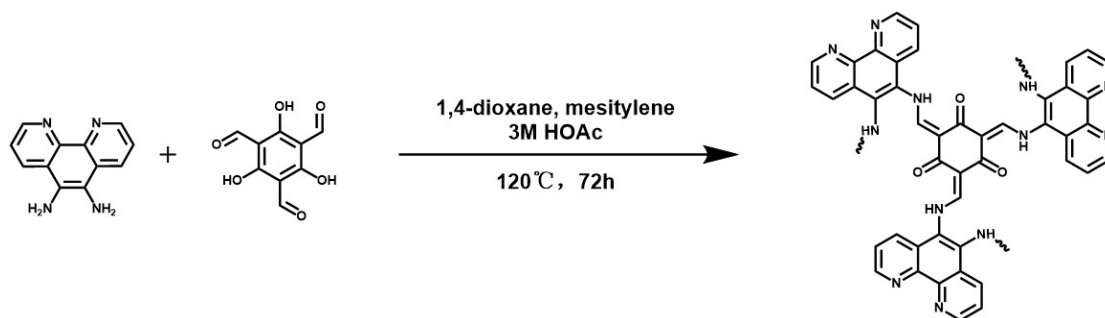
Terephthalaldehyde (TPA, 0.2 mmol) was added into a small bottle containing 1,4-dioxane (3 mL), and 5,6-Diamino-1,10-phenanthroline (DAP, 0.2 mmol) was added into a small bottle containing mesitylene (1 mL). After each bottle was sonicated uniformly for 30 min, the solution of TPA was dropped into DAP solution and the mixture was sonicated for another 30 min. Subsequently, 0.2 mL of 3 M aqueous acetic acid was added into the above mixture and the mixed solution was transferred into a Pyrex tube. Before the reaction, the tube needed to be frozen with liquid N₂ and degassed by freeze-pump-thaw 3 times. Then, the tube was sealed and heated to 120 °C for 72 h. After being naturally cooled to room temperature, the product was washed with absolute ethanol and tetrahydrofuran several times, and then freeze-dried in vacuum for 12 h.

Synthesis of TFB-DAP



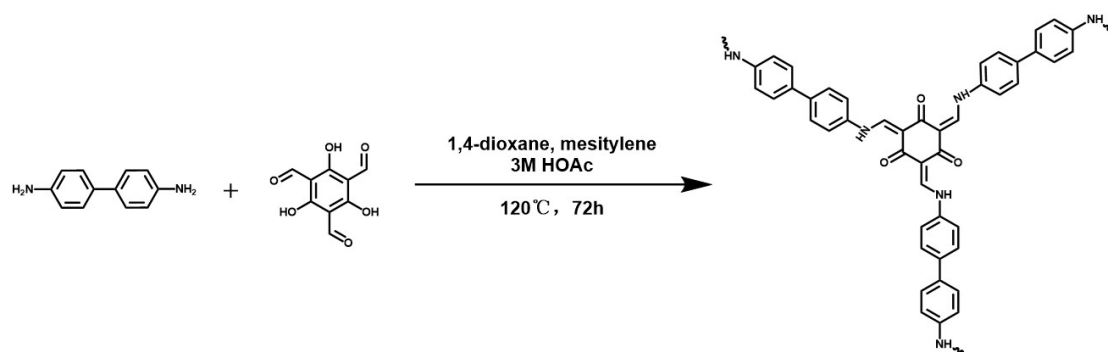
1,3,5-triformylbenzene (TFB, 0.2 mmol) was added into a small bottle containing 1,4-dioxane (3 mL), and 5,6-diamino-1,10-phenanthroline (DAP, 0.3 mmol) was added into a small bottle containing mesitylene (1 mL). After each bottle was sonicated uniformly for 30 min, the solution of TFB was dropped into DAP solution and the mixture was sonicated for another 30 min. The remaining synthetic steps and conditions keep the same as that of TPA-DAP.

Synthesis of TP-DAP



1,3,5-triformylphloroglucinol (TP, 0.2 mmol) was added into a small bottle containing 1,4-dioxane (3 mL), and 5,6-Diamino-1,10-phenanthroline (DAP, 0.3 mmol) was added into a small bottle containing mesitylene (1 mL), respectively. After each bottle was sonicated uniformly for 30 min, the solution of TP was dropped into DAP solution and the mixture was sonicated for another 30 min. The remaining synthetic steps and conditions keep the same as that of TPA-DAP.

Synthesis of TP-BD



1,3,5-triformylphloroglucinol (TP, 0.2 mmol) was added into a small bottle containing 1,4-dioxane (3 mL), and 4,4'-diaminobiphenyl Benzidine (BD, 0.3 mmol) was added into a small bottle containing mesitylene (1 mL), respectively. After each bottle was sonicated uniformly for 30 min, the solution of TP was dropped into BD solution and the mixture was sonicated for another 30 min. The remaining synthetic steps and conditions keep the same as that of TPA-DAP.

1.4 Photoelectrochemical measurements

The photocatalytic experiments were measured using a CHI 660E electrochemical workstation equipped with a three-electrode unit. The carbon rod and saturated calomel electrode were used as the counter electrode and the reference electrode, respectively. The working electrode was obtained as follows: 1 mg of photocatalyst was mixed with 200 μL of isopropanol and 10 μL Nafion 117 solution uniformly by ultrasonication. The mixture was dropped onto a 1x1 cm^2 carbon paper. The electrolyte was 0.5 M Na_2SO_4 aqueous solution. Photocurrent tests and electrochemical impedance spectrum (EIS) tests were performed in an electrolytic cell in air. Photocurrents were measured at open circuit voltage using a 300 W Xenon lamp as light source. The EIS tests were performed in the frequency range of 10^{-5} to 10^{-2} Hz. The flat band potentials of the

working electrodes for the obtained COPs were measured by the Mott-Schottky curves in the range of -1.0~1.0 V at the frequencies of 500, 800 and 1000 Hz.

1.5 Photocatalytic H₂O₂ production

Under visible light irradiation, the photocatalytic H₂O₂ formation performance of the different COPs obtained was tested. Specific experimental procedures: 5 mg of photocatalyst and 30 mL of deionized water were added to the reactor, and the photocatalyst was sonicated for 10 min in order to disperse it in the solution. After that, oxygen was introduced continuously to maintain the saturated state in the system, and then the reactor was illuminated by turning on the light source (300 W Xenon lamp with 420 nm cut-off filter). In order to control the reaction temperature, a circulating water system is used, and the temperature is controlled at 25°C. 2mL of the suspension was withdrawn every 30 minutes and passed through 0.45µm microporous filter. In the active species trapping test, ethanol (10 vol% aqueous solution) was used as a trapping agent for holes (h⁺), AgNO₃ solution (1 mmol/L) was used to trap electrons (e⁻), p-benzoquinone (p-BQ, 0.5 mmol/L) was used to detect superoxide radicals (•O₂⁻), 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.5 mmol/L) was used as a trapping agent for single linear oxygen (¹O₂), and tert-butanol (TBA, 10 vol% aqueous solution) was used to trap hydroxyl radicals (•OH). In each trapping experiment, 5 mg of photocatalysts was added into 30 mL of each trapping agent solution. The potassium titanium oxalate method was used to quantify the concentration of H₂O₂¹. Typically, take 1.5ml of the above filtrate in a test tube and add 1ml of 0.02M potassium titanium (IV) oxalate solution and shake to mix. The change in color of the mixed solution from clear to

yellow is indicative of the formation of titanium peroxides. Absorbance at 400 nm was quantified using a UV-visible spectrophotometer, enabling the calculation of H_2O_2 concentration according to the Lambert-Beer law at various time points.

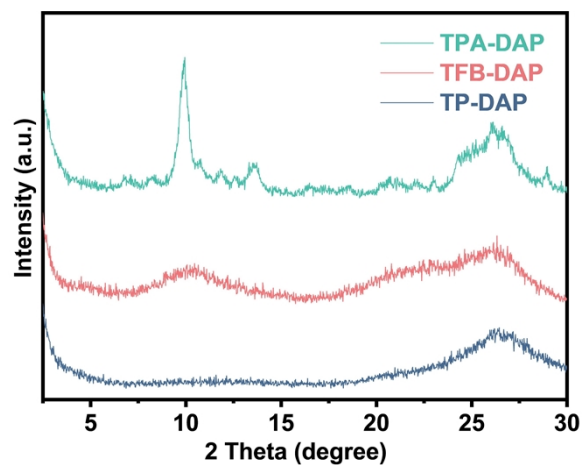


Fig. S1 XRD patterns of TPA-DAP, TFB-DAP and TP-DAP.

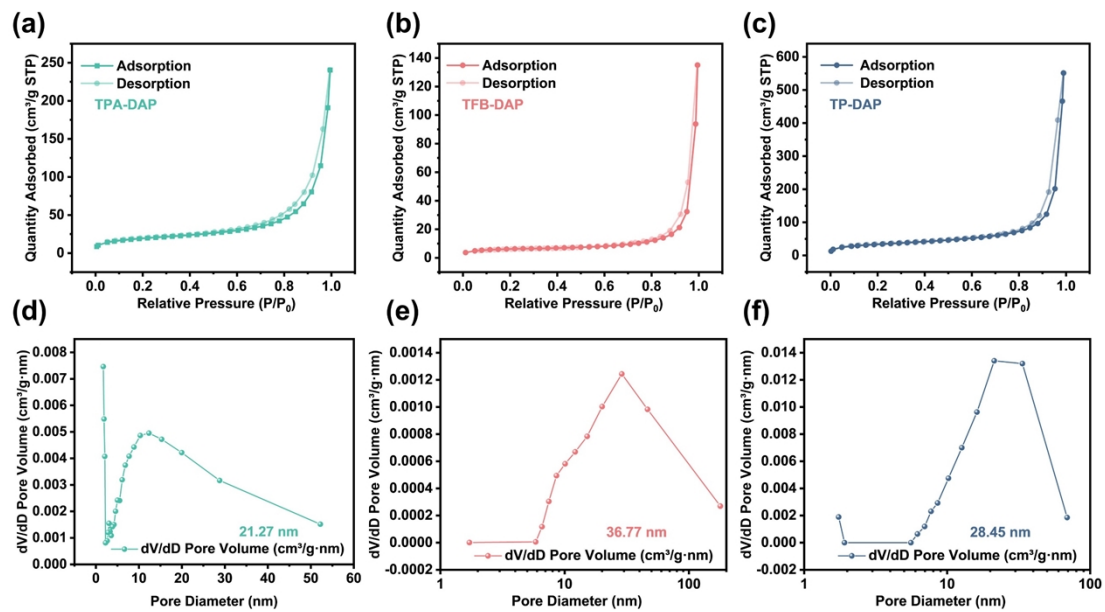


Fig. S2 N_2 sorption isotherms of (a) TPA-DAP, (b) TFB-DAP, (c) TP-DAP. And pore size distribution curve (d) TPA-DAP, (e) TFB-DAP, (f) TP-DAP.

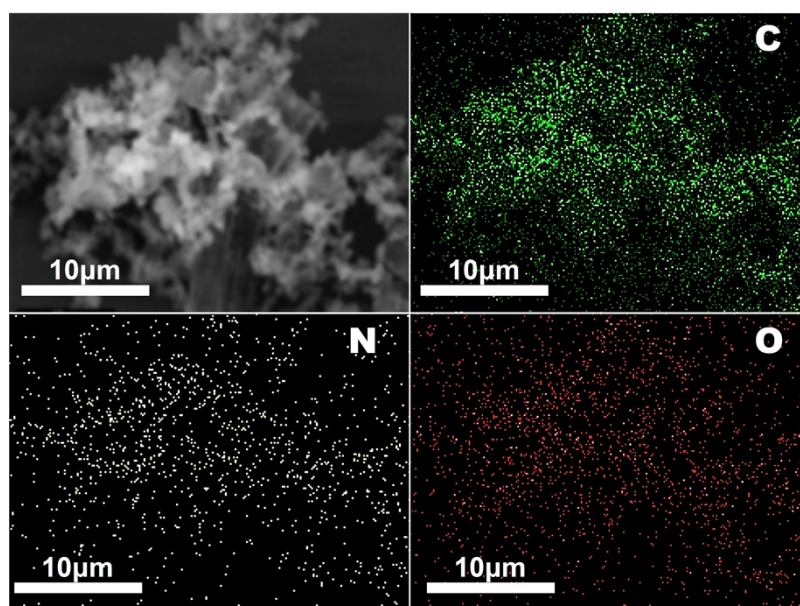


Fig. S3 EDX elemental mapping of TPA-DAP.

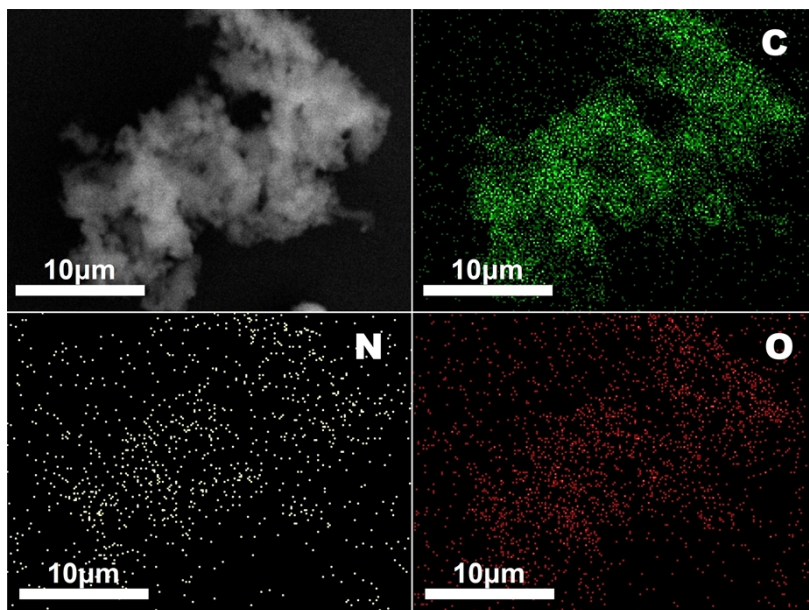


Fig. S4 EDX elemental mapping of TFB-DAP.

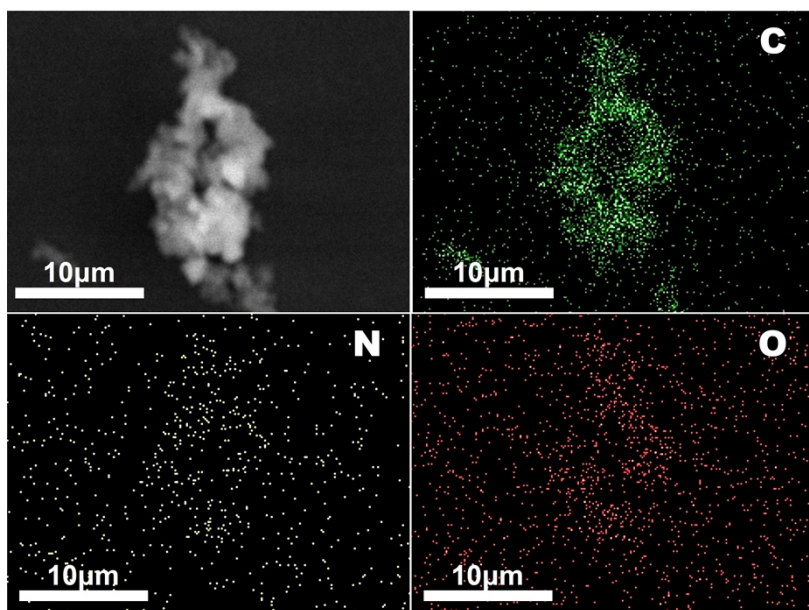


Fig. S5 EDX elemental mapping of TP-DAP.

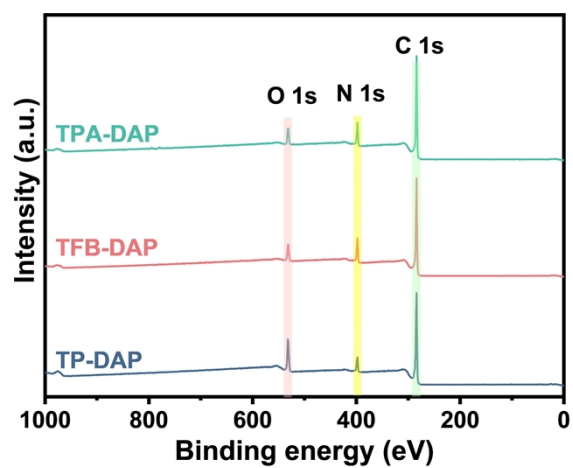


Fig. S6 XPS survey spectra of TPA-DAP, TFB-DAP and TP-DAP.

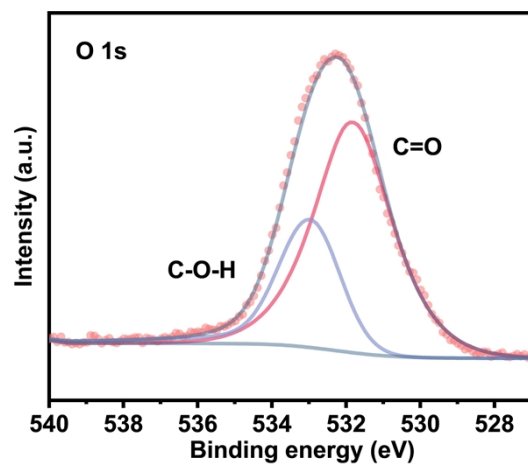


Fig. S7 O 1s spectrum of TP-DAP

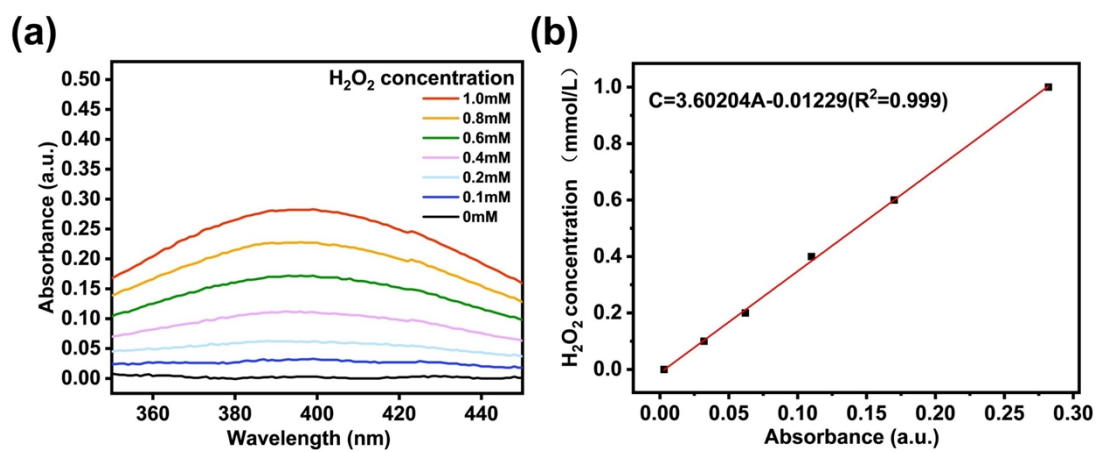


Fig. S8 (a) The UV spectra and (b) standard curve of H₂O₂ obtained by the potassium titanium oxalate method.

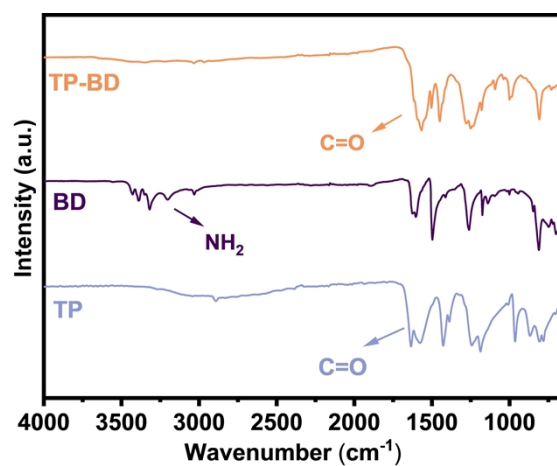


Fig. S9 FT-IR spectra of TP-BD.

The disappearance of the -NH₂ vibration and the appearance of a new C=O signal at 1567 cm⁻¹ indicated the formation of keto-enol tautomerization.

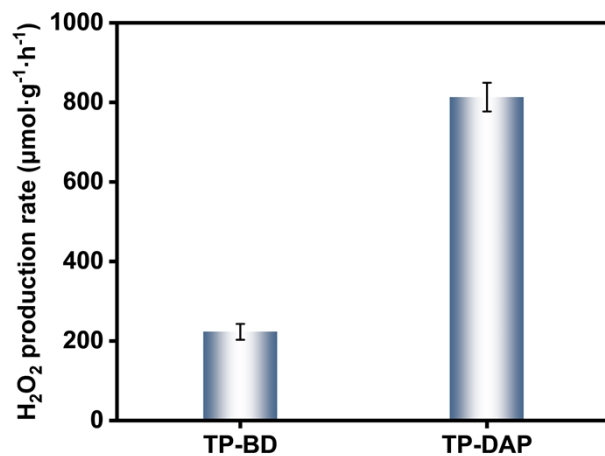


Fig. S10 Photocatalytic production rate of H₂O₂ by TP-BD and TP-DAP.

The properties of TP-BD were tested and compared with TP-DAP, the hydrogen peroxide yield of TP-DAP was about 3.65 times higher than that of TP-BD.

Table S1 Comparison of photocatalytic performance for TP-DAP and other reported photocatalyst

photocatalyst	Irradiation conditions	Reaction system	H ₂ O ₂ production rate (μmol·g ⁻¹ h ⁻¹)	Ref.
TP-DAP	λ ≥ 420 nm	5 mg Cat., 30 mL of H ₂ O	814	This work
COF-TfpBpy	λ ≥ 420 nm	5 mg Cat., 10 mL of H ₂ O	695	2
DHAA-Tp-COF	λ ≥ 420 nm	10 mg Cat., 10 mL of H ₂ O	220	3
Py-Da-COF	λ ≥ 420 nm	5 mg Cat., 5 mL of H ₂ O	461	4
COP-TT	λ ≥ 425 nm	10 mg Cat., 50 mL of H ₂ O	382	5
COF-N32	λ ≥ 420 nm	25 mg Cat., 50 mL of H ₂ O	605	6
COF-Tfp-BDDA	λ ≥ 420 nm	10 mg Cat., 20 mL of H ₂ O	880	7
COF-BPDA-DTP	λ ≥ 420 nm	5 mg Cat., 40 mL of H ₂ O	1164	8
WO ₃ /Tp-TAPB	λ ≥ 420 nm	5 mg Cat., 10 mL of H ₂ O	1488	9
COF-2CN	λ ≥ 420 nm	12.5 mg Cat., 50 mL of H ₂ O	1601	10
TpTt-COF	400-780 nm	20 mg Cat., 40 mL of H ₂ O	2627	11
NMT400	AM 1.5G	20 mg Cat., 45 mL of H ₂ O, 5 mL ethanol	270	12
Bi ₂ O ₂ CO ₃ /Bi-MOF	λ ≥ 420 nm	5 mg Cat., 45 mL of H ₂ O, 5 mL CH ₃ OH	280	13
BTT-MD-COF	λ ≥ 420 nm	2 mg Cat., 10 mL of H ₂ O, 1 mL ethanol	5912	14

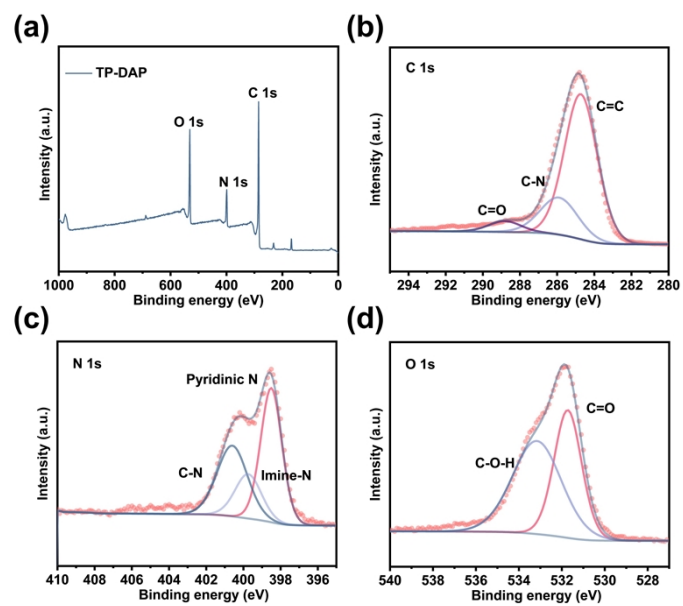


Fig. S11 XPS spectra of the as-synthesized TP-DAP before and after eight cycles of photocatalytic reaction: (a) survey spectra, (b) C 1s, (c) N 1s, (d) O 1s.

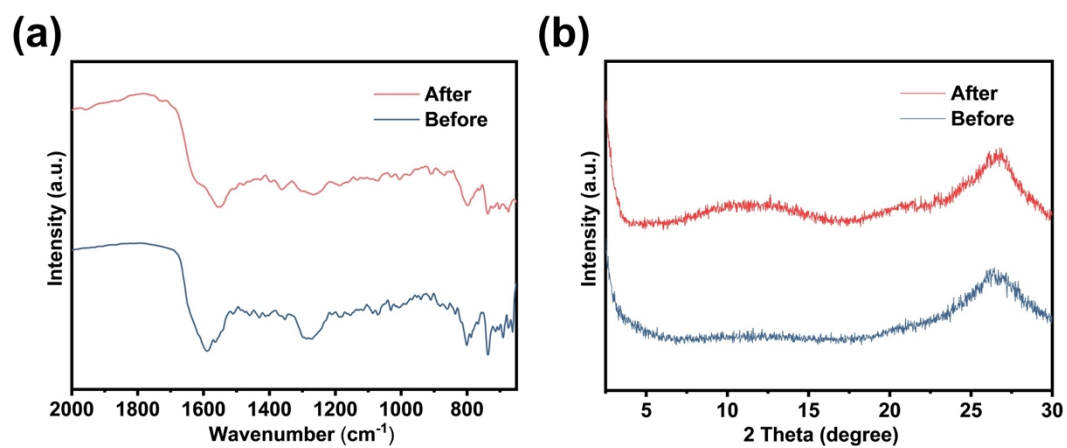


Fig. S12 (a) FT-IR and (b) XRD spectra of the as-synthesized TP-DAP before and after eight cycles of photocatalytic reaction.

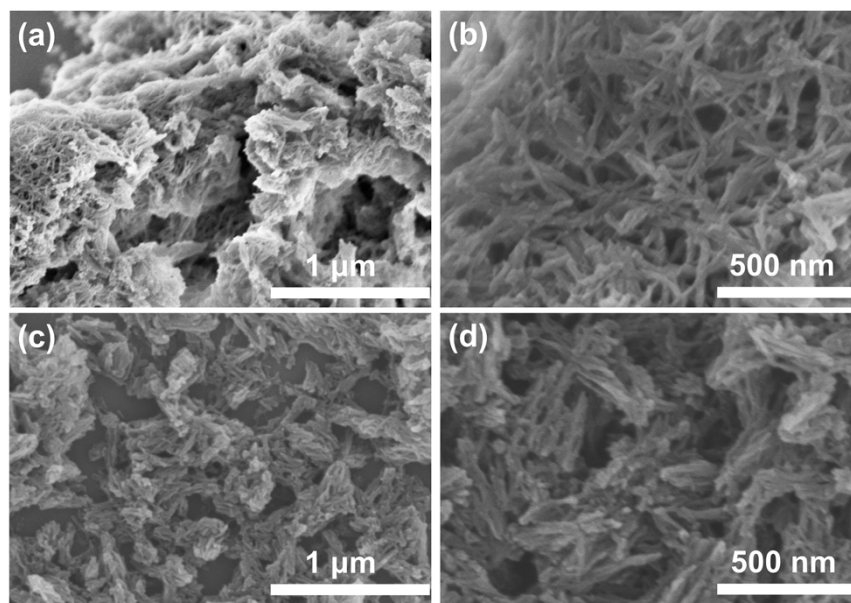


Fig. S13 SEM images of TP-DAP sample before (a, b) and after (c, d) cyclic photocatalysis.

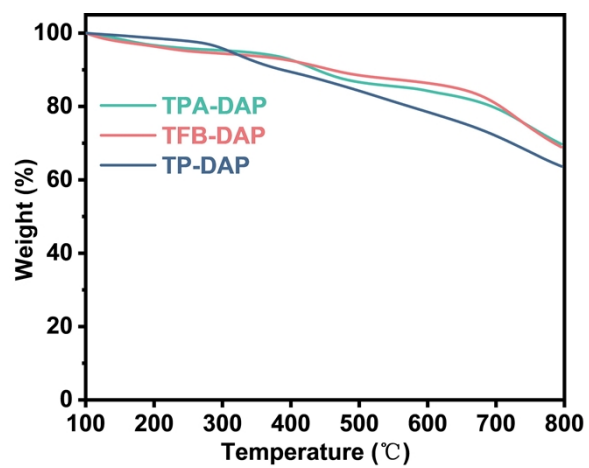


Fig. S14 TGA curves of TPA-DAP, TFB-DAP and TP-DAP.

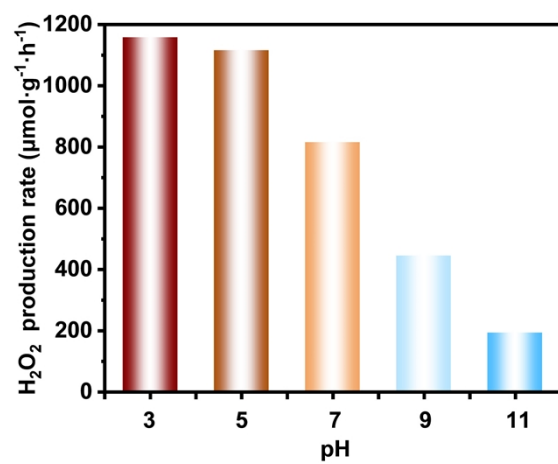


Fig. S15 Photocatalytic H₂O₂ production by TP-DAP at different pH values.

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